PEETER JOOT

BASIC STATISTICAL MECHANICS

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peeter joot

Notes and problems from UofT PHY452H1S 2013

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DOCUMENT VERSION

Version V0.1.13

Sources for this notes compilation can be found in the github repository

https://github.com/peeterjoot/phy452-basicstatmech

The last commit (Sep/10/2020), associated with this pdf was

309bc76da70f3dd7aa38ee343f5f40750f516da0

Should you wish to actively contribute typo fixes (or even more significant changes) to this book, you can do so by contacting me, or by forking your own copy of the associated git repositories and building the book pdf from source, and submitting a subsequent merge request.

```
#!/bin/bash

git clone git@github.com:peeterjoot/latex-notes-
    compilations.git peeterjoot
cd peeterjoot

submods="figures/phy452−basicstatmech phy452−
    basicstatmech mathematica latex"
for i in $submods ; do
   git submodule update --init $i
   (cd $i && git checkout master)
done

export PATH=‘pwd‘/latex/bin:$PATH

cd phy452-basicstatmech
make all
```

I reserve the right to impose dictatorial control over any editing and content decisions, and may not accept merge requests as-is, or at all. That said, I will probably not refuse reasonable suggestions or merge requests.

Dedicated to:
Aurora and Lance, my awesome kids, and
Sofia, who not only tolerates and encourages my studies, but is also awesome enough to think that math is sexy.

PREFACE

This book contains lecture notes taken during the Winter 2013 session of Basic Statistical Mechanics (PHY452H1S), a University of Toronto course that was taught by Prof. Arun Paramekanti.

Official course description: "Classical and quantum statistical mechanics of noninteracting systems; the statistical basis of thermodynamics; ensembles, partition function; thermodynamic equilibrium; stability and fluctuations; formulation of quantum statistics; theory of simple gases; ideal Bose and Fermi systems."

This book contains:

- Plain old lecture notes. These mirror what was covered in class, possibly augmented with additional details.
- Personal notes exploring details that were not clear to me from the lectures, or from the texts associated with the lecture material.
- Assigned problems. Like anything else take these as is. I may or may not have gone back and corrected errors, and did not see the graded versions of the last two problem sets.
- Some worked problems attempted as course prep, for fun, for test preparation, or post test reflection.
- Links to Mathematica workbooks associated with these notes.

On conventions These notes include worked problems from a few difference sources, which lead to some notational inconsistencies. In particular the problems from [11] work with a fundamental temperature $\tau = k_{\mathrm{B}} T$ having dimensions of energy and a nondimensionalized entropy $\sigma = S/k_{\mathrm{B}}$.

I've attempted to use k_{B} consistently. We used this or k in the class and our text [13] uses k.

For expressing the grand canonical partition function, I've settled on the Ω notation from the final exam (not actually used at all in class). This is less cumbersome than the Z_{G} that we used in class, and easier to interpret than the script Q used in the text [13]. That Q from the text looks like $\mathcal{Q}$, but with the circular part of the Q all detached and pushed up. It took me a long time to even figure out what that symbol was supposed to be.

Thanks My thanks go to Professor Paramekanti, who knows his subject well, for teaching this course and for his excellent elaborations of a number of tricky seeming concepts. I feel I learned a lot, despite also feeling like I've only scratched the surface of this subject.

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CONTENTS

LIST OF FIGURES

1

WHAT IS STATISTISTICAL MECHANICS AND EQUILIBRIUM.

1.1 EQUILIBRIUM.

This is the study of systems in equilibrium. What is equilibrium? [1]

- Mechanical equilibrium example: ball in bowl
- Chemical equilibrium: when all the reactants have been consumed, or rates of forward and backwards reactions have become more constant.

More generally, equilibrium is a matter of time scales!

Feynman “Fast things have happened and all slow things have not”

Example 1.1: Water in a cup

After 1 min - 1 hour, when any sloshing has stopped, we can say it’s in equilibrium. However, if we consider a time scale like 10 days, we see that there are changes occurring (evaporation).

Example 1.2: Hot water in a cup

Less than 10 minute time scale: Not in equilibrium (evaporating). At a longer time scale we may say it’s reached equilibrium, but again on a, say, 10 day time scale, we’d again reach the conclusion that this system is also not in equilibrium.

We go through state transitions

- Cooling: Not in equilibrium

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[1] There’s an excellent discussion of this in §1 [12]

- Stay: In equilibrium
- Evaporate: Not in equilibrium

Example 1.3: Window glass

- ~ 10 years $\rightarrow$ equilibrium.
- $\sim 100 - 1000$ years $\rightarrow$ not in equilibrium.

While this was given in class as an example, [15] refutes this.

Example 1.4: Battery and resistor

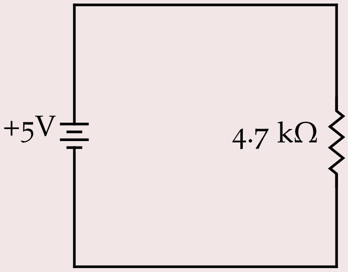


Figure 1.1: Steady non-equilibrium state.

Steady current over a small time scale, but we are persistently generating heat and draining the battery.

How do we reach equilibrium?

- We'll be looking at small systems connected to a very much larger "heat bath" or "environment". Such a system will eventually, after perhaps exchange of particles, radiation, ... will eventually take on a state that is dictated by the state of the environment.
- Completely isolated system! Molecules in a box, say, may all initially be a corner of a box. We'll have exchange of energy and momentum, and interaction with the walls of the box.

The “final” state of the system will be determined by the initial state of the molecules. Experiments of this sort have recently been performed and studied in depth (actually a very tricky problem).

2

PROBABILITY.

2.1 PROBABILITY.

2.2 PROBABILITIES.

Why do I need probabilities?

- QM: Ultimately there's an underlying quantum state, and we can only talk about probabilities. Any measurement has uncertainties, and this microscopic state forces us to use statistical methods.
- Classical chaos and unpredictability: In a many particle system, or even a system of a few interacting particles with non-linear interaction, even given an initial state to 10 decimal places, we'll end up with uncertainties. Given enough particles, even with simple interactions, we'll be forced to use statistical methods.
- Too much information: Even if we suppose that we could answer the question of where is and how fast every particle in a large collection was, what would we do with that info. We don't care about such a fine granularity state. We want to know about things like gas pressure. We are forced to discard information.

We need a systematic way of dealing with and discarding specific details. We want to use statistical methods to throw away useless information.

Analogy: Election We can poll a sample of the population if we want to attempt to predict results. We want to know things, but not what every person thinks.

A discrete probability distribution is a function satisfying

$$P(x) \geq 0 \tag{2.1a}$$

$$\sum_x P(x) = 1. \tag{2.1b}$$

Such a distribution is sketched in fig. 2.1. The probability that event is in the interval $x_1 - x_0 = \Delta x$ is

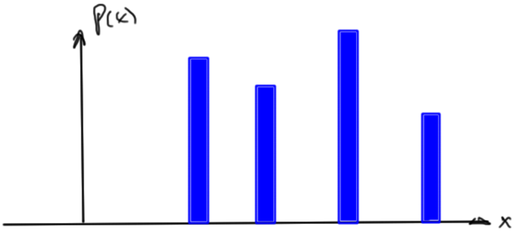


Figure 2.1: Discrete probability distribution.

$$\sum_{k=x_0}^{x_1} P(k). \tag{2.2}$$

A continuous probability is a function satisfying

$$\mathcal{P}(x) \ge 0 \tag{2.3a}$$

$$\int \mathcal{P}(x)dx = 1. \tag{2.3b}$$

One such function is sketched in fig. 2.2. The probability that an event is in the interval $x_1 - x_0 = \Delta x$ is

$$\int_{x_0}^{x_1} \mathcal{P}(x)dx. \tag{2.4}$$

2.3 CENTRAL LIMIT THEOREM.

$$x \leftrightarrow P(x). \tag{2.5}$$

Suppose we construct a sum of random variables

$$X = \sum_{i=1}^{N} x_i. \tag{2.6}$$

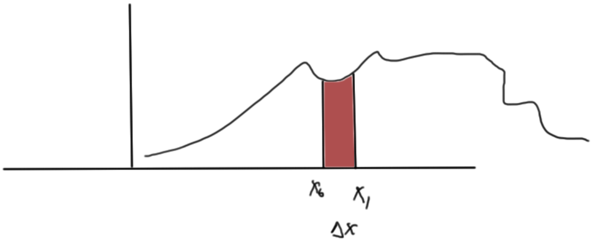


Figure 2.2: Continuous probability distribution.

Example 2.1: Gambling, coin toss

$$x \rightarrow \begin{cases} +1 & \text{Heads} \\ -1 & \text{Tails} \end{cases} \tag{2.7}$$

If we ask the question about what the total number of heads minus the total number of tails (do we have excess heads, and by how much).

Given an average of

$$\langle x \rangle = \mu, \tag{2.8}$$

and a variance (or squared standard deviation) of

$$\left\langle x^2 \right\rangle - \langle x \rangle^2 = \sigma^2, \tag{2.9}$$

we have for the sum of random variables

$$\boxed{\lim_{N \rightarrow \infty} P(X) = \frac{1}{\sigma\sqrt{2\pi N}} \exp\left(-\frac{(x - N\mu)^2}{2N\sigma^2} \right)} \tag{2.10a}$$

$$\langle X \rangle = N\mu \tag{2.10b}$$

$$\left\langle X^2 \right\rangle - \langle X \rangle^2 = N\sigma^2. \tag{2.10c}$$

A proof of this can be found in [25].

2.4 BINOMIAL DISTRIBUTION.

Example 2.2: Coin toss

Given

$$P(\text{Heads}) = \frac{1}{2} \tag{2.11a}$$

$$P(\text{Tails}) = \frac{1}{2}. \tag{2.11b}$$

Our probability distribution may look like fig. 2.3.

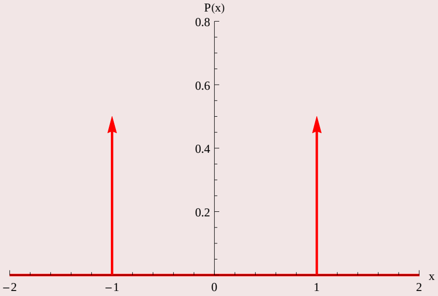


Figure 2.3: Discrete probability distribution for coin tosses.

Aside: continuous analogue Note that the continuous analogue of a distribution like this is

$$\mathcal{P}(x) = \frac{1}{2}\delta(x-1) + \frac{1}{2}\delta(x+1). \tag{2.12}$$

2 tosses:

$$(x_1, x_2) \in \{(1,1),(1,-1),(-1,1),(-1,-1)\} \tag{2.13}$$

$$X \in \{-2,0,0,2\}. \tag{2.14}$$

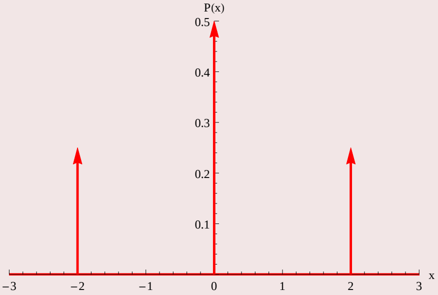


Figure 2.4: 2 tosses distribution.

3 tosses

$$(x_1, x_2, x_3) \in \{(1, 1, 1), \cdots (-1, -1, -1)\} \tag{2.15}$$

- $X = 3$: 1 way
- $X = 1$: 3 ways
- $X = -1$: 3 ways
- $X = -3$: 1 way

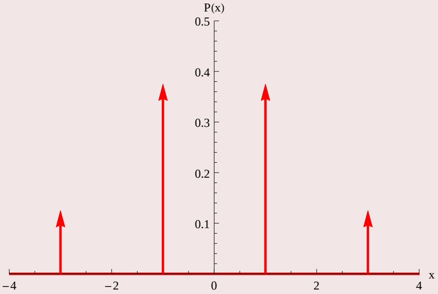


Figure 2.5: 3 tosses.

N tosses We want to find $P_N(X)$. We have

$$\text{Total Heads} - \text{Total Tails} = X \tag{2.16}$$

$$\text{Total tosses} = \text{Total Tails} + \text{Total Heads} = N. \tag{2.17}$$

So that

- Total Heads: $\frac{N+X}{2}$
- Total Tails: $\frac{N-X}{2}$

How many ways can we find a specific event such as the number of ways we find 2 heads and 1 tail? We can enumerate these $\{(H,H,T),(H,T,H),(T,H,H)\}$.

The number of ways of choosing just that combination is

$$P_N(X) = \left(\frac{1}{2}\right)^N \binom{N}{\frac{N-X}{2}} \quad \text{or} \quad \left(\frac{1}{2}\right)^N \binom{N}{\frac{N+X}{2}}, \tag{2.18}$$

we find the binomial distribution

$$P_N(X) = \begin{cases} \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N-X}{2}\right)!\left(\frac{N+X}{2}\right)!} & \text{if } X \text{ and } N \text{ have same parity} \\ 0 & \text{otherwise} \end{cases} \tag{2.19}$$

The reason for special casing this depending on the parity is because we'll have only X even or X odd, depending on whether N is even or odd. For example when $N = 3$ we have $X \in \{-3,-1,1,3\}$, and for $N = 2$ we have $X \in \{-2,0,2\}$. In particular once we have the Gaussian approximation that we are looking for (for large N), should we use an integral to approximate sum, and check for normalization as in fig. 2.6, we'd find a normalization of two instead of unity, because we are integrating over all "integers" (approximated by the continuum), instead of just the odd or the even integers.

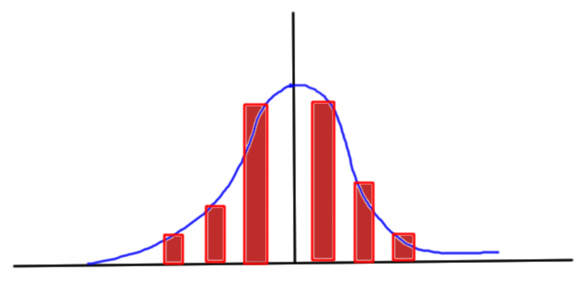


Figure 2.6: Gaussian approx. discrete distribution with parity.

For the approximation itself, we'll use the Stirling formula eq. (2.39), to find

$$P_N(X) = \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N-X}{2}\right)!\left(\frac{N+X}{2}\right)!}. \tag{2.20}$$

This can be simplified to

$$P_N(X) = \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{X^2}{2N}\right). \tag{2.21}$$

Demonstrating this limit is left to problem 2.1.

2.5 STIRLING FORMULA.

To prove the Stirling formula we'll use the Gamma (related) function

$$I(\alpha) = \Gamma(\alpha+1) = \int_0^\infty dy e^{-y} y^\alpha. \tag{2.22}$$

Observe that we have

$$I(0) = \int_0^\infty dy e^{-y} = 1, \tag{2.23}$$

and

$$\begin{aligned} I(\alpha+1) &= \int_0^\infty dy e^{-y} y^{\alpha+1} \\ &= \int_0^\infty d\left(\frac{e^{-y}}{-1}\right) y^{\alpha+1} \\ &= \cancel{\left.\left(\frac{e^{-y}}{-1} y^{\alpha+1}\right)\right|_0^\infty} - \int_0^\infty dy \left(\frac{e^{-y}}{-1}\right)(\alpha+1) y^\alpha \\ &= (\alpha+1) I(\alpha). \end{aligned} \tag{2.24}$$

This induction result means that

$$I(\alpha = N) = N!, \tag{2.25}$$

so we can use the large α behavior of this function to find approximations of the factorial. What does the innards of this integral (integrand) look like. We can plot these fig. 2.7, and find a hump for any non-zero value of α ($\alpha = 0$ is just a line)

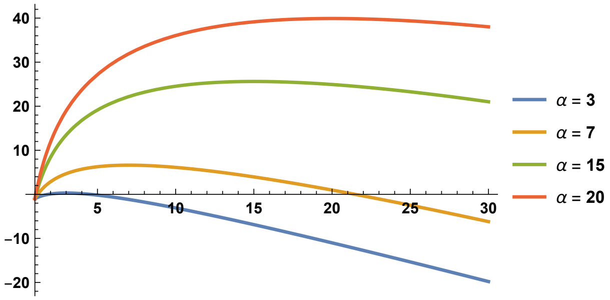


Figure 2.7: Some values of $f(y, \alpha)$.

There's a peak for large alpha that can be approximated by a Gaussian function. When α is large enough then we can ignore the polynomial boundary effects. We want to look at where this integrand is peaked. We can write

$$I(\alpha) = \int_0^\infty dy e^{-y+\alpha \ln y} = \int_0^\infty dy f(y), \tag{2.26}$$

and look for where $f(y)$ is the largest. We've set

$$f(y) = -y + \alpha \ln y, \tag{2.27}$$

and want to look at where

$$\begin{aligned} 0 &= f'(y)\big|_{y^*} \\ &= -1 + \frac{\alpha}{y^*}, \end{aligned} \tag{2.28}$$

so that the peak value

$$y^* = \alpha. \tag{2.29}$$

We now want to expand the integrand around this peak value

$$I(\alpha) = \int_0^\infty \exp\left(f(y^*) + \overset{=0}{\boxed{\left.\frac{\partial f}{\partial y}\right|_{y^*}}} (y - y^*) + \frac{1}{2} \left.\frac{\partial^2 f}{\partial y^2}\right|_{y^*} (y - y^*)^2 + \cdots \right).$$

$$(2.30)$$

We'll drop all but the quadratic term, and first need the second derivative

$$\begin{aligned} f''(y) &= \frac{d}{dy}\left(-1 + \alpha\frac{1}{y}\right) \\ &= -\alpha\frac{1}{y^2}, \end{aligned} \tag{2.31}$$

at $y = y^* = \alpha$ we have $f''(y^*) = -\frac{1}{\alpha}$, so

$$\begin{aligned} I(\alpha \gg 1) &\approx e^{f(y^*)} \int_0^\infty \exp\left(\frac{1}{2}\left.\frac{\partial^2 f}{\partial y^2}\right|_{y^*} (y - y^*)^2\right) \\ &= e^{f(\alpha)} \int_0^\infty dy e^{-\frac{(y-\alpha)^2}{2\alpha}}. \end{aligned} \tag{2.32}$$

With a substitution $x = (y - \alpha)/\sqrt{2\alpha}$, this integral can be split into a constant term and an error function component, where the error function is

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt. \tag{2.33}$$

That is

$$\begin{aligned} \int_0^\infty dy e^{-\frac{(y-\alpha)^2}{2\alpha}} &= \sqrt{2\alpha} \int_{-\alpha/\sqrt{2\alpha}}^\infty dx e^{-x^2} \\ &= \sqrt{2\alpha} \int_{-\sqrt{\alpha/2}}^0 dx e^{-x^2} + \sqrt{2\alpha} \int_0^\infty dx e^{-x^2} \\ &= \sqrt{2\alpha}\left(\frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\sqrt{\frac{\alpha}{2}}\right) + \frac{\sqrt{\pi}}{2}\right), \end{aligned} \tag{2.34}$$

or (as also verified in lecture2Figures.nb)

$$\int_0^\infty dy e^{-\frac{(y-\alpha)^2}{2\alpha}} = \sqrt{\frac{\pi\alpha}{2}}\left(\operatorname{erf}\left(\sqrt{\frac{\alpha}{2}}\right) + 1\right). \tag{2.35}$$

Note that $\operatorname{erf}(z)$ tends to unity as $x \rightarrow \infty$, as illustrated in fig. 2.8. So we have for large α

$$\int_0^\infty dy e^{-\frac{(y-\alpha)^2}{2\alpha}} \approx \sqrt{2\pi\alpha}. \tag{2.36}$$

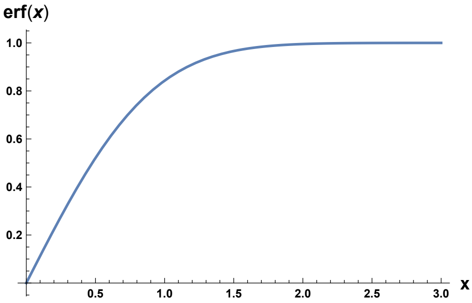


Figure 2.8: Error function.

With

$$e^{f(\alpha)} = e^{-\alpha+\alpha\ln\alpha}, \tag{2.37}$$

we have for $\alpha \gg 1$

$$I(\alpha) \approx e^{-\alpha} \overset{\alpha^\alpha}{\boxed{e^{\alpha\ln\alpha}}} \sqrt{2\pi\alpha}. \tag{2.38}$$

This gives us the Stirling approximation

$$\boxed{N! \approx \sqrt{2\pi N} N^N e^{-N}.} \tag{2.39}$$

A plot of the relative difference between the stirling approximation and the factorial $(N! - \sqrt{2\pi N} N^N e^{-N})/N!$ is given in fig. 2.9

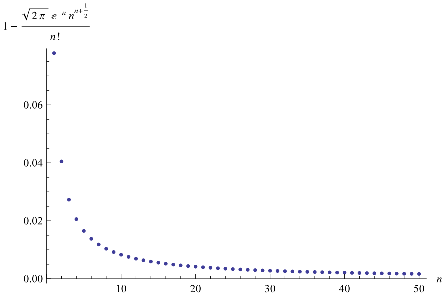


Figure 2.9: Relative error of the Stirling approximation.

2.6 STIRLING LOG APPROXIMATION.

If we only want an approximation for the logarithm, then we can get a Stirling like approximation in an easier way. I found this derivation on a scrap in my old undergrad text [11] from the thermal/quantum course I took taught by Prof. Marjoribanks.

First write the factorial in product form

$$N! = \prod_{k=0}^{N-1} (N-k), \tag{2.40}$$

so that it's logarithm is a sum

$$\ln N! = \sum_{k=0}^{N-1} \ln(N-k). \tag{2.41}$$

We can now derivatives of both sides with respect to N, ignoring the fact that N is a discrete variable. For the left hand side, writing $f = N!$, we have

$$\frac{d \ln f}{dN} = \frac{1}{f}\frac{df}{dN}. \tag{2.42}$$

Now for the right hand side

$$\begin{aligned}
&\frac{d}{dN}\sum_{k=0}^{N-1} \ln(N-k) \\
&= \sum_{k=0}^{N-1} \frac{1}{N-k} \\
&\approx \int_0^{N-1} \frac{dk}{\underbrace{\boxed{N-k}}_{\rightarrow u}} \\
&= \int_N^1 \frac{-du}{u} \\
&= \ln N - \ln 1 \\
&= \ln N.
\end{aligned} \tag{2.43}$$

Merging eq. (2.42) and eq. (2.43) into two differentials and integrating we have

$$\frac{df}{f} \approx \ln N dN. \tag{2.44}$$

Observing that

$$\begin{aligned}(x \ln x - x)' &= x\frac{1}{x} + \ln x - 1 \\ &= \ln x,\end{aligned} \tag{2.45}$$

we have

$$\ln N! \approx N \ln N - N + C. \tag{2.46}$$

Even though we are interested in large N, we note that with $N = 1$ we have

$$0 = -1 + C, \tag{2.47}$$

but this is small compared to N for large N, so we have

$$\boxed{\ln N! \approx \ln N^N - N.} \tag{2.48}$$

Exponentiating, this is

$$\boxed{N! \approx N^N e^{-N}.} \tag{2.49}$$

I think that our Professor's point at the time was that when we only care about the logarithm of $N!$ we can get away with eq. (2.48), and can avoid the complexity and care required to do a proper Stirling approximation.

2.7 PROBLEMS.

Exercise 2.1 Limit of binomial distribution (*2013 ps1, p1*)

Starting from the simple case of the binomial distribution

$$P_N(X) = 2^{-N} \frac{N!}{\left(\frac{N+X}{2}\right)!\left(\frac{N-X}{2}\right)!}, \tag{2.50}$$

derive the Gaussian distribution which results when $N \gg 1$ and $|X| \ll N$.

Answer for Exercise 2.1

We'll work with the logarithms of $P_N(X)$.

Note that the logarithm of the Stirling approximation takes the form

$$\begin{aligned}\ln a! &\approx \ln\sqrt{2\pi} + \frac{1}{2}\ln a + a\ln a - a \\ &= \ln\sqrt{2\pi} + \left(a + \frac{1}{2}\right)\ln a - a.\end{aligned} \tag{2.51}$$

Using this we have

$$\begin{aligned}&\ln\left((N+X)/2\right)! = \ln\sqrt{2\pi} \\ &\quad + \left(\frac{N+1+X}{2}\right)\left(\ln\left(1+\frac{X}{N}\right) + \ln\frac{N}{2}\right) - \frac{N+X}{2}.\end{aligned} \tag{2.52}$$

Adding $\ln\left((N+X)/2\right)! + \ln\left((N-X)/2\right)!$, we have

$$\begin{aligned}&2\ln\sqrt{2\pi} - N + \left(\frac{N+1+X}{2}\right) \times \\ &\quad \left(\ln\left(1+\frac{X}{N}\right) + \ln\frac{N}{2}\right) + \left(\frac{N+1-X}{2}\right)\left(\ln\left(1-\frac{X}{N}\right) + \ln\frac{N}{2}\right) \\ &= 2\ln\sqrt{2\pi} - N + \left(\frac{N+1}{2}\right) \times \\ &\left(\ln\left(1-\frac{X^2}{N^2}\right) + 2\ln\frac{N}{2}\right) + \frac{X}{2}\left(\ln\left(1+\frac{X}{N}\right) - \ln\left(1-\frac{X}{N}\right)\right)\end{aligned} \tag{2.53}$$

Recall that we can expand the log around 1 with the slowly converging Taylor series

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \tag{2.54a}$$

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4}, \tag{2.54b}$$

but if $x \ll 1$ the first order term will dominate, so in this case where we assume $X \ll N$, we can approximate this sum of factorial logs to first order as

$$\begin{aligned} &2 \ln \sqrt{2\pi} - N + \left(\frac{N+1}{2} \right) \left(-\frac{X^2}{N^2} + 2 \ln \frac{N}{2} \right) + \frac{X}{2} \left(\frac{X}{N} + \frac{X}{N} \right) \\ &= 2 \ln \sqrt{2\pi} - N + \frac{X^2}{N} \left(-\frac{N+1}{2N} + 1 \right) + (N+1) \ln \frac{N}{2} \\ &\approx 2 \ln \sqrt{2\pi} - N + \frac{X^2}{2N} + (N+1) \ln \frac{N}{2}. \end{aligned} \tag{2.55}$$

Putting the bits together, we have

$$\begin{aligned} \ln P_N(X) &\approx -N \ln 2 + \left(N + \frac{1}{2} \right) \ln N \\ &\quad - \cancel{N} - \ln \sqrt{2\pi} + \cancel{N} - \frac{X^2}{2N} - (N+1) \ln \frac{N}{2} \\ &= \left(-\cancel{N} + (\cancel{N}+1) \ln 2 \right) + \left(\cancel{N} + \frac{1}{2} - \cancel{N} - 1 \right) \ln N - \ln \sqrt{2\pi} - \frac{X^2}{2N} \\ &= \ln \left(\frac{2}{\sqrt{2\pi N}} \right) - \frac{X^2}{2N}. \end{aligned} \tag{2.56}$$

Exponentiating gives us the desired result

$$\boxed{P_N(X) \rightarrow \frac{2}{\sqrt{2\pi N}} e^{-\frac{X^2}{2N}}.} \tag{2.57}$$

Exercise 2.2 Binomial distribution, biased coin (*2013 ps1, p2*)

Consider the more general case of a binomial distribution where the probability of a head is r and a tail is $(1-r)$ (a biased coin). With head = -1 and tail = $+1$, obtain the binomial distribution $P_N(r, X)$ for obtaining a total of X from N coin tosses. What is the limiting form of this distribution when $N \gg 1$ and $\langle X - \langle X \rangle \rangle \ll N$? The latter condition simply means that I need to carry out any Taylor expansions in X about its mean value $\langle X \rangle$. The mean $\langle X \rangle$ can be easily computed first in terms of "r".

Answer for Exercise 2.2

Let's consider 1, 2, 3, and N tosses in sequence to understand the pattern.

1 toss The base case has just two possibilities

- Heads, $P = r$, $X = -1$
- Tails, $P = (1 - r)$, $X = 1$

If $k = 0, 1$ for $X = -1, 1$ respectively, we have

$$P_1(r, X) = r^{1-k}(1 - r)^k \tag{2.58}$$

As a check, when $r = 1/2$ we have $P_1(X) = 1/2$

2 tosses Our sample space is now a bit bigger

- (h, h), $P = r^2$, $X = -2$
- (h, t), $P = r(1 - r)$, $X = 0$
- (t, h), $P = r(1 - r)$, $X = 0$
- (t, t), $P = (1 - r)^2$, $X = 2$

Here P is the probability of the ordered sequence, but we are interested only in the probability of each specific value of X. For $X = 0$ there are $\binom{2}{1} = 2$ ways of picking a heads, tails combination.

Enumerating the probabilities, as before, with $k = 0, 1, 2$ for $X = -1, 0, 1$ respectively, we have

$$P_2(r, X) = r^{2-k}(1 - r)^k \binom{2}{k} \tag{2.59}$$

3 tosses Increasing our sample space by one more toss our possibilities for all ordered triplets of toss results is

- (h, h, h), $P = r^3$, $X = -3$
- (h, h, t), $P = r^2(1 - r)$, $X = -1$
- (h, t, h), $P = r^2(1 - r)$, $X = -1$
- (h, t, t), $P = r(1 - r)^2$, $X = 1$
- (t, h, h), $P = r^2(1 - r)$, $X = -1$

- (t, h, t), $P = r(1-r)^2$, $X = 1$
- (t, t, h), $P = r(1-r)^2$, $X = 1$
- (t, t, t), $P = r(1-r)$, $X = 0$
- (t, t, t), $P = (1-r)^3$, $X = 3$

Here P is the probability of the ordered sequence, but we are still interested only in the probability of each specific value of X. We see that we have $\binom{3}{1} = \binom{3}{2} = 3$ ways of picking some ordering of either (h, h, t) or (t, t, h)

Now enumerating the possibilities with $k = 0, 1, 2, 3$ for $X = -3, -1, 1, 3$ respectively, we have

$$P_3(r, X) = r^{3-k}(1-r)^k \binom{3}{k} \tag{2.60}$$

n tosses To generalize we need a mapping between our random variable X, and the binomial index k, but we know what that is from the fair coin problem, one of $(N - X)/2$ or $(N + X)/2$. To get the signs right, let's evaluate $(N \pm X)/2$ for $N = 3$ and $X \in \{3, -1, 1, 3\}$

Table 2.1: Mapping between k and $(N \pm X)/2$ for $N = 3$

X	$\frac{N-X}{2}$	$\frac{N+X}{2}$
-3	3	0
-1	2	1
1	1	2
3	0	3

Using this, we see that the generalization to unfair coins of the binomial distribution is

$$\boxed{P_N(r, X) = r^{\frac{N-X}{2}}(1-r)^{\frac{N+X}{2}} \frac{N!}{\left(\frac{N+X}{2}\right)!\left(\frac{N-X}{2}\right)!}} \tag{2.61}$$

Checking against the fair result, we see that we have the $1/2^N$ factor when $r = 1/2$ as expected. Let's check for $X = -1$ (two heads, one tail) to see if the exponents are right. That is

$$\begin{aligned} P_3(r,-1) &= r^{\frac{3+1}{2}}(1-r)^{\frac{3-1}{2}} \frac{3!}{\left(\frac{3-1}{2}\right)!\left(\frac{3+1}{2}\right)!} \\ &= r^2(1-r)\frac{3!}{1!\,2!} \\ &= r^2(1-r). \end{aligned} \tag{2.62}$$

Good, we've got a r^2 (two heads) term as desired.

Limiting form To determine the limiting behavior, we can utilize the Central limit theorem. We first have to calculate the mean and the variance for the $N = 1$ case. The first two moments are

$$\langle X \rangle = -1r + 1(1-r) = 1 - 2r \tag{2.63a}$$

$$\left\langle X^2 \right\rangle = (-1)^2 r + 1^2(1-r) = 1, \tag{2.63b}$$

and the variance is

$$\begin{aligned} \left\langle X^2 \right\rangle - \langle X \rangle^2 &= 1 - (1-2r)^2 \\ &= 1 - (1 - 4r + 4r^2) \\ &= 4r - 4r^2 \\ &= 4r(1-r). \end{aligned} \tag{2.64}$$

The Central Limit Theorem gives us

$$P_N(r,X) \rightarrow \frac{1}{\sqrt{8\pi N r(1-r)}} \exp\left(-\frac{(X - N(1-2r))^2}{8Nr(1-r)} \right), \tag{2.65}$$

however, we saw in [25] that this theorem was derived for continuous random variables. Here we have random variables that only take on either odd or even integer values, with parity depending on whether N is odd or even. We'll need to double the CLT result to account for this. This gives us

$$\boxed{P_N(r,X) \rightarrow \frac{1}{\sqrt{2\pi N r(1-r)}} \exp\left(-\frac{(X - N(1-2r))^2}{8Nr(1-r)} \right).}$$

(2.66)

As a check we note that for $r = 1/2$ we have $r(1-r) = 1/4$ and $1 - 2r = 0$, so we get

$$P_N(1/2, X) \to \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{X^2}{2N}\right). \tag{2.67}$$

Observe that both this and eq. (2.57) do not integrate to unity, but to 2. This is expected given the parity of the discrete random variable X. An integral normalization check is really only approximating the sum over integral values of our discrete random variable, and here we want to skip half of those values.

Exercise 2.3 Large N limit for unfair coin (*2013 ps1, p2*)

We calculated the distribution for the sum of random variables associated with N unfair coin tosses, where the probabilities were r, and $s = 1 - r$ for heads and tails respectively. Assigning heads and tails values of -1 and $+1$ respectively, the probability distribution of the sum X of the total numbers of heads and tails values for N such tosses was found to be

$$P_N(r, k) = \binom{N}{k} r^{N-k} s^k, \tag{2.68a}$$

$$k = \frac{N+X}{2}. \tag{2.68b}$$

Calculate the limit for $N \gg 1$ and $N \gg X$, without using the central limit theorem (i.e. using Stirling's approximation and Taylor series expansion for the logs.)

Answer for Exercise 2.3

Application of Stirling's approximation gives us

$$\begin{aligned} P_N(r,k) &\approx \frac{\sqrt{2\pi N}\cancel{e^{-N}}N^N}{\sqrt{2\pi(N-k)}\cancel{e^{-N+k}}(N-k)^{N-k}\sqrt{2\pi k}\cancel{e^{-k}}k^k} r^{N-k}s^k \\ &\qquad\qquad\qquad\qquad\qquad \text{Add and subtract} \\ &= \sqrt{\frac{N}{2\pi k(N-k)}} N^{N\boxed{-k+k}} \left(\frac{r}{N-k}\right)^{N-k} \left(\frac{s}{k}\right)^{k} \\ &= \sqrt{\frac{N}{2\pi k(N-k)}} \left(\frac{Nr}{N-k}\right)^{N-k} \left(\frac{Ns}{k}\right)^{k}. \end{aligned} \tag{2.69}$$

The $Nr/(N-k)$ term looks like it can probably be coerced into $1/(1-y/N)$ form that will allow for Taylor expansion of the log. With that change of variables, we find

$$k = N(1-r) - yr = Ns + yr, \tag{2.70}$$

so

$$\frac{k}{Ns} = 1 + \frac{yr}{Ns} \tag{2.71a}$$

$$\frac{N-k}{Nr} = 1 - \frac{y}{N}. \tag{2.71b}$$

This is a bit unsymmetrical, so let's write $yr = x$ so that

$$\frac{N-k}{Nr} = 1 - \frac{x}{Nr} \tag{2.72a}$$

$$\frac{k}{Ns} = 1 + \frac{x}{Ns}. \tag{2.72b}$$

We've also got terms in k and $N-k$ above that we need to express. With $k = Ns + x$, we have $N - k = Nr - x$, and

$$\begin{aligned} \frac{(N-k)k}{N} &= \frac{1}{N}(Nr-x)(Ns+x) \\ &= \frac{1}{N}(-x^2 + N^2 rs + xN(r-s)) \\ &= -\frac{x^2}{N} + Nrs + x(2r-1) \\ &\approx Nrs. \end{aligned} \tag{2.73}$$

Taking logs of eq. (2.69) we have

$$\begin{aligned}
\ln P_N(r,k) &\approx \ln\sqrt{\frac{1}{2\pi Nrs}} - (Nr-x)\ln\left(1-\frac{x}{Nr}\right) \\
&\quad - (Ns+x)\ln\left(1+\frac{x}{Ns}\right) \\
&\approx \ln\sqrt{\frac{1}{2\pi Nrs}} + (x-Nr)\left(-\frac{x}{Nr}-\frac{1}{2}\left(\frac{x}{Nr}\right)^2\right) \\
&\quad - (x+Ns)\left(\frac{x}{Ns}-\frac{1}{2}\left(\frac{x}{Ns}\right)^2\right) \\
&= \ln\sqrt{\frac{1}{2\pi Nrs}} + \frac{1}{2}\frac{x^2}{N}\left(\frac{1}{r}+\frac{1}{s}\right) \\
&\quad - \frac{x^2}{N}\left(\frac{1}{r}+\frac{1}{s}\right) + \frac{x^3}{(N)^2}\left(\frac{1}{r^2}-\frac{1}{s^2}\right).
\end{aligned} \tag{2.74}$$

Dropping the $O(1/N^2)$ term and noting that

$$\begin{aligned}
-\frac{1}{2}\left(\frac{1}{r}+\frac{1}{s}\right) &= -\frac{1}{2rs}\left(r+(1-r)\right) \\
&= -\frac{1}{2rs}.
\end{aligned} \tag{2.75}$$

We have

$$P_N(r,k) \approx \frac{1}{\sqrt{2\pi Nrs}} \exp\left(-\frac{x^2}{2Nrs}\right). \tag{2.76}$$

With

$$\begin{aligned}
x &= k - Ns \\
&= \frac{1}{2}(N+X) - Ns \\
&= \frac{1}{2}(N+X-2Ns) \\
&= \frac{1}{2}(X+N(1-2s)) \\
&= \frac{1}{2}(X-N(1-2r)),
\end{aligned} \tag{2.77}$$

we have

$$\boxed{P_N(r,k) \approx \frac{1}{\sqrt{2\pi Nrs}} \exp\left(-\frac{(X-N(1-2r))^2}{8Nrs}\right).} \tag{2.78}$$

This recovers the result obtained with the central limit theorem (after that result was adjusted to account for parity).

Exercise 2.4 Large N approximation of binomial distribution

In §11.1 [12] it is stated that the binomial distribution

$$\rho(n) = \binom{N}{n} p^n (1-p)^{N-n}, \tag{2.79}$$

has the large N approximation of a Poisson distribution

$$\rho(n) = \frac{(\alpha v)^n}{n!} e^{-\alpha v}, \tag{2.80}$$

where $N/V = \alpha$ is the density and $p = v/V$, the probability (of finding the particle in a volume v of a total volume V in this case).

Show this.

Answer for Exercise 2.4

This is another Stirling's approximation problem. With $p = v\alpha/N$, and working with log expansion of the $N!$ and $(N-n)!$ terms of the binomial coefficient we have

$$\begin{aligned}
\ln \rho &\approx \left(N + \frac{1}{2}\right) \ln N - \cancel{N} - \left(N - n + \frac{1}{2}\right) \ln(N-n) \\
&\quad + (\cancel{N} - n) - \ln n! + n \ln p + (N-n) \ln(1-p) \\
&= \left(N + \frac{1}{2}\right) \ln N - \left(N - n + \frac{1}{2}\right) \ln(N-n) \\
&\quad - n - \ln n! + n \ln \frac{v\alpha}{N} + (N-n) \ln \left(1 - \frac{v\alpha}{N}\right) \\
&= \left(N + \frac{1}{2} - N + n - \frac{1}{2} - n\right) \ln N - \left(N - n + \frac{1}{2}\right) \ln \left(1 - \frac{n}{N}\right) \\
&\quad - n - \ln n! + n \ln v\alpha + (N-n) \ln \left(1 - \frac{v\alpha}{N}\right) \\
&\approx \ln \frac{(v\alpha)^n}{n!} - n - \left(N - n + \frac{1}{2}\right) \left(-\frac{n}{N} - \frac{1}{2}\frac{n^2}{N^2}\right) \\
&\quad + (N-n) \left(-\frac{v\alpha}{N} - \frac{1}{2}\frac{v^2\alpha^2}{N^2}\right) \\
&= \ln \frac{(v\alpha)^n}{n!} - n + n \left(1 - \frac{n}{N} + \frac{1}{2N}\right) \left(1 + \frac{1}{2}\frac{n}{N}\right) \\
&\quad - v\alpha \left(1 - \frac{n}{N}\right) \left(1 + \frac{1}{2}\frac{v\alpha}{N}\right) \\
&\approx \ln \frac{(v\alpha)^n}{n!} - n + n - v\alpha.
\end{aligned} \tag{2.81}$$

Here all the $1/N$ terms have been dropped, and we are left with

$$\ln \rho \approx \ln \frac{(v\alpha)^n}{n!} - v\alpha, \tag{2.82}$$

which is the logarithm of the Poisson distribution as desired.

Exercise 2.5 Central limit theorem, IID. (*2013 midterm 1, q1*)

Our midterm had a question asking what the central limit theorem said about a product of random variables. Say, $Y = X_1 X_2 \cdots X_N$, where the random variables X_k had mean and variance μ and σ^2 respectively.

Answer for Exercise 2.5

Following https://math.stackexchange.com/q/82133, the central limit theorem can be applied to the logarithm of such a product (provided all the random variables are strictly positive). For example, if we write

$$Z = \ln Y = \sum_{k=1}^{N} \ln X_k, \tag{2.83}$$

now we have something that the central limit theorem can be applied to. It will be interesting to see if this is the answer that the midterm was looking for. It is one that wasn't obvious enough for me to think of it at the time. In fact, it's also not something that we can even state a precise central limit theorem result for, because we don't have enough information to state the mean and variance of the logarithm of the random vars X_k. For example, if the random vars are continuous, we have

$$\langle \ln X \rangle = \int \rho(X) \ln X dX. \tag{2.84}$$

Conceivably, if we knew all the moments of X we could expand the logarithm in Taylor series. In fact we need more than that. If we suppose that $0 < X < 2\mu$, so that $|X/\mu - 1| \le 1$, we can write

$$\begin{aligned}\ln X &= \ln \mu + (X - \mu) \\ &= \ln \mu + \ln \left(1 + \left(\frac{X}{\mu} - 1 \right) \right) \\ &= \ln \mu + \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\left(\frac{X}{\mu} - 1 \right)^k}{k}.\end{aligned} \tag{2.85}$$

With such a bounding for the random variable X we'd have

$$\langle \ln X \rangle = \ln \mu + \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} \left\langle \left(\frac{X}{\mu} - 1 \right)^k \right\rangle. \tag{2.86}$$

We need all the higher order moments of $X/\mu - 1$ (or equivalently all the moments of X), and can't just assume that $\langle \ln X \rangle = \ln \mu$.

Suppose instead that we just assume that it is possible to find the mean and variance of the logarithm of the random variables X_k, say

$$\mu_{\ln} = \langle \ln X \rangle \tag{2.87a}$$

$$\sigma_{\ln}^2 = \left\langle (\ln X)^2 \right\rangle - \langle \ln X \rangle^2 . \tag{2.87b}$$

Now we can state that for large N the random variable Z has a distribution approximated by

$$\rho(Z) = \frac{1}{\sigma_{\ln}\sqrt{2\pi N}} \exp\left(-\frac{(\ln X - N\mu_{\ln})^2}{2N\sigma_{\ln}^2} \right) . \tag{2.88}$$

Given that, we can say that the random variable $Y = X_1 X_2 \cdots X_N$, is the exponential of random variable with the distribution given approximately (for large N) by eq. (2.88).

As it turned out, this is exactly the sort of answer that was expected of us on the midterm. Had I thought of application of the logarithm to the problem, I would have been able to answer that correctly. As it turned out, I wasn't that clever.

DIFFUSION, MAXWELL DISTRIBUTION.

3

3.1 SPATIAL RANDOM WALK.

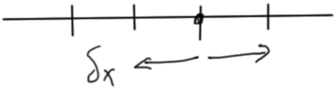


Figure 3.1: One dimensional random walk.

One dimensional case With a time interval δt, our total time is

$$t = N \delta t. \tag{3.1}$$

We form a random variable for the total distance moved

$$X = \sum_{i=1}^{N} \delta x_i \tag{3.2}$$

$$\left\langle X \right\rangle = \sum_{i=1}^{N} \left\langle \delta x_i \right\rangle = 0 \tag{3.3}$$

$$\begin{aligned}
\left\langle X^2 \right\rangle &= \left\langle \sum_{i=1}^{N} \delta x_i \sum_{j=1}^{N} \delta x_j \right\rangle \\
&= \sum_{i,j=1}^{N} \left\langle \delta x_i \delta x_j \right\rangle \\
&= \sum_{i=1}^{N} \left\langle (\delta x_i)^2 \right\rangle \\
&= \sum_{i=1}^{N} \left\langle (\pm \delta x)^2 \right\rangle \\
&= (\delta x)^2 \sum_{i=1}^{N} 1 \\
&= N (\delta x)^2 .
\end{aligned} \tag{3.4}$$

In the above, I assume that the cross terms were killed with an assumption of uncorrelation.

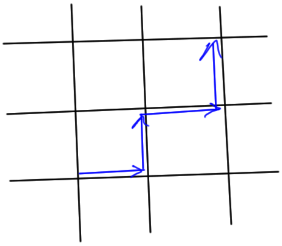


Figure 3.2: Two dimensional random walk.

Two dimensional case The two dimensional case can be used for either spatial generalization of the above, or a one dimensional problem with time evolution as illustrated in fig. 3.3.

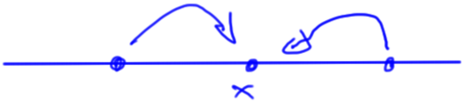


Figure 3.3: Spatial and temporal evolution.

$$
\begin{aligned}
\mathcal{P}(x,t) &= \frac{1}{2}\mathcal{P}(x+\delta x, t-\delta t) + \frac{1}{2}\mathcal{P}(x-\delta x, t-\delta t) \\
&\approx \frac{1}{2}\left(\mathcal{P}(x, t-\delta t) + \cancel{\frac{\partial \mathcal{P}}{\partial x}(x, t-\delta t)}\delta x + \frac{1}{2}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x, t-\delta t)(\delta x)^2 \right) \\
&\quad + \frac{1}{2}\left(\mathcal{P}(x, t-\delta t) - \cancel{\frac{\partial \mathcal{P}}{\partial x}(x, t-\delta t)}\delta x + \frac{1}{2}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x, t-\delta t)(\delta x)^2 \right) \\
&= \mathcal{P}(x, t-\delta t) + \frac{1}{2}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x, t-\delta t)(\delta x)^2.
\end{aligned}
\tag{3.5}
$$

Since we have a small correction $(\delta x)^2 \approx 0$, this is approximately

$$
\mathcal{P}(x,t) \approx \mathcal{P}(x, t-\delta t) + \frac{1}{2}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x,t)(\delta x)^2. \tag{3.6}
$$

$$\delta t \frac{\partial \mathcal{P}}{\partial t}(x,t) \approx \frac{1}{2}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x,t)(\delta x)^2 \tag{3.7}$$

$$\frac{\partial \mathcal{P}}{\partial t}(x,t) = \overset{\equiv D\text{, the diffusion constant}}{\boxed{\frac{1}{2}\frac{(\delta x)^2}{\delta t}}} \frac{\partial^2 \mathcal{P}}{\partial x^2}(x,t) \tag{3.8}$$

We see that random microscopics lead to a well defined macroscopic equation.

$$N\mathcal{P}(x,t) = \overset{\text{particle density or concentration}}{\boxed{C(x,t)}}. \tag{3.9}$$

3.2 CONTINUITY EQUATION AND FICKS LAW.

Requirements for well defined diffusion results

1. Particle number conservation (local)

   Imagine that we put a drop of ink in water. We'll see the ink gradually spread out and appear to disappear. But the particles are still there. We require particle number concentration for well defined diffusion results.

   This is expressed as a continuity equation and illustrated in fig. 3.4.

   $$\frac{\partial \mathcal{P}}{\partial t} + \frac{\partial J}{\partial x} = 0. \tag{3.10}$$

   Here J is the probability current density, and $\mathcal{P}$ is the probability density.

2. Phenomenological law, or Fick's law.

   $$J = -D\frac{\partial \mathcal{P}}{\partial x}. \tag{3.11}$$

   The probability current is linearly proportional to the gradient of the probability density.

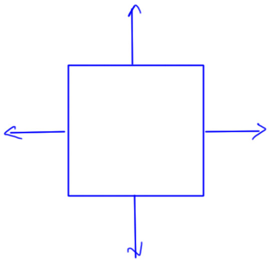


Figure 3.4: probability changes by flows through the boundary.

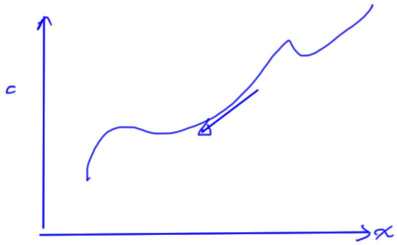


Figure 3.5: Probability current proportional to gradient.

Combining the above we have

$$0 = \frac{\partial \mathcal{P}}{\partial t} + \frac{\partial}{\partial x}\left(-D\frac{\partial \mathcal{P}}{\partial x}\right). \tag{3.12}$$

So for constant diffusion rates D we also arrive at the random walk diffusion result

$$\boxed{\frac{\partial \mathcal{P}}{\partial t} = D\frac{\partial^2 \mathcal{P}}{\partial x^2}.} \tag{3.13}$$

3.3 RANDOM WALK IN VELOCITY SPACE.

We are imagining that we are following one particle (particle i) in a gas, initially propagating without interaction at some velocity $\mathbf{v}_i$. After one collision we have

$$\mathbf{v}_i(1) = \mathbf{v}_i(0) + \Delta\mathbf{v}_i(1). \tag{3.14}$$

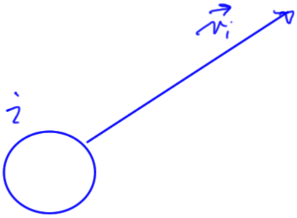


Figure 3.6: Single atom velocity view.

After two collisions

$$\mathbf{v}_i(2) = \mathbf{v}_i(1) + \Delta\mathbf{v}_i(2). \tag{3.15}$$

After N_c collisions

$$\mathbf{v}_i(N_c) = \mathbf{v}_i(0) + \Delta\mathbf{v}_i(1) + \Delta\mathbf{v}_i(2) + \cdots + \Delta\mathbf{v}_i(N_c). \tag{3.16}$$

Where N_c is the number of collisions. We expect

$$\left\langle \mathbf{v}_i \right\rangle = \mathbf{v}_i(0) \tag{3.17a}$$

$$\left\langle \mathbf{v}_i^2 \right\rangle \propto N_c \tag{3.17b}$$

$$\mathcal{P}_{N_c}(\mathbf{v}) \propto e^{-\frac{(\mathbf{v}-\mathbf{v}_0)^2}{2N_c}}. \tag{3.17c}$$

Here the mean is expected to be zero because the individual collisions are thought to be uncorrelated.

We'll see that there is something wrong with this, and will figure out how to fix this in the next lecture.

In particular, the kinetic energy of any given particle is

$$\mathrm{KE}_i = \frac{1}{2} m \mathbf{v}_i^2, \tag{3.18}$$

and the sum of this is fixed for the complete system.

However, if we sum the kinetic energy squares above eq. (3.17b) shows that it is growing with the number of collisions. Fixing this we will arrive at the Maxwell Boltzmann distribution.

3.4 LEAD UP TO MAXWELL DISTRIBUTION FOR GASES.

For the random walk, after a number of collisions N_c, we found that a particle (labeled the ith) will have a velocity

$$\mathbf{v}_i(N_c) = \mathbf{v}_i(0) + \sum_{l=1}^{N_c} \Delta \mathbf{v}_i(l). \tag{3.19}$$

We argued that the probability distribution for finding a velocity $\mathbf{v}$ was as in fig. 3.7, and

$$\mathcal{P}_{N_c}(\mathbf{v}_i) \propto \exp\left(-\frac{(\mathbf{v}_i - \mathbf{v}_i(0))^2}{2N_c}\right). \tag{3.20}$$

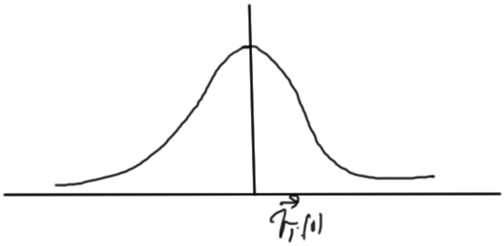


Figure 3.7: Velocity distribution w/o KE conservation.

3.5 WHAT WENT WRONG?.

However, we know that this must be wrong, since we require

$$T = \frac{1}{2}\sum_{i=1}^{n} \mathbf{v}_i^2 = \text{conserved}. \tag{3.21}$$

Where our argument went wrong is that when the particle has a greater than average velocity, the effect of a collision will be to slow it down. We have to account for

- Fluctuations → "random walk"
- Dissipation → "slowing down"

There were two ingredients to diffusion (the random walk), these were

- Conservation of particles

  $$\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} = 0. \tag{3.22}$$

  We can also think about a conservation of a particles in a velocity space

  $$\frac{\partial c}{\partial t}(v, t) + \frac{\partial j_v}{\partial v} = 0 \tag{3.23}$$

  where j_v is a probability current in this velocity space.

- Fick's law in velocity space takes the form

  $$j_v = -D \frac{\partial c}{\partial v}(v, t) \tag{3.24}$$

The diffusion results in an "attempt" to flatten the distribution of the concentration as in fig. 3.8.

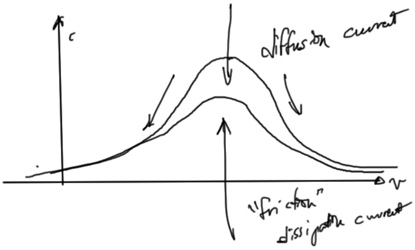


Figure 3.8: Friction required to oppose diffusion pressure.

We'd like to add to the diffusion current an extra frictional like term

$$j_v = -D \frac{\partial c}{\partial v}(v, t) - \eta v c(v) \tag{3.25}$$

We want something directed opposite to the velocity and the concentration

$$\text{Diffusion current} \equiv -D \frac{\partial c}{\partial v}(v, t) \tag{3.26a}$$

$$\text{Dissipation current} \equiv -\eta v c(v,t). \tag{3.26b}$$

This gives

$$\begin{aligned}
\frac{\partial c}{\partial t}(v,t) &= -\frac{\partial j_v}{\partial v} \\
&= -\frac{\partial}{\partial v}\left(-D\frac{\partial c}{\partial v}(v,t) - \eta v c(v)\right) \\
&= D\frac{\partial^2 c}{\partial v^2}(v,t) + \eta\frac{\partial}{\partial v}\left(v c(v,t)\right).
\end{aligned} \tag{3.27}$$

Can we find a steady state solution to this equation when $t \rightarrow \infty$? For such a steady state we have

$$0 = \frac{d^2 c}{dv^2} + \frac{\eta}{D}\frac{d}{dv}\left(vc\right). \tag{3.28}$$

Integrating once we have

$$\frac{dc}{dv} = -\frac{\eta}{D} v c + \text{constant}, \tag{3.29}$$

and supposing that $dc/dv = 0$ at $v = 0$, integrating once more we have

$$\boxed{c(v) \propto \exp\left(-\frac{\eta v^2}{2D}\right).} \tag{3.30}$$

This is the Maxwell-Boltzmann distribution, illustrated in fig. 3.9.

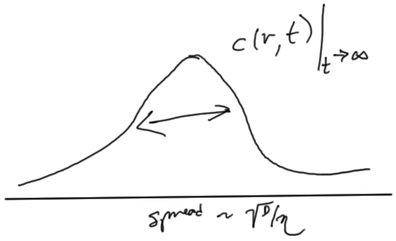


Figure 3.9: Maxwell-Boltzmann distribution.

The concentration $c(v)$ has a probability distribution.

Calculating $\left\langle v^2 \right\rangle$ from this distribution we can identify the D/η factor.

$$\begin{aligned}
\left\langle v^2 \right\rangle &= \frac{\int v^2 e^{-\eta v^2/2D} dv}{\int e^{-\eta v^2/2D} dv} \\
&= \frac{\frac{D}{\eta} \int v \frac{d}{dv} \left(-e^{-\eta v^2/2D} \right) dv}{\int e^{-\eta v^2/2D} dv} \\
&= -\frac{D}{\eta} \frac{\int -e^{-\eta v^2/2D} dv}{\int e^{-\eta v^2/2D} dv} \\
&= \frac{D}{\eta}.
\end{aligned} \tag{3.31}$$

This also happens to be the energy in terms of temperature (we can view this as a definition of the temperature for now), writing

$$\frac{1}{2} m \left\langle \mathbf{v}^2 \right\rangle = \frac{1}{2} m \left(\frac{D}{\eta} \right) = \frac{1}{2} k_{\mathrm{B}} T. \tag{3.32}$$

Here

$$k_{\mathrm{B}} = \text{Boltzmann constant} \tag{3.33a}$$

$$T = \text{absolute temperature.} \tag{3.33b}$$

3.6 EQUILIBRIUM STEADY STATES.

Fluctuations ↔ Dissipation

$$\boxed{\frac{D}{\eta} = \frac{k_{\mathrm{B}} T}{m}.} \tag{3.34}$$

This is a specific example of the more general fluctuation-dissipation theorem.

Generalizing to 3D Fick's law and the continuity equation in 3D are respectively

$$\mathbf{j} = -D \boldsymbol{\nabla}_{\mathbf{v}} c(\mathbf{v}, t) - \eta \mathbf{v} c(\mathbf{v}, t) \tag{3.35a}$$

$$\frac{\partial}{\partial t} c(\mathbf{v}, t) + \boldsymbol{\nabla}_{\mathbf{v}} \cdot \mathbf{j}(\mathbf{v}, t) = 0. \tag{3.35b}$$

As above we have for the steady state

$$\begin{aligned} 0 &= \frac{\partial}{\partial t} c(\mathbf{v}, t) \\ &= \boldsymbol{\nabla}_{\mathbf{v}} \cdot \left(-D \boldsymbol{\nabla}_{\mathbf{v}} c(\mathbf{v}, t) - \eta \mathbf{v} c(\mathbf{v}, t) \right) \\ &= -D \boldsymbol{\nabla}_{\mathbf{v}}^2 c - \eta \boldsymbol{\nabla}_{\mathbf{v}} \cdot (\mathbf{v} c). \end{aligned} \tag{3.36}$$

Integrating once over all space

$$D \boldsymbol{\nabla}_{\mathbf{v}} c = -\eta \mathbf{v} c + \text{vector constant, assumed zero} \tag{3.37}$$

This is three sets of equations, one for each component v_α of $\mathbf{v}$

$$\frac{\partial c}{\partial v_\alpha} = -\frac{\eta}{D} v_\alpha c. \tag{3.38}$$

So that our steady state equation is

$$c(\mathbf{v}, t \to \infty) \propto \exp \left(-\frac{v_x^2 + v_y^2 + v_z^2}{2(D/\eta)} \right). \tag{3.39}$$

Computing the average 3D squared velocity for this distribution, we have

$$\begin{aligned} \frac{1}{2} m \left\langle \mathbf{v} \cdot \mathbf{v} \right\rangle &= \frac{\int dv_x dv_y dv_z \left(v_x^2 + v_y^2 + v_z^2 \right) \exp \left(-\frac{v_x^2+v_y^2+v_z^2}{2(D/\eta)} \right)}{\int dv_x dv_y dv_z \exp \left(-\frac{v_x^2+v_y^2+v_z^2}{2(D/\eta)} \right)} \\ &= \frac{\int dv_x v_x^2 \exp \left(-\frac{v_x^2}{2(D/\eta)} \right)}{\int dv_x \exp \left(-\frac{v_x^2}{2(D/\eta)} \right)} + \frac{\int dv_y v_y^2 \exp \left(-\frac{v_y^2}{2(D/\eta)} \right)}{\int dv_y \exp \left(-\frac{v_y^2}{2(D/\eta)} \right)} \\ &\quad + \frac{\int dv_z v_z^2 \exp \left(-\frac{v_z^2}{2(D/\eta)} \right)}{\int dv_z \exp \left(-\frac{v_z^2}{2(D/\eta)} \right)} \\ &= 3 \left(\frac{1}{2} k_{\mathrm{B}} T \right) \\ &= \frac{3}{2} k_{\mathrm{B}} T. \end{aligned} \tag{3.40}$$

For each component v_α the normalization kills off all the contributions for the other components, leaving us with the usual $3k_\mathrm{B}T/2$ ideal gas law kinetic energy.

3.7 PROBLEMS.

Exercise 3.1 Diffusion (*2013 ps2, p1*)

The usual diffusion equation for the probability density in one dimension is given by

$$\frac{\partial P}{\partial t}(x,t) = D\frac{\partial^2 P}{\partial x^2}(x,t), \tag{3.41}$$

where D is the diffusion constant. Define the Fourier components of the probability distribution via

$$P(x,t) = \int_{-\infty}^{\infty} \frac{dk}{2\pi}\tilde{P}(k,t)\exp\left(ikx\right) \tag{3.42a}$$

$$\tilde{P}(k,t) = \int_{-\infty}^{\infty} dx P(x,t)\exp\left(-ikx\right). \tag{3.42b}$$

This is useful since the diffusion equation is linear in the probability and each Fourier component will evolve independently. Using this, solve the diffusion equation to obtain $P(k,t)$ in Fourier space given the initial $\tilde{P}(k,0)$.

a. Assuming an initial Gaussian profile

$$P(x,0) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{x^2}{2\sigma^2}\right), \tag{3.43}$$

obtain the probability density $P(x,t)$ at a later time t. (NB: Fourier transform, get the solution, transform back.) Schematically plot the profile at the initial time and a later time.

b. A small modulation on top of a uniform value Let the probability density be proportional to

$$\frac{1}{L} + A\sin(k_0 x), \tag{3.44}$$

at an initial time $t = 0$. Assume this is in a box of large size L, but ignore boundary effects except to note that it will help to normalize the constant piece, assuming the oscillating piece integrates to zero. Also note that we have to assume $A < 1/L$ to ensure that the probability density is positive. Obtain $P(x,t)$ at a later time t. Roughly how long does the modulation take to decay away? Schematically plot the profile at the initial time and a later time.

Answer for Exercise 3.1

Inserting the transform definitions we have

$$\begin{aligned}
0 &= \left(\frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} \right) P \\
&= \left(\frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} \right) \int_{-\infty}^{\infty} \frac{dk}{2\pi} \tilde{P}(k,t) \exp\left(ikx\right) \\
&= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \left(\frac{\partial}{\partial t} \tilde{P}(k,t) + k^2 D \tilde{P}(k,t) \right) \exp\left(ikx\right),
\end{aligned} \tag{3.45}$$

We conclude that

$$0 = \tilde{P}(k,t) + k^2 D \tilde{P}(k,t), \tag{3.46}$$

or

$$\tilde{P}(k,t) = A(k) e^{-k^2 D t}. \tag{3.47}$$

If the Fourier transform of the distribution is constant until time t, so that $\tilde{P}(k, t < 0) = \tilde{P}(k, 0)$, we can write

$$\boxed{\tilde{P}(k,t) = \tilde{P}(k,0) e^{-k^2 D t}.} \tag{3.48}$$

The time evolution of the distributions transform just requires multiplication by the decreasing exponential factor $e^{-k^2 D t}$.

Propagator for the diffusion equation We can also use this to express the explicit time evolution of the distribution

$$\begin{aligned}
P(x,t) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \tilde{P}(k,0) e^{-k^2 D t} \exp\left(ikx\right) \\
&= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{-\infty}^{\infty} dx' P(x',0) \exp\left(-ikx'\right) e^{-k^2 D t} \exp\left(ikx\right) \\
&= \int_{-\infty}^{\infty} dx' P(x',0) \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left(-k^2 D t + ik(x - x')\right).
\end{aligned} \tag{3.49}$$

Our distribution time evolution is given by convolve with a propagator function

$$P(x,t) = \int dx' P(x',0) G(x',x) \tag{3.50a}$$

$$G(x',x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left(-k^2 Dt + ik(x-x')\right). \tag{3.50b}$$

For $t \ge 0$ we can complete the square, finding that this propagator is

$$\begin{aligned} G(x',x) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left(-k^2 Dt + ik(x-x')\right) \\ &= \exp\left(\left(\frac{i(x-x')}{2\sqrt{Dt}}\right)^2\right) \times \\ &\quad \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left(-\left(k\sqrt{Dt} + \frac{i(x-x')}{2\sqrt{Dt}}\right)^2\right), \end{aligned} \tag{3.51}$$

or

$$\boxed{G(x',x) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x-x')^2}{4Dt}\right).} \tag{3.52}$$

A schematic plot of this function as a function of t for fixed $x - x'$ is plotted in fig. 3.10.

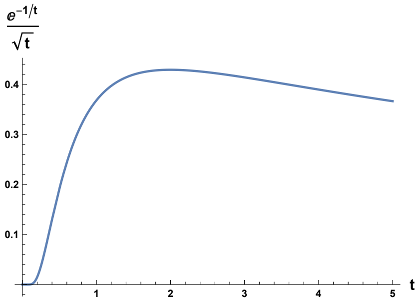


Figure 3.10: Propagator for the diffusion equation.

Part a. Gaussian For the Gaussian of eq. (3.43) we compute the initial time Fourier transform

$$\begin{aligned}\tilde{P}(k) &= \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2} - ikx\right) \\ &= \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\left(\frac{\sqrt{2\sigma^2}}{2} ki\right)^2\right) \\ &\int_{-\infty}^{\infty} dx \exp\left(-\left(\frac{x}{\sqrt{2\sigma^2}} + \frac{\sqrt{2\sigma^2}}{2} ki\right)^2\right) = \exp\left(-\frac{\sigma^2 k^2}{2}\right).\end{aligned} \tag{3.53}$$

The time evolution of the generating function is

$$\tilde{P}(k,t) = \exp\left(-\frac{\sigma^2 k^2}{2} - Dk^2 t\right), \tag{3.54}$$

and we can find our time evolved probability density by inverse transforming

$$\begin{aligned}P(x,t) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left(-\frac{\sigma^2 k^2}{2} - Dk^2 t + ikx\right) \\ &= \exp\left(i \frac{x}{2\sqrt{\frac{\sigma^2}{2} + Dt}}\right)^2 \int_{-\infty}^{\infty} \frac{dk}{2\pi} \\ &\quad \exp\left(-\left(k\sqrt{\frac{\sigma^2}{2} + Dt} + i\frac{x}{2\sqrt{\frac{\sigma^2}{2} + Dt}}\right)^2\right).\end{aligned} \tag{3.55}$$

For $t \geq 0$ this is

$$\boxed{P(x,t) = \frac{1}{\sqrt{2\pi\left(\sigma^2 + 2Dt\right)}} \exp\left(-\frac{x^2}{2\left(\sigma^2 + 2Dt\right)}\right).} \tag{3.56}$$

As a check, we see that this reproduces the $t = 0$ value as expected. A further check using Mathematica (attemptAtProblemSet2Problem1iiIntegrals.nb) applying the propagator eq. (3.52), also finds the same result as this manual calculation.

This is plotted for $D = \sigma = 1$ in fig. 3.11 for a couple different times $t \geq 0$.

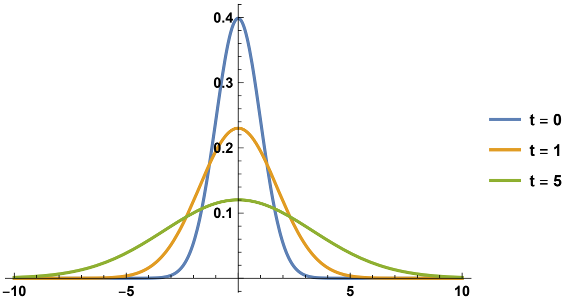


Figure 3.11: Gaussian PDF time evolution with diffusion.

Part b. Boxed constant with small oscillation The normalization of the distribution depends on the interval boundaries. With the box range given by $x \in [a, a+L]$ we have

$$\int_a^{a+L} dx \left(\frac{1}{L} + A \sin(k_0 x) \right) dx = 1 - \frac{A}{k_0} \left(\cos(k_0(a+L)) - \cos(k_0 a) \right). \tag{3.57}$$

With an even range for box $x \in [-L/2, L/2]$ this is unity.

To find the distribution at a later point in time we can utilize the propagator

$$P(x,t) = \int_{-L/2}^{L/2} dx' \frac{1}{2\sqrt{\pi D t}} \left(\frac{1}{L} + A \sin(k_0 x') \right) \exp\left(-\frac{(x'-x)^2}{2\sqrt{Dt}} \right). \tag{3.58}$$

Let's write this as

$$P(x,t) = P_{\text{rect}}(x,t) + P_{\sin}(x,t) \tag{3.59a}$$

$$P_{\text{rect}}(x,t) = \frac{1}{2L\sqrt{\pi D t}} \int_{-L/2}^{L/2} dx' \exp\left(-\frac{(x'-x)^2}{2\sqrt{Dt}} \right) \tag{3.59b}$$

$$\begin{aligned} P_{\sin}(x,t) = \frac{A}{2\sqrt{\pi D t}} &\int_{-L/2}^{L/2} dx' \sin(k_0 x') \\ &\exp\left(-\frac{(x'-x)^2}{2\sqrt{Dt}} \right). \end{aligned} \tag{3.59c}$$

Applying a $u = (x' - x)/\sqrt{4Dt}$ change of variables for the first term, we can reduce it to a difference of error functions

$$\begin{aligned}P_{\text{rect}}(x,t) &= \frac{1}{L}\int_{-L/2}^{L/2} dx' \frac{1}{2\sqrt{\pi D t}} \exp\left(-\frac{(x'-x)^2}{2\sqrt{Dt}}\right) \\ &= \frac{1}{L\sqrt{\pi}} \int_{-\frac{L/2+x}{2\sqrt{Dt}}}^{\frac{L/2-x}{2\sqrt{Dt}}} du e^{-u^2} \\ &= \frac{1}{2L}\left(\operatorname{erf}\left(\frac{L/2-x}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}}\right)\right).\end{aligned} \tag{3.60}$$

Following Mathematica, lets introduce a two argument error function for the difference between two points

$$\operatorname{erf}(z_0, z_1) \equiv \operatorname{erf}(z_1) - \operatorname{erf}(z_0). \tag{3.61}$$

Using that our rectangular function's time evolution can be written

$$P_{\text{rect}}(x,t) = \frac{1}{2L} \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}}, \frac{L/2-x}{2\sqrt{Dt}}\right). \tag{3.62}$$

For $L = D = 1$, and $t = 10^{-8}$, this is plotted in fig. 3.12. Somewhat surprisingly, this difference of error functions does appear to result in a rectangular function for small t.

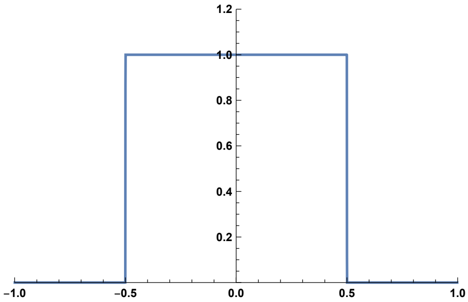


Figure 3.12: Rectangular part of the probability distribution, small t.

The time evolution of this non-oscillation part of the probability distribution is plotted as a function of both t and x in fig. 3.13.

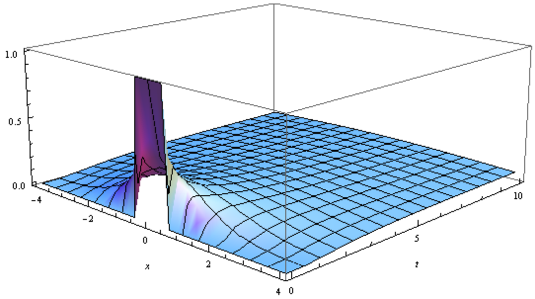


Figure 3.13: Time evolution of the rectangular part of the probability distribution.

For the sine piece we can also find a solution in terms of (complex) error functions

$$\begin{aligned}
&P_{\sin}(x,t) \\
&= A\int_{-L/2}^{L/2} dx' \frac{1}{2\sqrt{\pi D t}} \sin(k_0 x') \exp\left(-\frac{(x'-x)^2}{2\sqrt{Dt}}\right) \\
&= \frac{A}{\sqrt{\pi}} \int_{-\frac{L/2+x}{2\sqrt{Dt}}}^{\frac{L/2-x}{2\sqrt{Dt}}} du \sin(k_0(x+2u\sqrt{Dt}))e^{-u^2} \\
&= \frac{A}{2i\sqrt{\pi}} \int_{-\frac{L/2+x}{2\sqrt{Dt}}}^{\frac{L/2-x}{2\sqrt{Dt}}} du \left(e^{ik_0(x+2u\sqrt{Dt})} - e^{-ik_0(x+2u\sqrt{Dt})}\right) e^{-u^2}
\end{aligned} \tag{3.63}$$

,

which reduces to

$$\begin{aligned}
&P_{\sin}(x,t) = \\
&\quad \frac{A}{4i} e^{-k_0^2 D t} e^{ik_0 x} \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}} - ik_0\sqrt{Dt}, \frac{L/2-x}{2\sqrt{Dt}} - ik_0\sqrt{Dt}\right) \\
&\quad - \frac{A}{4i} e^{-k_0^2 D t} e^{-ik_0 x} \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}} + ik_0\sqrt{Dt}, \frac{L/2-x}{2\sqrt{Dt}} + ik_0\sqrt{Dt}\right).
\end{aligned} \tag{3.64}$$

This is plotted for $A = D = L = 1$, $k_0 = 8\pi$, and $t = 10^{-8}$ in fig. 3.14.

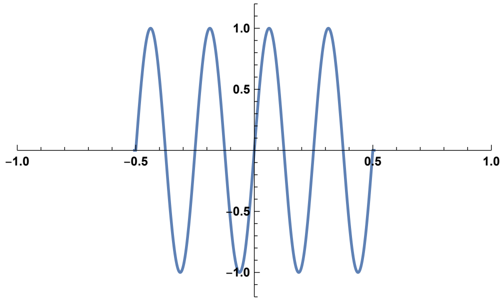


Figure 3.14: Verification at $t \rightarrow 0$, sine like diffusion.

The diffusion of this, again for $A = D = L = 1$, $k_0 = 8\pi$, and $t \in [10^{-5}, 0.01]$ is plotted in fig. 3.15. Again we see that we have the expected sine for small t.

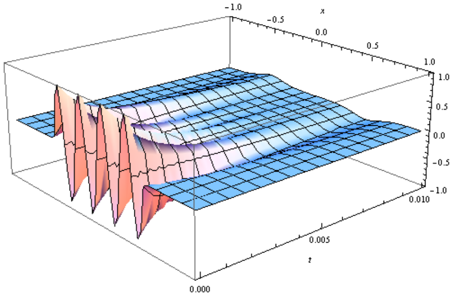


Figure 3.15: Diffusion of the oscillatory term.

Putting both the rectangular and the windowed sine portions of the probability distribution together, we have the diffusion result for the entire distribution

$$\boxed{\begin{aligned} P(x,t) &= \frac{1}{2L}\operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}}, \frac{L/2-x}{2\sqrt{Dt}}\right) \\ &\quad + \frac{A}{4i} e^{-k_0^2 Dt + ik_0 x} \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}} - ik_0\sqrt{Dt}, \frac{L/2-x}{2\sqrt{Dt}} - ik_0\sqrt{Dt}\right) \\ &\quad - \frac{A}{4i} e^{-k_0^2 Dt - ik_0 x} \operatorname{erf}\left(-\frac{L/2+x}{2\sqrt{Dt}} + ik_0\sqrt{Dt}, \frac{L/2-x}{2\sqrt{Dt}} + ik_0\sqrt{Dt}\right) \end{aligned}}$$

(3.65)

It is certainly ugly looking! We see that the oscillation die off is dependent on the $\exp(-k_0^2 D t)$ term. In time

$$t = \frac{1}{k_0^2 D}, \tag{3.66}$$

that oscillation dies away to $1/e$ of its initial amplitude. This dispersion is plotted at times $t = 10^{-5}$ and $t = 1/(k_0^2 D)$ for $L = D = 1$, $k_0 = 8\pi$ and $A = 1/2$ in fig. 3.16.

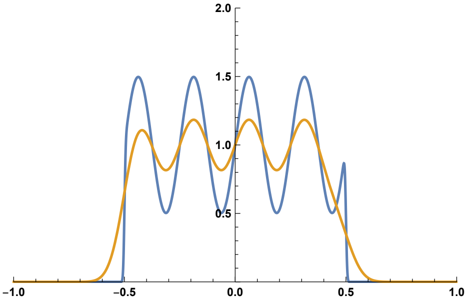


Figure 3.16: Initial time distribution and dispersion of the oscillatory portion to $1/e$ of initial amplitude.

Similar to the individual plots of $P_{\text{rect}}(x,t)$ and $P_{\sin}(x,t)$ above, we plot the time evolution of the total probability dispersion $P(x,t)$ in fig. 3.17. We see in the plots above that the rectangular portion of this distribution will also continue to flatten over time after most of the oscillation has also died off.

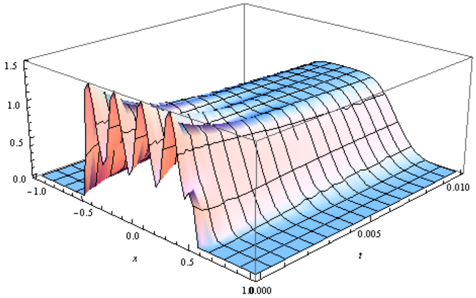


Figure 3.17: Diffusion of uniform but oscillating probability distribution.

An easier solution for the sinusoidal part After working this problem, talking with classmates about how they solved it (because I was sure I'd done this windowed oscillating distribution the hard way), I now understand what was meant by "ignore boundary effects". That is, ignore the boundary effects in the sinusoid portion of the distribution. I didn't see how we could ignore the boundary effects because doing so would make the sine Fourier transform non-convergent. Ignoring pesky ideas like convergence we can "approximate" the Fourier transform of the windowed sine as

$$\begin{aligned}\tilde{P}_{\mathrm{sin}}(k) &\approx A \int_{-\infty}^{\infty} \sin(k_0 x) e^{-ikx} dx \\ &= \frac{A}{2i} \int_{-\infty}^{\infty} \left(e^{i(k_0 - k)x} - e^{-i(k_0+k)x} \right) dx \\ &= \frac{A\pi}{i} \left(\delta(k - k_0) - \delta(k + k_0) \right).\end{aligned} \tag{3.67}$$

Now we can inverse Fourier transform the diffusion result with ease since we've got delta functions. That is

$$\begin{aligned}P_{\mathrm{sin}}(x,t) &\approx \frac{1}{2\pi} \frac{A\pi}{i} \int \left(\delta(k - k_0) - \delta(k + k_0) \right) e^{-Dk^2 t} e^{ikx} dk \\ &= A e^{-D k_0^2 t} \frac{e^{ik_0 x} - e^{-ik_0 x}}{2i} \\ &= A e^{-D k_0^2 t} \sin(k_0 x).\end{aligned} \tag{3.68}$$

Plotted in fig. 3.18 we see things die off uniformly, since we didn't start with a windowed sine. Together, the rectangular function and the sine, after diffusion is plotted in fig. 3.19. Because the sine wasn't confined to the window, we see initial time oscillations, but they die off, looking fairly similar to what we saw when the initial conditions were completely zero outside of the window.

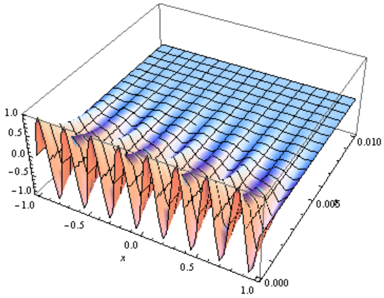


Figure 3.18: Diffusion of (non-windowed) sine.

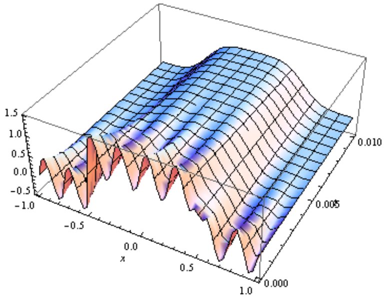


Figure 3.19: Diffusion of rectangular function and (non-windowed) sine composition.

My expectation is that we'd get exactly the same result with application of the propagator. Let's try that.

$$u = (x' - x)/\sqrt{4Dt}$$

$$\begin{aligned}
P_{\sin}(x,t) &= \frac{A}{\sqrt{4\pi D t}} \int \sin(k_0 x') \exp \boxed{\left(-\frac{(x'-x)^2}{4Dt}\right)} dx' \\
&= \frac{A}{\sqrt{\pi}} \int \sin\left(k_0\left(\sqrt{4Dt}u + x\right)\right) e^{-u^2} du \\
&= \frac{A}{2i\sqrt{\pi}} \int \left(e^{ik_0\left(\sqrt{4Dt}u + x\right)} - e^{-ik_0\left(\sqrt{4Dt}u + x\right)}\right) e^{-u^2} du \\
&= \frac{A}{2i\sqrt{\pi}} \int du \left(e^{ik_0 x} \exp\left(-\left(u - ik_0\sqrt{Dt}\right)^2\right) \exp\left(\left(-ik_0\sqrt{Dt}\right)^2\right)\right. \\
&\qquad \left. - e^{-ik_0 x} \exp\left(-\left(u + ik_0\sqrt{Dt}\right)^2\right) \exp\left(\left(ik_0\sqrt{Dt}\right)^2\right)\right).
\end{aligned} \tag{3.69}$$

This is just

$$P_{\text{sin}}(x,t) = Ae^{-k_0^2 Dt}\sin(k_0 x). \tag{3.70}$$

Observe that we get exactly the same result if we use the propagator on this non-windowed sine. It is just harder to do the calculation.

Given this, I wasn't sure what to make of the grading response: You cannot use the same Green function/propagator as the first case since the boundary conditions differ. This is why you have probability density leaking our of $\pm L/2$ at $t > 0$. Better to simply perform the Fourier transform on the initial condition and use the first order differential equation. e.g. propagate time and inverse Fourier transform back.

I'd asked of this: There was no use of boundary conditions in the derivation of the propagator, at least that I can see. This appears to be confirmed by using it to calculate the diffusion of the sine portion of the probability density (i.e. eq. (3.68) vs. eq. (3.70)). I think the leaking out of the probability density at $t > 0$ is strictly due to the diffusion of the rectangle function. It has to go somewhere if it diffuses. Because I applied the propagator to a windowed sine instead of an unbounded one, that leakage of the initial rectangular function is more evident in my first plot, but exists regardless.

Eric's response was interesting: There are two points of contention here, I think:

1. That the same propagator (or Green's function) can be applied equally to both situations,
2. That the sinusoidal decay can be obtained equally well with both the Green's function and the FT/iFT method.

Let's focus on 1. Finding Green's functions for the diffusion equation require specification of boundary conditions (much like how solving linear diff equations, one needs to specify boundary conditions). For instance, in the "box" problem, the Green's function should have the boundary condition of $G(x, x', t, t') = 0$ if $|x|$

or $|x'| > L/2$ (recall that Green's function is the density profile at time t' and location x' if one were to inject a delta function density profile at time t and location x). The Green's function you found in the "free" system case does not satisfy this condition, hence it is the wrong Green's function for the problem. As you found, performing exact calculations using that propagator results in densities flowing outside the box, which is not possible by definition.

Another way to see that the Green's function is wrong: the Green's function you found has translational symmetry. Namely, $G(x, x', t, t') = G(x - x', t, t')$. But imposing the box should break the translational symmetry of the problem, so the Green's function shouldn't have this symmetry any more (unlike the "free" system case in part 1).

Point here being that it is incorrect to use the same Green's function in both part 1 and part 2 and will lead to wrong answers like densities flowing out of the box.

Now the second contention: I agree that if you took the $L \rightarrow \infty$ limit, the two calculations should give you the same answer. This is simply because the $L \rightarrow \infty$ limit the boundaries don't matter any more. This is not in contradiction with what I just said because we are taking a limiting procedure.

All in all, marks were deducted because densities leaked out of $|x| > L/2$, which is unphysical (and if I'm not mistaken, looking at graphs fig. 3.13 and fig. 3.15, this behaviour plagued both the constant and the sinusoidal parts). I appreciate you solving the problem from a different angle, but the answer simply ended up being qualitatively wrong in that regard. You did obtain the decay factor which is good and your answer would've been correct if the boundaries of the box didn't exist. For problems like the box, it is far simpler (as you have found) to perform direct calculations since the boundary conditions are not trivial to into account.

My final thoughts. Because we are ignoring boundary conditions for the sine, treating it as unbounded, is why the Green's function works for that case (even if it isn't correct for the box itself).

I don't think there's actually any leakage of probability for the sine portion (I just shouldn't have graphed it outside of the "box"). I say this because using this symmetric interval, the sine doesn't contribute any non-zero total probability. The total area under the sine is zero (as a PV integral $\lim_{L->\infty}\int_{-L}^{L}$), and that's true for any point in time.

I'm curious how to calculate a Green's function for the box boundary conditions. I don't recall encountering one with boundary conditions before this, and obviously the usual Fourier transform method doesn't work.

Exercise 3.2 Generating function (*2013 ps2, p2*)

The Fourier transform of the probability distribution defined above $\tilde{P}(k)$ is called the "generating function" of the distribution. Show that the n-th derivative of this generating function $\partial^n \tilde{P}(k)/\partial k^n$ at the origin $k = 0$ is related to the n-th moment of the distribution function defined via $\langle x^n \rangle = \int dx P(x) x^n$. We will later see that the "partition function" in statistical mechanics is closely related to this concept of a generating function, and derivatives of this partition function can be related to thermodynamic averages of various observables.

Answer for Exercise 3.2

$$
\begin{aligned}
\left.\frac{\partial^n}{\partial k^n}\tilde{P}(k)\right|_{k=0} &= \frac{\partial^n}{\partial k^n}\left.\left(\int_{-\infty}^{\infty} dx P(x)\exp\left(-ikx\right)\right)\right|_{k=0} \\
&= \left.\left(\int_{-\infty}^{\infty} dx P(x)(-ix)^n \exp\left(-ikx\right)\right)\right|_{k=0} \\
&= (-i)^n \int_{-\infty}^{\infty} dx P(x) x^n \\
&= (-i)^n \left\langle x^n \right\rangle .
\end{aligned}
\tag{3.71}
$$

Exercise 3.3 State counting - polymer (*2013 ps3, p2*)

A typical protein is a long chain molecule made of very many elementary units called amino acids - it is an example of a class of such macromolecules called polymers. Consider a protein made N amino acids, and assume each amino acid is like a sphere of radius a. As a toy model assume that the protein configuration is like a random walk with each amino acid being one "step", i.e., the center-to-center vector from one amino acid to the next is a random vector of length $2a$ and ignore any issues with overlapping spheres (so-called "excluded volume" constraints). Estimate the spatial extent of this protein in space. Typical proteins assume a compact form in order to be functional. In this case, taking the constraint of nonoverlapping spheres, estimate the radius of such a compact protein assuming it has an overall spherical shape with fully packed amino acids (ignore holes in the packing, and use only volume ratios to make this estimate). With $N = 300$ and $a \approx 5\text{Å}$, estimate these sizes for the random walk case as well as the compact globular case.

Answer for Exercise 3.3

We are considering a geometry like that of fig. 3.20, depicted in two dimensions for ease of illustration.

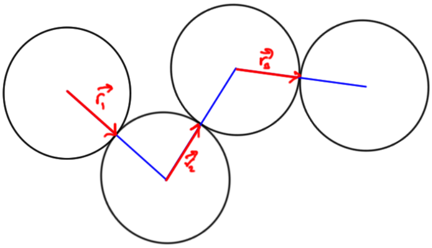


Figure 3.20: Touching "spheres".

From the geometry, if $\mathbf{c}_k$ is the vector to the center of the kth sphere, we have for some random unit vector $\hat{\mathbf{r}}_k$

$$\mathbf{c}_{k+1} = \mathbf{c}_k + 2a\hat{\mathbf{r}}_k. \tag{3.72}$$

Proceeding recursively, writing d_N, and $n = N - 1 > 0$, we have for the difference of the positions of the first and last centers of the chain

$$\begin{aligned} d_N &= \left|\mathbf{c}_N - \mathbf{c}_1\right| \\ &= 2a \left| \sum_{k=1}^{n} \hat{\mathbf{r}}_k \right| \\ &= 2a \left(\sum_{k,m=1}^{n} \hat{\mathbf{r}}_k \cdot \hat{\mathbf{r}}_m \right)^{1/2} \\ &= 2a \left(n + 2 \sum_{1 \le k < m \le n} \hat{\mathbf{r}}_k \cdot \hat{\mathbf{r}}_m \right)^{1/2} \\ &= 2a\sqrt{n} \left(1 + \frac{2}{n} \sum_{1 \le k < m \le n} \hat{\mathbf{r}}_k \cdot \hat{\mathbf{r}}_m \right)^{1/2} . \end{aligned} \tag{3.73}$$

The $\hat{\mathbf{r}}_k$'s clearly cannot be completely random since we have a constraint that $\hat{\mathbf{r}}_k \cdot \hat{\mathbf{r}}_{k+1} > -\cos \pi/3$, or else two adjacent spheres will overlap. There will also be overlapping constraints for longer portions of the chain that are harder to express. We are ignoring both such constraints, and seek the ensemble average of all systems of the form eq. (3.73).

Employing random azimuthal and polar angular variables θ_k, and ϕ_k, we have

$$\hat{\mathbf{r}}_k = \begin{bmatrix} \sin\theta_k \cos\phi_k \\ \sin\theta_k \sin\phi_k \\ \cos\theta_k, \end{bmatrix} \tag{3.74}$$

so that the average polymer length is

$$\begin{aligned}\langle d_N \rangle = 2a\sqrt{n}\left(\frac{1}{(2\pi)(\pi)}\right)^n \times \\ \int_{\theta_j\in[0,\pi]} d\theta_1 d\theta_2\cdots d\theta_n \int_{\phi_j\in[0,2\pi]} d\phi_1 d\phi_2\cdots d\phi_n \times \\ \left(1 + \frac{2}{n}\sum_{1\le k<m\le n} \sin\theta_k\cos\phi_k\sin\theta_m\cos\phi_m \right. \\ + \sin\theta_k\sin\phi_k\sin\theta_m\sin\phi_m \\ \left. + \cos\theta_k\cos\theta_m\right)^{1/2}.\end{aligned} \tag{3.75}$$

Observing that even $\int\sqrt{1+a\cos\theta}d\theta$ is an elliptic integral, we don't have any hope of evaluating this in closed form. However, to first order, we have

$$\begin{aligned}\langle d_N \rangle \approx 2a\sqrt{n}\left(\frac{1}{(2\pi)(\pi)}\right)^n \left(2\pi^2\right)^n \\ + 2a\sqrt{n}\left(\frac{1}{(2\pi)(\pi)}\right)^n \left(2\pi^2\right)^{n-2}\left(\frac{1}{2}n(n+1)\right)\frac{1}{n}\times \\ \int_0^\pi d\theta \int_0^\pi d\theta' \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \times \\ \left(\sin\theta\cos\phi\sin\theta'\cos\phi' + \sin\theta\sin\phi\sin\theta'\sin\phi' + \cos\theta\cos\theta'\right)\end{aligned} \tag{3.76}$$

The $\int_0^{2\pi}\cos\phi$ integrals kill off the first term, the $\int_0^{2\pi}\sin\phi$ integrals kill of the second, and the $\int_0^\pi\cos\theta$ integral kill of the last term, and we are left with just

$$d_N \approx 2a\sqrt{N-1}. \tag{3.77}$$

Ignoring the extra $2\times a$ of the end points, and assuming that for large N we have $\sqrt{N-1}\approx\sqrt{N}$, the spatial extent of the polymer chain is

$$\boxed{d_N \approx 2a\sqrt{N}.} \tag{3.78}$$

Grading remark: You have computed the end to end length. The radius of gyration is a better measure.

Spherical packing Assuming the densest possible spherical packing, a face centered cubic [22], as in fig. 3.21, we see that the density of such a spherical packing is

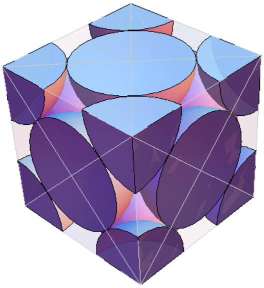


Figure 3.21: Element of a face centered cubic.

$$\eta_{\text{FCC}} = \frac{\left(8 \times \frac{1}{8} + 6 \times \frac{1}{2}\right) \frac{4}{3}\pi r^3}{\left(\sqrt{8r^2}\right)^3} = \frac{\pi}{\sqrt{18}}. \tag{3.79}$$

With a globular radius of R and an atomic radius of a, and density η we have

$$\eta \frac{4}{3}\pi R^3 = N \frac{4}{3}\pi a^3, \tag{3.80}$$

so that the globular radius R is

$$\boxed{R_N(\eta) = a \sqrt[3]{\frac{N}{\eta}}.} \tag{3.81}$$

Some numbers With $N = 300$ and $a \approx 5\text{Å}$, and ignoring spaces (i.e. $\eta = 1$, for a non-physical infinite packing), our globular diameter is approximately

$$2 \times 5\text{Å}\sqrt[3]{300} \approx 67\text{Å}. \tag{3.82}$$

This is actually not much different than the maximum spherical packing of an FCC lattice, which results a slightly larger globular cluster diameter

$$2 \times 5\text{Å}\sqrt[3]{300\sqrt{18}/\pi} \approx 74\text{Å}. \tag{3.83}$$

Both however, are much less than the end to end length of the random walk polymer chain

$$2(5\text{Å})\sqrt{300} \approx 173\text{Å}. \tag{3.84}$$

Exercise 3.4 1D random walk (*2013 midterm 1, pr. 2*)

Random walk in 1D by unit steps. With the probability to go right of p and a probability to go left of $1 - p$ what are the first two moments of the final position of the particle?

Answer for Exercise 3.4

First we need the probabilities.

One step: $N = 1$ Our distance (from the origin) can only be $X = \pm 1$.

$$P_{X=-1} = p^0(1-p)^1, \tag{3.85}$$

$$P_{X=1} = p^1(1-p)^{1-1}. \tag{3.86}$$

Two steps: $N = 2$ We now have three possibilities

$$P_{X=-2} = p^0(1-p)^{2-0}, \tag{3.87}$$

$$P_{X=0} = 2p^1(1-p)^{2-1}, \tag{3.88}$$

$$P_{X=2} = p^2(1-p)^{2-2}. \tag{3.89}$$

Three steps: $N = 3$ We now have three possibilities

$$P_{X=-3} = p^0(1-p)^{3-0}, \tag{3.90}$$

$$P_{X=-1} = 3p^1(1-p)^{3-1}, \tag{3.91}$$

$$P_{X=1} = 3p^2(1-p)^{3-2}, \tag{3.92}$$

$$P_{X=3} = p^3(1-p)^{3-3}. \tag{3.93}$$

General case The pattern is pretty clear, but we need a mapping from the binomial index to the final distance. With an index k, and a guess

$$D(k) = ak + b, \tag{3.94}$$

where

$$D(0) = -N = b, \tag{3.95}$$

and

$$D(N) = aN + b = (a-1)N = N. \tag{3.96}$$

So

$$D(k) = 2k - N, \tag{3.97}$$

and

$$k = \frac{D+N}{2}. \tag{3.98}$$

Our probabilities are therefore

$$\boxed{P_{X=D} = \binom{N}{(N+D)/2} p^{(N+D)/2}(1-p)^{(N-D)/2}.} \tag{3.99}$$

First moment For the expectations let's work with k instead of D, so that the expectation is

$$\begin{aligned}
\langle X \rangle &= \sum_{k=0}^{N}(2k-N)\binom{N}{k} p^k (1-p)^{N-k} \\
&= 2\sum_{k=0}^{N} k\frac{N!}{(N-k)!\,k!} p^k (1-p)^{N-k} - N \\
&= 2Np\sum_{k=1}^{N} \frac{(N-1)!}{(N-1-(k-1))!\,(k-1)!} p^{k-1}(1-p)^{N-1-(k-1)} - N \\
&= 2Np\sum_{s=0}^{N-1} \binom{N-1}{s} p^s (1-p)^{N-1-s} - N.
\end{aligned} \tag{3.100}$$

This gives us

$$\boxed{\langle X \rangle = N(2p-1).} \tag{3.101}$$

Second moment

$$\begin{aligned}
\left\langle X^2 \right\rangle &= \sum_{k=0}^{N} (2k - N)^2 \binom{N}{k} p^k (1-p)^{N-k} \\
&= 4 \sum_{k=0}^{N} k^2 \binom{N}{k} p^k (1-p)^{N-k} - 4N^2 p + N^2 \\
&= 4Np \sum_{k=1}^{N} k \frac{(N-1)!}{(N-1-(k-1))!\,(k-1)!} p^{k-1} (1-p)^{N-k} \\
&\quad + N^2 (1 - 4p) \\
&= 4Np \sum_{s=0}^{N} (s+1) \frac{(N-1)!}{(N-1-s)!\,s!} p^s (1-p)^{N-1-s} + N^2(1-4p) \\
&= 4Np((N-1)p + 1) + N^2(1-4p) \\
&= N^2(1 - 4p + 4p^2) + 4Np(1-p).
\end{aligned} \tag{3.102}$$

So the second moment is

$$\boxed{\left\langle X^2 \right\rangle = N^2 (1-2p)^2 + 4Np(1-p)} \tag{3.103}$$

From this we see that the variance is just this second term

$$\sigma^2 = \left\langle X^2 \right\rangle - \left\langle X \right\rangle^2 = 4Np(1-p). \tag{3.104}$$

Exercise 3.5 Ergodicity in 1D system (*2013 midterm pr. 4*)

Consider a system with N particles constrained to one dimension. Is this system ergodic?

Answer for Exercise 3.5

A portion of this system is illustrated in fig. 3.22.

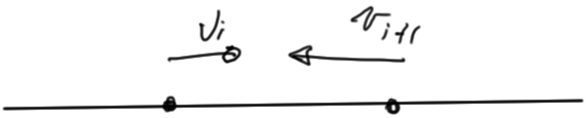


Figure 3.22: One dimensional collision of particles.

Start with a pair of collisions and work out that the velocities are exchanged.

$$(v_i, v_{i+1}) \rightarrow (v_{i+1}, v_i) \tag{3.105}$$

This is verified in midtermQ4twoEqualMassesCollision.nb , but is also easy to show. Our momentum and energy conservation relationships, for equal masses, are

$$v_1 + v_2 = w_1 + w_2, \tag{3.106a}$$

$$v_1^2 + v_2^2 = w_1^2 + w_2^2. \tag{3.106b}$$

Solving for w_1 we have

$$\begin{aligned} v_1^2 + v_2^2 &= w_1^2 + (v_1 + v_2 - w_1)^2 \\ &= 2w_1^2 + v_1^2 + v_2^2 + 2v_1 v_2 + 2(v_1 + v_2)w_1, \end{aligned} \tag{3.107}$$

or

$$\begin{aligned} 0 &= \left(w_1 - \frac{v_1 + v_2}{2}\right)^2 + v_1 v_2 - \left(\frac{v_1 + v_2}{2}\right)^2 \\ &= \left(w_1 - \frac{v_1 + v_2}{2}\right)^2 + \frac{4v_1 v_2 - v_1^2 - v_2^2 - 2v_1 v_2}{4} \\ &= \left(w_1 - \frac{v_1 + v_2}{2}\right)^2 - \frac{(v_1 - v_2)^2}{4}. \end{aligned} \tag{3.108}$$

This gives us

$$w_1 = \frac{v_1 + v_2}{2} \pm \left|\frac{v_1 - v_2}{2}\right|. \tag{3.109}$$

This yields solutions

$$\{w_1, w_2\} \in \{v_1, v_2\}, \{v_2, v_1\}. \tag{3.110}$$

The first corresponds to conservation of energy and momentum prior to the collision, and the second, the post collision event where we have an exchange of velocities. This won't result in all the phase space being explored (i.e. a non-ergodic process), and was meant to show that things are extremely restrictive in 1D.

PHASE SPACE.

4

4.1 PHASE SPACE.

Now let's switch directions a bit and look at how to examine a more general system described by the phase space of generalized coordinates

$$\{x_{i_\alpha}(t), p_{i_\alpha}(t)\} \tag{4.1}$$

Here

- i = molecule or particle number
- $\alpha \in \{x, y, z\}$
- Dimension = $N_{\text{particles}} \times 2 \times d$, where d is the physical space dimension.

The motion in phase space will be governed by the knowledge of how each of these coordinates change for all the particles. Assuming a Hamiltonian H and recalling that $H = \dot{x}p - \mathcal{L}$, gives us

$$\frac{\partial H}{\partial p} = \dot{x} \tag{4.2a}$$

$$\frac{\partial H}{\partial x} = -\frac{\partial \mathcal{L}}{\partial x} = -\frac{dp}{dt}, \tag{4.2b}$$

we have for the following set of equations describing the entire system

$$\frac{d}{dt} x_{i_\alpha}(t) = \frac{\partial H}{\partial p_{i_\alpha}} \tag{4.3a}$$

$$\frac{d}{dt} p_{i_\alpha}(t) = -\frac{\partial H}{\partial x_{i_\alpha}}. \tag{4.3b}$$

Example, 1D SHO

$$H = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}kx^2. \tag{4.4}$$

This has phase space trajectories as in fig. 4.1. An exploratory purely phase space review of this 1D harmonic oscillator system can be found in appendix C.

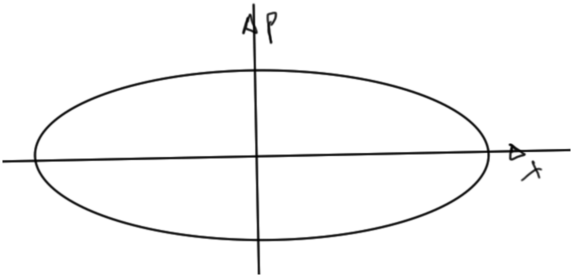


Figure 4.1: Classical SHO phase space trajectories.

4.2 MOTION IN PHASE SPACE.

Classical system: $\mathbf{x}_i, \mathbf{p}_i$ with dimensionality

$$\overset{x,p}{\boxed{2}}\underset{\text{space dimension}}{\boxed{d}}\overset{\text{Number of particles}}{\boxed{N}}. \tag{4.5}$$

Hamiltonian H is the "energy function"

$$H = \overset{\text{Kinetic energy}}{\boxed{\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}}} + \underset{\text{Potential energy}}{\boxed{\sum_{i=1}^N V(\mathbf{x}_i)}} + \overset{\text{Internal energy}}{\boxed{\sum_{i<j}^N \Phi(\mathbf{x}_i - \mathbf{x}_j)}} \tag{4.6}$$

$$\dot{\mathbf{p}}_i = \mathbf{F} = \text{force} \tag{4.7a}$$

$$\dot{\mathbf{x}}_i = \frac{\mathbf{p}_i}{m}. \tag{4.7b}$$

Expressed in terms of the Hamiltonian this is

$$\dot{p}_{i_\alpha} = -\frac{\partial H}{\partial x_{i_\alpha}} \tag{4.8a}$$

$$\dot{x}_{i_\alpha} = \frac{\partial H}{\partial p_{i_\alpha}}. \tag{4.8b}$$

In phase space we can have any number of possible trajectories as illustrated in fig. 4.2.

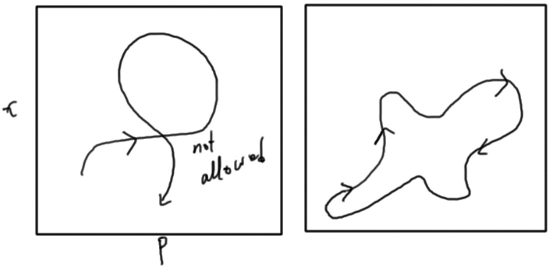


Figure 4.2: Disallowed and allowed phase space trajectories.

4.3 LIOUVILLE'S THEOREM.

We are interested in asking the question of how the density of a region in phase space evolves as illustrated in fig. 4.3. We define a phase space density

$$\rho(p_{i_\alpha}, x_{i_\alpha}, t), \tag{4.9}$$

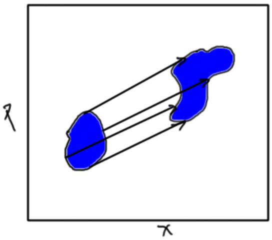


Figure 4.3: Evolution of a phase space volume.

and seek to demonstrate Liouville's theorem, that the phase space density does not change. To do so, consider the total time derivative of the phase space density

$$
\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial\rho}{\partial t} + \sum_{i_\alpha} \frac{\partial p_{i_\alpha}}{\partial t}\frac{\partial\rho}{\partial p_{i_\alpha}} + \frac{\partial x_{i_\alpha}}{\partial t}\frac{\partial\rho}{\partial x_{i_\alpha}} \\
&= \frac{\partial\rho}{\partial t} + \sum_{i_\alpha} \dot{p}_{i_\alpha}\frac{\partial\rho}{\partial p_{i_\alpha}} + \dot{x}_{i_\alpha}\frac{\partial\rho}{\partial x_{i_\alpha}} \\
&= \frac{\partial\rho}{\partial t} + \sum_{i_\alpha} \frac{\partial\left(\rho\dot{p}_{i_\alpha}\right)}{\partial p_{i_\alpha}} + \frac{\partial\left(\rho\dot{x}_{i_\alpha}\right)}{\partial x_{i_\alpha}} - \rho\left(\frac{\partial\dot{p}_{i_\alpha}}{\partial p_{i_\alpha}} + \frac{\partial\dot{x}_{i_\alpha}}{\partial x_{i_\alpha}}\right) \\
&= \frac{\partial\rho}{\partial t} + \underbrace{\boxed{\sum_{i_\alpha}\left(\frac{\partial p_{i_\alpha}}{\partial t}\frac{\partial(\rho\dot{p}_{i_\alpha})}{\partial p_{i_\alpha}} + \frac{\partial x_{i_\alpha}}{\partial t}\frac{\partial(\rho\dot{x}_{i_\alpha})}{\partial x_{i_\alpha}}\right)}}_{\equiv \boldsymbol{\nabla}\cdot\mathbf{j}} \\
&\quad - \rho\sum_{i_\alpha}\underbrace{\boxed{\left(-\frac{\partial^2 H}{\partial p_{i_\alpha}\partial x_{i_\alpha}} + \frac{\partial^2 H}{\partial x_{i_\alpha}\partial p_{i_\alpha}}\right)}}_{=0}.
\end{aligned}
\tag{4.10}
$$

We've implicitly defined a current density $\mathbf{j}$ above by comparing to the continuity equation

$$
\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{j} = 0. \tag{4.11}
$$

By inserting Hamilton's equations we find that

$$
\frac{\partial\dot{p}_{i_\alpha}}{\partial p_{i_\alpha}} + \frac{\partial\dot{x}_{i_\alpha}}{\partial x_{i_\alpha}} = 0. \tag{4.12}
$$

Here we have

$$\rho(\dot{x}_{i_\alpha}, \dot{p}_{i_\alpha}) \rightarrow \text{current in phase space.} \tag{4.13}$$

Usually we have

$$\mathbf{j}_{\text{usual}} \sim \rho \mathbf{v} \tag{4.14a}$$

$$\mathbf{j} = -D \boldsymbol{\nabla} \rho, \tag{4.14b}$$

but we don't care about this diffusion relation here. With this identification the implication is that

$$\frac{d\rho}{dt} = 0. \tag{4.15}$$

We can say that flow in phase space is very similar to an "incompressible fluid".

4.4 TIME AVERAGES, AND POINCARÉ RECURRENCE THEOREM.

We want to look at how various observables behave over time

$$\overline{A} = \frac{1}{T} \int_0^T dt \rho(x, p, t) A(p, x) \tag{4.16}$$

We'd like to understand how such averages behave over long time intervals, looking at $\rho(x, p, t \rightarrow \infty)$.

This long term behavior is described by the Poincaré recurrence theorem. If we wait long enough a point in phase space will come arbitrarily close to its starting point, recurring or "closing the trajectory loops".

A simple example of a recurrence is an undamped SHO, such as a pendulum. That pendulum bob when it hits the bottom of the cycle will have the same velocity (and position) each time it goes through a complete cycle. If we imagine a much more complicated system, such as N harmonic oscillators, each with different periods, we can imagine that it will take infinitely long for this cycle or recurrence to occur, and the trajectory will end up sweeping through all of phase space.

4.5 LIOUVILLE'S THEOREM QUESTIONS ON DENSITY AND CURRENT.

In the midterm today we were asked to state and prove Liouville's theorem. I couldn't remember the proof, having only a recollection that it had something to do with the continuity equation

$$0 = \frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x}, \tag{4.17}$$

but unfortunately couldn't remember what the j was. Looking up the proof, it's actually really simple, just the application of chain rule for a function ρ that's presumed to be a function of time, position and momentum variables. It didn't appear to me that this proof has anything to do with any sort of notion of density, so I posed the following questions.

Context The core of the proof can be distilled to one dimension, removing all the indices that obfuscate what's being one. For that case, application of the chain rule to a function $\rho(t, x, p)$, we have

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \frac{\partial x}{\partial t}\frac{\partial \rho}{\partial x} + \frac{\partial p}{\partial t}\frac{\partial \rho}{\partial p} \\
&= \frac{\partial \rho}{\partial t} + \dot{x}\frac{\partial \rho}{\partial x} + \dot{p}\frac{\partial \rho}{\partial p} \\
&= \frac{\partial \rho}{\partial t} + \frac{\partial \left(\dot{x}\rho\right)}{\partial x} + \frac{\partial \left(\dot{x}\rho\right)}{\partial p} - \rho\left(\frac{\partial \dot{x}}{\partial x} + \frac{\partial \dot{p}}{\partial p}\right) \\
&= \frac{\partial \rho}{\partial t} + \frac{\partial \left(\dot{x}\rho\right)}{\partial x} + \frac{\partial \left(\dot{x}\rho\right)}{\partial p} - \rho \overset{= 0}{\boxed{\left(\frac{\partial}{\partial x}\left(\frac{\partial H}{\partial p}\right) + \frac{\partial}{\partial p}\left(-\frac{\partial H}{\partial x}\right)\right)}}.
\end{aligned} \tag{4.18}$$

Wrong interpretation From this I'd thought that the theorem was about steady states. If we do have a steady state, where $d\rho/dt = 0$ we have

$$0 = \frac{\partial \rho}{\partial t} + \frac{\partial \left(\dot{x}\rho\right)}{\partial x} + \frac{\partial \left(\dot{p}\rho\right)}{\partial p}. \tag{4.19}$$

That would answer the question of what the current is, it's this tuple

$$\mathbf{j} = (\rho\dot{x}, \rho\dot{p}), \tag{4.20}$$

so if we introduce a "phase space" gradient

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial p}\right), \tag{4.21}$$

we've got something that looks like a continuity equation

$$0 = \frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{j}. \tag{4.22}$$

Given this misinterpretation of the theorem, I had the following two questions

1. This function ρ appears to be pretty much arbitrary. I don't see how this connects to any notion of density?
2. If we pick a specific Hamiltonian, say the 1D SHO, what physical interpretation do we have for this "current" $\mathbf{j}$?

The clarification Asking about this, the response was "Actually, eq. (4.19) has to be assumed for the proof. This equation holds if ρ is the phase space density and since the pair in eq. (4.20) is the current density in phase space. The theorem then states that $d\rho/dt = 0$ whether or not one is in the steady state. This means even as the system is evolving in time, if we sit on a particular phase space point and follow it around as it evolves, the density in our neighborhood will be a constant."

4.6 LIOUVILLE'S THEOREM.

We've looked at the continuity equation of phase space density

$$0 = \frac{\partial\rho}{\partial t} + \sum_{i_\alpha}\left(\frac{\partial(\rho\dot{p}_{i_\alpha})}{\partial p_{i_\alpha}} + \frac{\partial(\rho\dot{x}_{i_\alpha})}{\partial x_{i_\alpha}}\right), \tag{4.23}$$

which with

$$\frac{\partial\dot{p}_{i_\alpha}}{\partial p_{i_\alpha}} + \frac{\partial\dot{x}_{i_\alpha}}{\partial x_{i_\alpha}} = 0, \tag{4.24}$$

led us to Liouville's theorem

$$\boxed{\frac{d\rho}{dt}(x, p, t) = 0.} \tag{4.25}$$

We define ergodic, meaning that with time, as you wait for $t \rightarrow \infty$, all available phase space will be covered. Not all systems are necessarily ergodic, but the hope is that all sufficiently complicated systems will be so. We hope that

$$\rho(x, p, t \rightarrow \infty) \implies \frac{\partial \rho}{\partial t} = 0 \qquad \text{in steady state.} \tag{4.26}$$

In particular for ρ = constant, we see that our continuity equation eq. (4.23) results in eq. (4.24).

For example in a SHO system with a cyclic phase space, as in fig. 4.4.

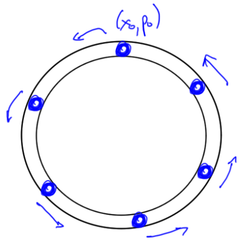


Figure 4.4: Phase space volume trajectory.

$$\langle A \rangle = \frac{1}{\tau} \int_0^\tau dt A(x_0(t), p_0(t)), \tag{4.27}$$

or equivalently with an ensemble average, imagining that we are averaging over a number of different systems

$$\langle A \rangle = \frac{1}{\tau} \int dx dp A(x, p) \overset{\text{constant}}{\boxed{\rho(x, p)}}. \tag{4.28}$$

If we say that

$$\rho(x, p) = \text{constant} = \frac{1}{\Omega}, \tag{4.29}$$

so that

$$\langle A \rangle = \frac{1}{\Omega} \int dx dp A(x, p), \tag{4.30}$$

then what is this constant? We fix this by the constraint

$$\int dx dp \rho(x, p) = 1. \tag{4.31}$$

So, Ω is the allowed "volume" of phase space, the number of states that the system can take that is consistent with conservation of energy.

What's the probability for a given configuration. We'll have to enumerate all the possible configurations. For a coin toss example, we can also ask how many configurations exist where the sum of "coin tosses" are fixed.

Relating Louiville's theorem to the number of configurations Some rough notes based on an after-class discussion:

We can examine the phase space trajectories of a number of particles. For example in a SHO configuration, we could have a number of particles moving along elliptic trajectories, all starting in a region of phase space. Drawing a boundary around this phase space points containing these initial conditions, this boundary will deform according to the Hamiltonian action, but will continue to contain all the particles. Given a number of different possible initial conditions, we can pick any volume containing these same number of particles and look at the evolution of that volume in time. All such configurations will have the same average behaviour over a large number of cycles, and it is this similarity in average that allows us to average over all the possible configurations instead of performing an average over time of a single configuration. This freedom to average over configurations is our starting point for the remainder of the statistical mechanics that we will proceed with shortly.

How does this relate to Louville's theorem? We start by demonstrating that phase space density is conserved, and then assume that we can approximate the systems of interest as ergodic systems. For such an ergodic system, we have constant phase space density, so the number of configurations will be proportional to the volume of phase space that we are investigating. It is really that idea, that the number of configurations is proportional to the region of phase space volume that is accessible given the energy constraints of the system that we want to use as the starting point for most of the rest of the course, and everything up to now is an attempt to justify this as a starting point.

Example 4.1: Ideal gas calculation of Ω

1. N gas atoms at phase space points $\mathbf{x}_i, \mathbf{p}_i$
2. constrained to volume V
3. Energy fixed at E.

$$\Omega(N, V, E) = \int_V d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \int d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N \times \delta\left(E - \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}_2^2}{2m} \cdots - \frac{\mathbf{p}_N^2}{2m}\right)$$

Real space volume, not N dimensional "volume"

$$= \boxed{V^N} \int d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N \delta\left(E - \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}_2^2}{2m} \cdots - \frac{\mathbf{p}_N^2}{2m}\right). \tag{4.32}$$

With γ defined implicitly by

$$\frac{d\gamma}{dE} = \Omega, \tag{4.33}$$

so that with Heavyside theta as in fig. 4.5.

$$\Theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \tag{4.34a}$$

$$\frac{d\Theta}{dx} = \delta(x), \tag{4.34b}$$

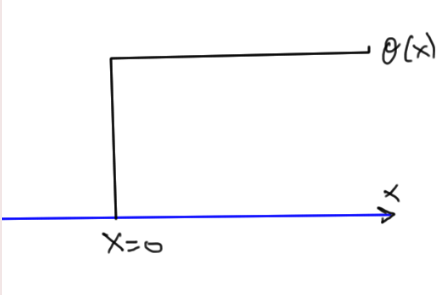


Figure 4.5: Heavyside theta, $\Theta(x)$.

we have

$$\gamma(N,V,E) = V^N \int d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N \Theta\left(E - \sum_i \frac{\mathbf{p}_i^2}{2m}\right). \tag{4.35}$$

In three dimensions (p_x, p_y, p_z), the dimension of momentum part of the phase space is 3. In general the dimension of the space is $3N$. Observe that the structure of this Heavyside integral

$$\int d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N \Theta\left(E - \sum_i \frac{\mathbf{p}_i^2}{2m}\right), \tag{4.36}$$

has the same structure as that of the volume of a sphere. If the radius of a 3D sphere is R, it's volume can be written

$$\int dxdydz \Theta\left(R - \sqrt{x^2+y^2+z^2}\right), \tag{4.37}$$

the integral of the volume element $dxdydz$ over the region $x^2+y^2+z^2 \le R^2$. By analogy eq. (4.36) has the structure of the volume of a "sphere" in $3N$- dimensions. Such a volume was found in the problems to be

$$V_m = \frac{\pi^{m/2} R^m}{\Gamma(m/2+1)}. \tag{4.38a}$$

$$\Gamma(x) = \int_0^\infty dy e^{-y} y^{x-1} \tag{4.38b}$$

$$\Gamma(x+1) = x\Gamma(x) = x!\,. \tag{4.38c}$$

Since we have

$$\mathbf{p}_1^2 + \cdots \mathbf{p}_N^2 \le 2mE, \tag{4.39}$$

the radius is

$$\text{radius} = \sqrt{2mE}. \tag{4.40}$$

This gives

$$\begin{aligned}\gamma(N, V, E) &= V^N \frac{\pi^{3N/2} (2mE)^{3N/2}}{\Gamma(3N/2 + 1)} \\ &= V^N \frac{2}{3N} \frac{\pi^{3N/2} (2mE)^{3N/2}}{\Gamma(3N/2)},\end{aligned} \tag{4.41}$$

and

$$\Omega(N, V, E) = V^N \pi^{3N/2} (2mE)^{3N/2-1} \frac{2m}{\Gamma(3N/2)} \tag{4.42}$$

This result is almost correct, and we have to correct in 2 ways. We have to fix the counting since we need an assumption that all the particles are indistinguishable.

1. Indistinguishability. We must divide by $N!$.
2. Ω is not dimensionless. We need to divide by h^{3N}, where h is Plank's constant.

In the real world we have to consider this as a quantum mechanical system. Imagine a two dimensional phase space. The allowed points are illustrated in fig. 4.6.

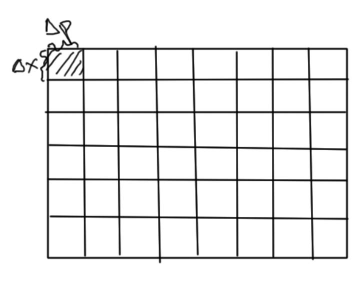


Figure 4.6: Uncertainty principle phase space volume adjustment.

Since $\Delta x \Delta p \sim \hbar$, the question of how many boxes there are, we calculate the total volume, and then divide by the volume of each box. This sort of handwaving wouldn't be required if we did a proper quantum mechanical treatment. The corrected result is

$$\boxed{\Omega_{\text{correct}} = \frac{V^N}{N!}\frac{1}{h^{3N}}\frac{(2\pi m E)^{3N/2}}{E}\frac{1}{\Gamma(3N/2)}} \tag{4.43}$$

4.7 IDEAL GAS AND SHO PHASE SPACE VOLUME CALCULATIONS.

Review. Classical phase space calculation

$$E_{\text{ideal}} = \sum_i \frac{\mathbf{p}_i^2}{2m}. \tag{4.44}$$

From this we calculated $\gamma(E)$, and

$$\frac{d\gamma(E)}{dE} = \Omega_{\text{classical}}(E). \tag{4.45}$$

Fudging with a requirement that $\Delta x \Delta p \sim h$, we corrected this as

$$\Omega_{\text{quantum}}(E) = \frac{\Omega_{\text{classical}}(E)}{N!\, h^{3N}}. \tag{4.46}$$

Recapping explicitly for a single particle, we have

$$\begin{aligned}\gamma^{3d}_{\text{classical}}(E) &= \overset{L^3}{\boxed{V}} \int d^3 p \Theta\left(E - \frac{\mathbf{p}^2}{2m}\right) \\ &= V \frac{4\pi}{3} (2mE)^{3/2},\end{aligned} \tag{4.47}$$

so that

$$\gamma^{3d}_{\text{corrected}}(E) = V \frac{4\pi}{3} \frac{(2mE)^{3/2}}{h^3}. \tag{4.48}$$

Now let's do the quantum calculation.

Quantum calculation Recall that for the solutions of the Quantum free particle in a box, as in fig. 4.7, our solutions are

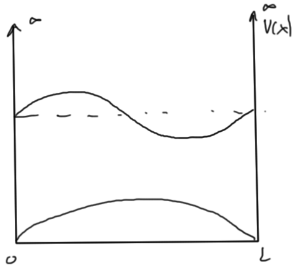


Figure 4.7: 1D Quantum free particle in a box.

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \tag{4.49}$$

where $n = 1, 2, \cdots$, and

$$\epsilon_n = \frac{n^2 h^2}{8 m L^2}. \tag{4.50}$$

.

In three dimensions, with $n_i = 1, 2, \cdots$ we have

$$\Psi_{n_1,n_2,n_3}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi x}{L}\right) \sin\left(\frac{n_3 \pi x}{L}\right),$$

(4.51)

and

$$\epsilon_{n_1,n_2,n_3} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right) \tag{4.52}$$

For the quantum case, we count exactly the number of states that satisfy the energy constraints

$$\gamma^{3d}_{\text{quantum}}(E) = \sum_{n_1,n_2,n_3} \Theta(E - \epsilon_{n_1,n_2,n_3}). \tag{4.53}$$

How do the multiplicities scale by energy? We'll have expect something like fig. 4.8.

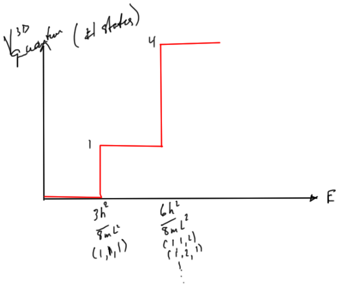


Figure 4.8: Multiplicities for free quantum particle in a 3D box.

Provided the energies $E \gg 3h^2/(8mL)$ are large enough, we can approximate the sum with

$$\sum_{n_1,n_2,n_3} \sim \int_0^\infty dn_1 dn_2 dn_3, \tag{4.54}$$

so

$$\begin{aligned}
\gamma^{3d}_{\text{quantum}}&\left(E \gg \frac{h^2}{8mL^2}\right) \\
&\approx \int_0^\infty dn_1 dn_2 dn_3 \Theta\left(E - \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)\right) \\
&= \frac{1}{8}\frac{4\pi}{3}\left(\frac{8mL^2E}{h^2}\right)^{3/2} \\
&= L^3 \frac{4\pi}{3}\frac{(2mE)^{3/2}}{h^3}.
\end{aligned} \tag{4.55}$$

Observe that this matches our corrected classical result eq. (4.48), justifying that correction procedure.

Example 4.2: Harmonic oscillator in 1D

Our phase space is of the form fig. 4.9.

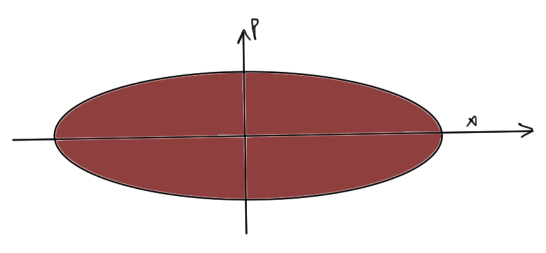


Figure 4.9: 1D classical SHO phase space.

Where the number of states in this classical picture are found with:

$$\gamma^{\text{classical}}(E) = \int dx dp \Theta \left(E - \left(\frac{1}{2} k x^2 + \frac{1}{2m} p^2 \right) \right). \tag{4.56}$$

Rescale

$$\tilde{x} = x \sqrt{\frac{k}{2}} \tag{4.57a}$$

$$\tilde{p} = \frac{p}{\sqrt{2m}}, \tag{4.57b}$$

so that we have

$$\begin{aligned}\gamma^{\text{classical}}(E) &= \int d\tilde{x} d\tilde{p} \sqrt{\frac{2 \times 2m}{k}} \Theta \left(E - \tilde{x}^2 - \tilde{p}^2 \right) \\ &= 2\sqrt{\frac{m}{k}} \pi E \\ &= 2\pi \sqrt{\frac{m}{k}} E.\end{aligned} \tag{4.58}$$

$$\gamma^{\text{SHO}}_{\text{corrected}}(E) = 2\pi \sqrt{\frac{m}{k}} \frac{E}{h}. \tag{4.59}$$

Example 4.3: Quantum Harmonic oscillator in 1D

How about the quantum calculation? We have for the energy

$$E_n^{\mathrm{SHO}} = \left(n + \frac{1}{2} \right) \hbar\omega \tag{4.60a}$$

$$\omega = \sqrt{\frac{k}{m}} \tag{4.60b}$$

$$\hbar = \frac{h}{2\pi}, \tag{4.60c}$$

graphing the counts fig. 4.10, we again have stepping as a function of energy, but no multiplicities this time

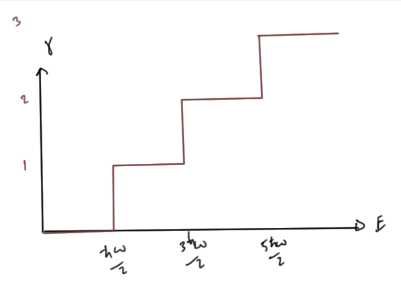


Figure 4.10: 1D quantum SHO states per energy level.

$$\gamma_{\mathrm{quantum}}(E) = \sum_{n=0}^{\infty} \Theta \left(E - \left(n + \frac{1}{2} \right) \hbar\omega \right). \tag{4.61}$$

We make the continuous approximation for the summation again and throw away the zero point energy

$$\gamma_{\mathrm{quantum}}(E \gg \hbar\omega) \approx \int_0^{\infty} dn \Theta \left(E - n\,\hbar\omega \right). \tag{4.62}$$

Let's think through what this Heaviside function means. It is unity only when

$$E - n\,\hbar\omega > 0, \tag{4.63}$$

or

$$\frac{E}{\hbar\omega} > n. \tag{4.64}$$

This gives us

$$\begin{aligned}\gamma_{\text{quantum}}(E \gg \hbar\omega) &\approx \int_0^{E/\hbar\omega} dn \\ &= \frac{E}{\hbar\omega} \\ &= 2\pi\frac{E}{h}\sqrt{\frac{m}{k}}.\end{aligned} \tag{4.65}$$

4.8 ENTROPY.

With the state counting that we've done, we want to look at entropy

$$S = k_{\text{B}} \ln \Omega_{\text{correct}}, \tag{4.66}$$

where S is the entropy, k_{B} is Boltzmann's constant, and Ω_{correct} is the phase space volume (number of configurations). For an ideal gas, with the quantum correction, but not the $N!$ correction of eq. (4.43), we have

$$\Omega = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{E} \frac{1}{\Gamma(3N/2)}. \tag{4.67}$$

For large N, Stirling's approximation gives us

$$\begin{aligned}\frac{S}{k_{\text{B}}} &= \ln \Omega \\ &\approx N \ln\left(\frac{V}{h^3}\right) + \frac{3N}{2}\ln(2\pi m) + \left(\frac{3N}{2} - 1\right)\ln E \\ &\quad - \frac{1}{2}\ln(2\pi) + \left(\frac{3N}{2} - 1\right) - \left(\frac{3N}{2} - 1 + \frac{1}{2}\right)\ln\left(\frac{3N}{2} - 1\right) \\ &\approx N \ln\left(\frac{V}{h^3}\right) + \frac{3N}{2}\ln\left(\frac{2\pi m E}{3N/2}\right) + \frac{3N}{2},\end{aligned} \tag{4.68}$$

or

$$S = k_{\mathrm{B}} N \left(\ln \left(\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right) + \frac{3}{2} \right). \tag{4.69}$$

This has a logical inconsistency that we'll now examine.

4.9 GIBBS PARADOX.

Why N!? We have a problem with our counting here. Consider some particles in a box as in fig. 4.11.

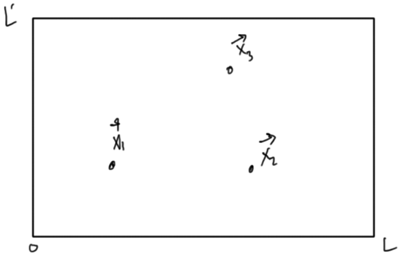


Figure 4.11: Three particles in a box.

- particle 1 at $\mathbf{x}_1$
- particle 2 at $\mathbf{x}_2$
- particle 3 at $\mathbf{x}_3$

or

- particle 1 at $\mathbf{x}_2$
- particle 2 at $\mathbf{x}_3$
- particle 3 at $\mathbf{x}_1$

This is fine in the classical picture, but in the quantum picture with an assumption of indistinguishability, no two particles (say electrons) cannot be labeled in this fashion.

Gibbs paradox

$$\overset{\text{Statistical entropy}}{\boxed{S^{(\mathrm{E,N,V})}_{\text{ideal}}}} = k_{\mathrm{B}} \ln\left(\frac{\Omega_{\text{classical}}}{h^{3N}}\right) \underset{N \gg 1}{\boxed{\approx}} k_{\mathrm{B}} \left(N\ln V + \frac{3N}{2}\ln\left(\frac{4\pi m E}{3Nh^2}\right) + \frac{3N}{2}\right). \tag{4.70}$$

Suppose we double the volume as in fig. 4.12, then our total entropy for the bigger system would be

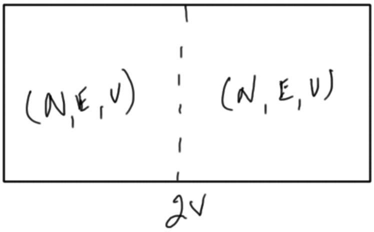


Figure 4.12: Gibbs volume doubling argument. Two identical systems allowed to mix.

$$\begin{aligned} S^{(\mathrm{E,N,V})}_{\text{total}} &= k_{\mathrm{B}} \ln\left(\frac{\Omega_{\text{classical}}}{h^{3N}}\right) \\ &\approx k_{\mathrm{B}} \left((2N)\ln(2V) + \frac{3(2N)}{2}\ln\left(\frac{4\pi m(2E)}{2(2N)h^2}\right) + \frac{3(2N)}{2}\right). \end{aligned} \tag{4.71}$$

We have

$$S_{\text{total}} = S_1 + S_2 + k_{\mathrm{B}}(2N)\ln 2V = S_1 + S_2 + k_{\mathrm{B}}\ln(2V)^{2N}. \tag{4.72}$$

This is telling us that each particle could be in either the left or the right side, but we know that this uncertainty shouldn't be in the final answer. We must drop this k_{B} term.

It turns out that we can do exactly this by dividing Ω by $N!$. Working directly from eq. (4.69) this adjusted statistical entropy is

$$\begin{aligned}
S_{\text{ideal}} &\rightarrow k_{\text{B}} \left(N \ln \left(\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right) + \frac{3N}{2} - \ln N! \right) \\
&\approx k_{\text{B}} \Bigg(N \ln \left(\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right) + \frac{3N}{2} \\
&\qquad - N \ln N + N \Bigg) \\
&= k_{\text{B}} N \left(\ln \left(\frac{V}{N h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right) + \frac{5}{2} \right).
\end{aligned} \tag{4.73}$$

If we use this as the starting point of our doubling argument, we see that we'd have a $\ln(2V/2N) = 0$ term and the entropies would be strictly additive as desired.

4.10 HYPERSPHERE VOLUME CALCULATION THE EASY WAY.

Motivation In exercise 4.3 I solved the hypersphere volume problem the hard way. I did it the way that I thought was obvious, starting with the spherical coordinate hypervolume element for an Euclidean space. That build on the volume element calculation I'd previously done for four dimensional Euclidean and Hyperbolic spaces in [9]. This time I avoided any use of Geometric Algebra and wrote out the volume element directly using a Jacobian transformation instead of a wedge product (that leads to the same Jacobian). I then proceeded to integrate the volume element, come up with a recurrence relation for the volume, solve that for even and odd powers, and find a common expression using Gamma functions that was correct for even and odd powers. It was a laborious process, but satisfying since I'd previously tried this calculation and not succeeded.

As and after I did this calculation, I figured there had to have been an easier way. In the midterm prep reading of §5.5 of [12] I found just that method. It's done there in about six lines, using a trick that seemed really sneaky! I was left with a frustrated feeling, wondering how on earth somebody figured out to do it that way.

After a bit of reflection, I see that the trick is a very sensible approach. I'll outline that here for 2 and 3 dimensions to show the technique, and the reader can generalize if desired.

The trick Switching to spherical or circular coordinates when there is radial symmetry isn't anything that we could describe as trickery. For example, with $r^2 = x^2 + y^2$ in a two dimensional problem or $r^2 = x^2 + y^2 + z^2$ in a three dimensional problem, it's clear that we'd do the following respectively if we were evaluating an integral

$$\iint f(r) dx dy = \iint f(r) r dr d\theta = 2\pi \int f(r) r dr \tag{4.74a}$$

$$\iiint f(r) dx dy = \iiint f(r) r^2 dr \sin d\theta d\theta d\phi = 4\pi \int f(r) r^2 dr. \tag{4.74b}$$

In fact, for $f(r) = 1$ these give us the area and volume of the circle and sphere respectively.

So, what's the trick? The first part is the observation that the "area" of a "volume" for the circle and the sphere are found by the derivatives of the "volumes"

$$\frac{d}{dr} \pi r^2 = 2\pi r \tag{4.75a}$$

$$\frac{d}{dr} \frac{4\pi}{3} r^3 = 4\pi r^2. \tag{4.75b}$$

I recall being surprised that this is the case back in high school calculus. When I lost marks for not having the formula for the surface area of a sphere memorized on some test, my calculus teacher told me this title tidbit.

Back then this wasn't obvious to me, and I complained that it was true only for the perfect symmetry of a sphere. For example, the derivative of an volume of a cube doesn't give the surface area of a cube ($dx^3/dx = 3x^2 \neq 6x^2$).

Once we believe or assume that the surface "area" of a hypervolume is the derivative of the volume, we can proceed with the trick. That trick is to express the volume in terms of an unknown constant. For example, for the circle and sphere the generalized "volume"s are respectively

$$V_2 = Br^2 \tag{4.76a}$$

$$V_3 = Cr^3. \tag{4.76b}$$

The perimeter of the circle and surface area of the sphere are then

$$A_2 = 2Br \tag{4.77a}$$

$$A_3 = 3Cr^2. \tag{4.77b}$$

So, if we want to calculate integrals of the form eq. (4.74) we can write

$$\iint f(r) dx dy = 2B \int f(r) r dr \tag{4.78a}$$

$$\iiint f(r) dx dy = 3C \int f(r) r^2 dr. \tag{4.78b}$$

The essence of the trick is to do such an integral in both Cartesian coordinates to get the left hand sides, and then do the radial right hand side integrals. Comparing these provides the constants B and C and thus completes the "volume" formulas for the circle and sphere.

The function chosen for this integral in the text was a Gaussian exponential $f(r) = e^{-r^2/2}$, something that is strictly radial, and can be integrated over all space. For the 2D case, we'll integrate

$$\iint e^{-(x^2+y^2)/2} dx dy = (\sqrt{2\pi})^2 = 2B \int_0^\infty dr r e^{-r^2/2} = -2B e^{-r^2/2}\Big|_0^\infty = 2B. \tag{4.79}$$

We find that $B = \pi$, so the 2D spherical "volume" (the area of the circle) is $V = \pi r^2$.

For the 3D sphere, we have

$$\begin{aligned}\iiint e^{-(x^2+y^2+z^2)/2} dx dy &= (\sqrt{2\pi})^3 \\ &= 3C \int_0^\infty dr r^2 e^{-r^2/2} \\ &= 3C \int_0^\infty dr e^{-r^2/2} \\ &= 3C\sqrt{2\pi}.\end{aligned} \tag{4.80}$$

So we have for the volume of the 3D sphere, $V = 4\pi r^3/3$ as expected.

It's also clear that the exponential integral isn't a requirement for this trick. It's just convienent because boundary value conditions aren't required. For example, suppose we want to calculate the area of a circle using this trick. We can do so by integrating

$$4 \int_0^r dx \int_0^{\sqrt{r^2-x^2}} dy (x^2+y^2) = \int_0^r r^2 2B r dr. \tag{4.81}$$

The LHS can be integrated using a sine or cosine substitution and then integrating by parts (or by Mathematica as in nVolumeTrickToCalculateAreaOfCircle.nb). Comparison of the two gives

$$4r^4 \frac{\pi}{8} = 2B \frac{r^4}{4}, \tag{4.82}$$

So that $B = \pi$ and $V_2 = \pi r^2$ as expected.

The same idea can be extended to higher dimensional spheres. The text does the even values of N. Treating both even and odd values, this would have to yield the result calculated using the Jacobian volume element method

$$V_m = \frac{\pi^{m/2} R^m}{\Gamma\left(m/2+1\right)}. \tag{4.83}$$

4.11 PROBLEMS.

Exercise 4.1 2D phase space, cartesian to cylindrical.

In [13] problem 2.2, it's suggested to try a spherical change of vars to verify explicitly that phase space volume is preserved, and to explore some related ideas. As a first step let's try a similar, but presumably easier change of variables, going from Cartesian to cylindrical phase spaces.

Answer for Exercise 4.1

Our cylindrical velocity is

$$\mathbf{v} = \dot{r}\hat{\mathbf{r}} + r\dot{\theta}\hat{\boldsymbol{\theta}}, \tag{4.84}$$

so a purely kinetic Lagrangian would be

$$\begin{aligned}\mathcal{L} &= \frac{1}{2}m\mathbf{v}^2 \\ &= \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2\right).\end{aligned} \tag{4.85}$$

Our canonical momenta are

$$p_r = \frac{\partial \mathcal{L}}{\partial \dot{r}} = m\dot{r} \tag{4.86a}$$

$$p_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = mr^2\dot{\theta}, \tag{4.86b}$$

and our kinetic energy is

$$H = \mathcal{L} = \frac{1}{2m}p_r^2 + \frac{1}{2mr^2}p_\theta^2. \tag{4.87}$$

Now we need to express our momenta in terms of the Cartesian coordinates. We have for the radial momentum

$$\begin{aligned}p_r &= m\dot{r} \\ &= m\frac{d}{dt}\sqrt{x^2 + y^2} \\ &= \frac{1}{2}\frac{2m}{r}\left(x\dot{x} + y\dot{y}\right),\end{aligned} \tag{4.88}$$

or

$$p_r = \frac{1}{r}\left(xp_x + yp_y\right). \tag{4.89}$$

$$\begin{aligned}p_\theta &= mr^2\frac{d\theta}{dt} \\ &= mr^2\frac{d}{dt}\operatorname{atan}\left(\frac{y}{x}\right).\end{aligned} \tag{4.90}$$

After some reduction cyclindrialMomenta.nb , we find

$$p_\theta = p_y x - p_x y. \tag{4.91}$$

We can assemble these into a complete set of change of variable equations

$$r = \sqrt{x^2 + y^2} \tag{4.92a}$$

$$\theta = \operatorname{atan}\left(\frac{y}{x}\right) \tag{4.92b}$$

$$p_r = \frac{1}{\sqrt{x^2 + y^2}}\left(x p_x + y p_y\right) \tag{4.92c}$$

$$p_\theta = p_y x - p_x y. \tag{4.92d}$$

Our phase space volume element change of variables is

$$\begin{aligned}
dr d\theta dp_r dp_\theta &= \frac{\partial(r, \theta, p_r, p_\theta)}{\partial(x, y, p_x, p_y)} dx dy dp_x dp_y \\
&= \begin{vmatrix}
\frac{x}{\sqrt{x^2+y^2}} & \frac{y}{\sqrt{x^2+y^2}} & 0 & 0 \\
-\frac{y}{x^2+y^2} & \frac{x}{x^2+y^2} & 0 & 0 \\
\frac{y\left(y p_x - x p_y\right)}{\left(x^2+y^2\right)^{3/2}} & \frac{x\left(x p_y - y p_x\right)}{\left(x^2+y^2\right)^{3/2}} & \frac{x}{\sqrt{x^2+y^2}} & \frac{y}{\sqrt{x^2+y^2}} \\
p_y & -p_x & -y & x
\end{vmatrix} \times \\
&\quad dx dy dp_x dp_y \\
&= \frac{x^2 + y^2}{\left(x^2 + y^2\right)^{3/2}} \frac{x^2 + y^2}{\left(x^2 + y^2\right)^{1/2}} \\
&= dx dy dp_x dp_y.
\end{aligned} \tag{4.93}$$

We see explicitly that this point transformation has a unit Jacobian, preserving area.

Exercise 4.2 3D phase space, Cartesian to spherical (*[13] pr. 2.2 (a)*)

Try a spherical change of vars to verify explicitly that phase space volume is preserved.

Answer for Exercise 4.2

Our kinetic Lagrangian in spherical coordinates is

$$\begin{aligned}\mathcal{L} &= \frac{1}{2}m\left(\dot{r}\hat{\mathbf{r}} + r\sin\theta\dot{\phi}\hat{\boldsymbol{\phi}} + r\dot{\theta}\hat{\boldsymbol{\theta}}\right)^2 \\ &= \frac{1}{2}m\left(\dot{r}^2 + r^2\sin^2\theta\dot{\phi}^2 + r^2\dot{\theta}^2\right).\end{aligned} \tag{4.94}$$

We read off our canonical momentum

$$p_r = \frac{\partial\mathcal{L}}{\partial r} = m\dot{r} \tag{4.95a}$$

$$p_\theta = \frac{\partial\mathcal{L}}{\partial\theta} = mr^2\dot{\theta} \tag{4.95b}$$

$$p_\phi = \frac{\partial\mathcal{L}}{\partial\phi} = mr^2\sin^2\theta\dot{\phi}, \tag{4.95c}$$

and can now express the Hamiltonian in spherical coordinates

$$\begin{aligned}H &= \frac{1}{2}m\left(\left(\frac{p_r}{m}\right)^2 + r^2\sin^2\theta\left(\frac{p_\phi}{mr^2\sin^2\theta}\right) + r^2\left(\frac{p_\theta}{mr^2}\right)\right) \\ &= \frac{p_r^2}{2m} + \frac{p_\phi^2}{2mr^2\sin^2\theta} + \frac{p_\theta^2}{2mr^2}.\end{aligned} \tag{4.96}$$

Now we want to do a change of variables. The coordinates transform as

$$x = r\sin\theta\cos\phi \tag{4.97a}$$

$$y = r\sin\theta\sin\phi \tag{4.97b}$$

$$z = r\cos\theta, \tag{4.97c}$$

or

$$r = \sqrt{x^2 + y^2 + z^2} \tag{4.98a}$$

$$\theta = \arccos(z/r) \tag{4.98b}$$

$$\phi = \arctan(y/x). \tag{4.98c}$$

It's not too hard to calculate the change of variables for the momenta (verified in sphericalPhaseSpaceChangeOfVars.nb). We have

$$p_r = \frac{x p_x + y p_y + z p_z}{\sqrt{x^2 + y^2 + z^2}} \tag{4.99a}$$

$$p_\theta = \frac{(p_x x + p_y y) z - p_z (x^2 + y^2)}{\sqrt{x^2 + y^2}} \tag{4.99b}$$

$$p_\phi = x p_y - y p_x. \tag{4.99c}$$

Now let's compute the volume element in spherical coordinates. With $\rho^2 = x^2 + y^2$, this is

$$\begin{aligned} d\omega &= dr d\theta d\phi dp_r dp_\theta dp_\phi \\ &= \frac{\partial(r, \theta, \phi, p_r, p_\theta, p_\phi)}{\partial(x, y, z, p_x, p_y, p_z)} dx dy dz dp_x dp_y dp_z, \end{aligned} \tag{4.100}$$

but

$$\frac{\partial(r, \theta, \phi, p_r, p_\theta, p_\phi)}{\partial(x, y, z, p_x, p_y, p_z)} =$$

$$\begin{vmatrix} \frac{x}{r} & \frac{y}{r} & \frac{z}{r} & 0 & 0 & 0 \\ \frac{xz}{\rho r^2} & \frac{yz}{\rho r^2} & -\frac{\rho}{r^2} & 0 & 0 & 0 \\ -\frac{y}{\rho^2} & \frac{x}{\rho^2} & 0 & 0 & 0 & 0 \\ \frac{\left(y^2+z^2\right) p_x - x y p_y - x z p_z}{r^3} & \frac{\left(x^2+z^2\right) p_y - y (x p_x + z p_z)}{r^3} & \frac{\left(\rho^2\right) p_z - z\left(x p_x + y p_y\right)}{r^3} & \frac{x}{r} & \frac{y}{r} & \frac{z}{r} \\ \frac{yz\left(y p_x - x p_y\right) - x\left(\rho^2\right) p_z}{\rho^3} & \frac{xz\left(x p_y - y p_x\right) - y\left(\rho^2\right) p_z}{\rho^3} & \frac{x p_x + y p_y}{\rho} & \frac{xz}{\rho} & \frac{yz}{\rho} & -\rho \\ p_y & -p_x & 0 & -y & x & 0 \end{vmatrix}.$$

We find after a bit of computation that this determinant is also unity, as we found in the similar cylindrical change of phase space variables, so we have

$$dr d\theta d\phi p_r p_\theta p_\phi = dx dy dz dp_x dp_y dp_z, \tag{4.101}$$

without the $r^2 \sin\theta$ dependence that we have in the volume element for a change of variables from Cartesian to spherical coordinates in the spatial domain.

Exercise 4.3 Surface area of a d-sphere (*2013 ps3, p1*)

Consider a d-dimensional sphere with radius R. Derive the volume of the sphere $V_d(R)$ and its surface area $S_d(R)$ using $S_d(R) = dV_d(R)/dR$.

Answer for Exercise 4.3

Let's start with some terminology and notation, borrowing from [21]

- 1-sphere : 2D circle, with "volume" V_2
- 2-sphere : 3D sphere, with volume V_3
- 3-sphere : 4D Euclidean hypersphere, with "volume" V_4
- 4-sphere : 5D Euclidean hypersphere, with "volume" V_5
- $\cdots$

To calculate the volume, we require a parameterization allowing for expression of the volume element in an easy to integrate fashion. For the 1-sphere, we can use the usual circular and spherical coordinate volume elements

$$\begin{aligned} V_2(R) &= 4 \int_0^R r dr \int_0^{\pi/2} d\theta \\ &= 4 \frac{R^2}{2} \frac{\pi}{2} \\ &= \pi R^2 \end{aligned} \tag{4.102a}$$

$$\begin{aligned} V_3(R) &= 8 \int_0^R r^2 dr \int_0^{\pi/2} \sin\theta d\theta \int_0^{\pi/2} d\phi \\ &= 8 \frac{R^3}{3} (1) \frac{\pi}{2} \\ &= \frac{4}{3} \pi R^3. \end{aligned} \tag{4.102b}$$

Here, to simplify the integration ranges, we've calculated the "volume" integral for just one quadrant or octet of the circle and sphere respectively, as in fig. 4.13.

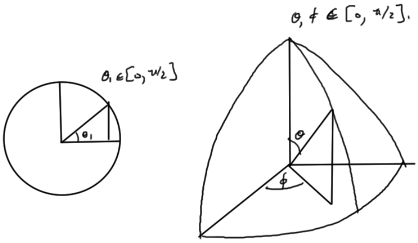


Figure 4.13: Integrating over just one quadrant of circle or octet of sphere.

How will we generalize this to higher dimensions? To calculate the volume elements in a systematic fashion, we can introduce a parameterization and use a Jacobian to change from Cartesian coordinates. For the 1-volume and 2-volume cases those parameterizations were the familiar

$$\begin{aligned} x_1 &= r \cos\theta \\ x_0 &= r \sin\theta \end{aligned} \tag{4.103a}$$

$$\begin{aligned} x_2 &= r \cos\theta \\ x_1 &= r \sin\theta \cos\phi \\ x_0 &= r \sin\theta \sin\phi. \end{aligned} \tag{4.103b}$$

Some reflection shows that this generalizes nicely. Let's use shorthand

$$C_k = \cos\theta_k \tag{4.104a}$$

$$S_k = \sin\theta_k, \tag{4.104b}$$

and pick V_5, say, a dimension bigger than the 2D or 3D cases that we can do by inspection, we can parameterize with

$$\begin{aligned}
x_4 &= rC_4 \\
x_3 &= rS_4C_3 \\
x_2 &= rS_4S_3C_2 \\
x_1 &= rS_4S_3S_2C_1 \\
x_0 &= rS_4S_3S_2S_1.
\end{aligned} \tag{4.105}$$

Our volume element

$$dV_5 = \overbrace{\boxed{\frac{\partial(x_4, x_3, x_2, x_1, x_0)}{\partial(r, \theta_4, \theta_3, \theta_2, \theta_1)}}}^{\equiv J_5} dr d\theta_4 d\theta_3 d\theta_2 d\theta_1. \tag{4.106}$$

After factoring out common terms, that Jacobian reduces to

$$J5 = r^4 S_4^3 S_3^2 S_2^1 S_1^0 \times$$

$$\begin{vmatrix}
C_4 & & -S_4 & & 0 & 0 & 0 \\
S_4 & C_3 & C_4 & C_3 & -S_3 & 0 & 0 \\
S_4 & S_3C_2 & C_4 & S_3C_2 & C_3C_2 & -S_2 & 0 \\
S_4 & S_3S_2C_1 & C_4 & S_3S_2C_1 & C_3S_2C_1 & C_2C_1 & -S_1 \\
S_4 & S_3S_2S_1 & C_4 & S_3S_2S_1 & C_3S_2S_1 & C_2S_1 & C_1
\end{vmatrix}. \tag{4.107}$$

Observe above that the cofactors of both the $1,1$ and the $1,2$ elements, when expanded along the first row, have a common factor. This allows us to work recursively

$$\begin{aligned}
J_5 &= r^4 S_4^3 S_3^2 S_2^1 S_1^0 (C_4^2 - -S_4^2)
\begin{vmatrix}
C_3 & -S_3 & 0 & 0 \\
S_3C_2 & C_3C_2 & -S_2 & 0 \\
S_3S_2C_1 & C_3S_2C_1 & C_2C_1 & -S_1 \\
S_3S_2S_1 & C_3S_2S_1 & C_2S_1 & C_1
\end{vmatrix} \\
&= rS_4^3 J_4.
\end{aligned} \tag{4.108}$$

Similarly for the 4D volume

$$\begin{aligned}
J_4 &= r^3 S_3^2 S_2^1 S_1^0 \begin{vmatrix} C_3 & -S_3 & 0 & 0 \\ S_3 C_2 & C_3 C_2 & -S_2 & 0 \\ S_3 S_2 C_1 & C_3 S_2 C_1 & C_2 C_1 & -S_1 \\ S_3 S_2 S_1 & C_3 S_2 S_1 & C_2 S_1 & C_1 \end{vmatrix} \\
&= r^3 S_3^2 S_2^1 S_1^0 (C_2^2 + S_2^2) \begin{vmatrix} C_2 & -S_2 & 0 \\ S_2 C_1 & C_2 C_1 & -S_1 \\ S_2 S_1 & C_2 S_1 & C_1 \end{vmatrix} \\
&= r S_3^2 J_3,
\end{aligned} \tag{4.109}$$

and for the 3D volume

$$\begin{aligned}
J_3 &= r^2 S_2^1 S_1^0 \begin{vmatrix} C_2 & -S_2 & 0 \\ S_2 C_1 & C_2 C_1 & -S_1 \\ S_2 S_1 & C_2 S_1 & C_1 \end{vmatrix} \\
&= r^2 S_2^1 S_1^0 (C_2^2 + S_2^2) \begin{vmatrix} C_1 & -S_1 \\ S_1 & C_1 \end{vmatrix} \\
&= r S_2^1 J_2,
\end{aligned} \tag{4.110}$$

and finally for the 2D volume

$$\begin{aligned}
J_2 &= r S_1^0 \begin{vmatrix} C_1 & -S_1 \\ S_1 & C_1 \end{vmatrix} \\
&= r S_1^0.
\end{aligned} \tag{4.111}$$

Putting all the bits together, the "volume" element in the n-D space is

$$dV_n = dr d\theta_{n-1} \cdots d\theta_1 r^{n-1} \prod_{k=0}^{n-2} (\sin\theta_{k+1})^k, \tag{4.112}$$

and the total volume is

$$\begin{aligned}
V_n(R) &= 2^n \int_0^R r^{n-1} dr \prod_{k=0}^{n-2} \int_0^{\pi/2} d\theta \sin^k \theta \\
&= 2^n \frac{R^n}{n} \prod_{k=0}^{n-2} \int_0^{\pi/2} d\theta \sin^k \theta \\
&= \frac{4R^2}{n} (n-2) 2^{n-2} \frac{R^{n-2}}{n-2} \prod_{k=n-3}^{n-2} \int_0^{\pi/2} d\theta \sin^k \theta \prod_{k=0}^{n-4} \int_0^{\pi/2} d\theta \sin^k \theta \\
&= 4R^2 \frac{n-2}{n} V_{n-2}(R) \int_0^{\pi/2} d\theta \sin^{n-2} \theta \int_0^{\pi/2} d\theta \sin^{n-3} \theta \\
&= 4R^2 \frac{n-2}{n} V_{n-2}(R) \frac{\pi}{2(n-2)}.
\end{aligned} \tag{4.113}$$

Note that a single of these sine power integrals has a messy result (see: statMechProblemSet3.nb)

$$\int_0^{\pi/2} d\theta \sin^k \theta = \frac{\sqrt{\pi}\Gamma\left(\frac{k+1}{2}\right)}{2\Gamma\left(\frac{k}{2}+1\right)}, \tag{4.114}$$

but the product is simple, and that result, computed in statMechProblemSet3.nb , is inserted above, providing an expression for the n-D volume element as a recurrence relation

$$\boxed{V_n = \frac{2\pi}{n} R^2 V_{n-2}(R).} \tag{4.115}$$

With this recurrence relation we can find the volume V_{2n} or V_{2n+1} in terms of V_2 and V_3 respectively. For the even powers we have

$$\begin{array}{lll}
V_{2(2)} & = \frac{2\pi R^2}{4} V_2 & = \frac{2^1 \pi R^2}{2(2)} V_2 \\
V_{2(3)} & = \frac{(2\pi R^2)^2}{(6)(4)} V_2 & = \frac{2^2 (\pi R^2)^2}{2^2(3)(2)} V_2 \\
V_{2(4)} & = \frac{(2\pi R^2)^3}{(8)(6)(4)} V_2 & = \frac{2^3 (\pi R^2)^3}{2^3(4)(3)(2)} V_2
\end{array} \tag{4.116}$$

$$\begin{aligned}
V_{2(n)} &= \frac{2^n (\pi R^2)^{n-1}}{(2n)!!} V_2 \\
&= \frac{(\pi R^2)^{n-1}}{(n)!} V_2 \\
&= \frac{(\pi R^2)^{n-1}}{(n)!} \pi R^2.
\end{aligned} \tag{4.117}$$

This gives us a closed form expression for the even powers for $n \ge 2$

$$\boxed{V_{2(n)} = \frac{(\pi R^2)^n}{n!}.} \tag{4.118}$$

Observe that this also conveniently gives $V_2 = \pi R^2$, so is actually valid for $n \ge 1$. Now for the odd powers

$$\begin{aligned} V_{2(2)+1} &= \tfrac{2\pi R^2}{5} V_3 & &= 3\tfrac{2^1 \pi R^2}{5!!} V_3 \\ V_{2(3)+1} &= 3\tfrac{(2\pi R^2)^2}{753} V_3 & &= 3\tfrac{2^2 (\pi R^2)^2}{7!!} V_2 \\ V_{2(4)+1} &= 3\tfrac{(2\pi R^2)^3}{(9)(7)(5)(3)} V_2 & &= 3\tfrac{2^3 (\pi R^2)^3}{9!!} V_2 \end{aligned} \tag{4.119}$$

$$\begin{aligned} V_{2(n)+1} &= 3\frac{2^{n-1}(\pi R^2)^{n-1}}{(2n+1)!!} V_2 \\ &= 3\frac{2^{n-1}(\pi R^2)^{n-1}}{(2n+1)!!} \frac{4}{3} \pi R^3. \end{aligned} \tag{4.120}$$

So, for $n \ge 2$ we have

$$\boxed{V_{2(n)+1} = \frac{2^{n+1} \pi^n R^{2n+1}}{(2n+1)!!}.} \tag{4.121}$$

As with the even powered expression eq. (4.118) we see that this is also good for $n = 1$, yielding $V_3 = 4\pi R^2/3$ as required for the 3D spherical volume.

The even and odd power expressions don't look quite different on the surface, but can be put into a consistent form, when expressed in terms of the gamma function.

For the even powers, using a substitution $2n = m$ we have for even values of $m \ge 2$

$$V_m = \frac{\pi^{m/2} R^m}{\Gamma(n+1)} = \frac{\pi^{m/2} R^m}{\Gamma(m/2+1)}. \tag{4.122}$$

For the even powers, with the help of [1] we find

$$(2n+1)!! = \frac{2^{n+1} \Gamma\left(n + \frac{3}{2}\right)}{\sqrt{\pi}}. \tag{4.123}$$

This gives us

$$\begin{aligned} V_{2(n)+1} &= \frac{\pi^{n+1/2}R^{2n+1}}{\Gamma\left(n+\frac{3}{2}\right)} \\ &= \frac{\pi^{n+1/2}R^{2n+1}}{\Gamma\left(\frac{(2n+1)+2}{2}\right)}. \end{aligned} \tag{4.124}$$

Writing $m = 2n+1$, or $n = (m-1)/2$ we have for odd values of $m \geq 3$ a match with the even powered expression of eq. (4.122)

$$\boxed{V_m = \frac{\pi^{m/2}R^m}{\Gamma\left(m/2+1\right)}.} \tag{4.125}$$

We've shown that this is valid for any dimension $m \geq 2$.

Tabulating some values of these for $n \in [2,7]$ we have respectively

$$\pi r^2, \frac{4\pi r^3}{3}, \frac{\pi^2 r^4}{2}, \frac{8\pi^2 r^5}{15}, \frac{\pi^3 r^6}{6}, \frac{16\pi^3 r^7}{105}, \tag{4.126}$$

The only task left is computation of the surface area. That comes by inspection and is

$$S_m(R) = \frac{dV_m(R)}{dR} = \frac{\pi^{m/2} m R^{m-1}}{\Gamma\left(m/2+1\right)}. \tag{4.127}$$

Again for $m \in [2,7]$ we have

$$2\pi r, 4\pi r^2, 2\pi^2 r^3, \frac{8\pi^2 r^4}{3}, \pi^3 r^5, \frac{16\pi^3 r^6}{15}. \tag{4.128}$$

Exercise 4.4 State counting - spins (*2013 ps3, p3*)

Consider a toy model of a magnet where the net magnetization arises from electronic spins on each atom which can point in one of only two possible directions - Up/North or Down/South. If we have a system with N spins, and if the magnetization can only take on values ± 1 (Up = +1, Down = -1), how many configurations are there which have a total magnetization m, where $m = (N_\uparrow - N_\downarrow)/N$ (note that $N_\uparrow + N_\downarrow = N$)? Simplify this result assuming $N \gg 1$ and a generic m (assume we are not interested in the extreme case of a fully magnetized system where $m = \pm 1$). Find the value of the magnetization m for which the number of such microscopic states is a maximum. For $N = 20$, make a numerical plot of the number of states as a function of the magnetization (note: $-1 \le m \le 1$) without making the $N \gg 1$ assumption.

Answer for Exercise 4.4

For the first couple values of N, lets enumerate the spin sample spaces, their magnetization.

$N = 1$

- $\uparrow : m = 1$
- $\downarrow, m = -1$

$N = 2$

- $\uparrow\uparrow : m = 1$
- $\uparrow\downarrow : m = 0$
- $\downarrow\uparrow, m = 0$
- $\downarrow\downarrow, m = -1$

$N = 3$

- $\uparrow\uparrow\uparrow : m = 1$
- $\uparrow\uparrow\downarrow : m = 1/3$
- $\uparrow\downarrow\uparrow : m = 1/3$
- $\uparrow\downarrow\downarrow : m = -1/3$
- $\downarrow\uparrow\uparrow : m = 1/3$
- $\downarrow\uparrow\downarrow : m = -1/3$
- $\downarrow\downarrow\uparrow : m = -1/3$
- $\downarrow\downarrow\downarrow : m = 1$

The respective multiplicities for $N = 1, 2, 3$ are $\{1\}$, $\{1, 2, 1\}$, $\{1, 3, 3, 1\}$. It's clear that these are just the binomial coefficients. Let's write for the multiplicities

$$g(N, m) = \binom{N}{i(m)}, \tag{4.129}$$

where $i(m)$ is a function that maps from the magnetization values m to the integers $[0, N]$. Assuming

$$i(m) = am + b, \tag{4.130}$$

where $i(-1) = 0$ and $i(1) = N$, we solve

$$\begin{aligned} a(-1) + b &= 0 \\ a(1) + b &= N, \end{aligned} \tag{4.131}$$

so

$$i(m) = \frac{N}{2}(m + 1), \tag{4.132}$$

and

$$g(N, m) = \binom{N}{\frac{N}{2}(1 + m)} = \frac{N!}{\left(\frac{N}{2}(1 + m)\right)!\left(\frac{N}{2}(1 - m)\right)!}. \tag{4.133}$$

From

$$\begin{aligned} 2m &= N_\uparrow - N_\downarrow \\ N &= N_\uparrow + N_\downarrow, \end{aligned} \tag{4.134}$$

we see that this can also be written

$$\boxed{g(N, m) = \frac{N!}{(N_\uparrow)!\,(N_\downarrow)!}} \tag{4.135}$$

Simplification for large N Using Stirlings approximation

$$
\begin{aligned}
\ln g(N,m) &= \ln N! - \ln N_\downarrow! - \ln N_\uparrow! \\
&\approx \left(N + \frac{1}{2}\right)\ln N - \cancel{N} + \cancel{\frac{1}{2}\ln 2\pi} \\
&\quad - \left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow + \cancel{N_\uparrow} - \cancel{\frac{1}{2}\ln 2\pi} \\
&\quad - \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow + \cancel{N_\downarrow} - \frac{1}{2}\ln 2\pi \\
&= \left(N_\uparrow + N_\downarrow + \frac{1}{2} + \overset{\text{add}}{\boxed{\frac{1}{2}}}\right)\ln N - \frac{1}{2}\ln 2\pi - \overset{\text{then subtract}}{\boxed{\frac{1}{2}\ln N}} \\
&\quad - \left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow \quad - \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow \\
&= -\left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow/N - \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow/N - \frac{1}{2}\ln 2\pi N \\
&= -\left(N_\uparrow + \frac{1}{2}\right)\ln \frac{1}{2}(1+m) - \left(N_\downarrow + \frac{1}{2}\right)\ln \frac{1}{2}(1-m) - \frac{1}{2}\ln 2\pi N \\
&\approx \left(N_\uparrow + \frac{1}{2}\right)\ln 2 + \left(N_\downarrow + \frac{1}{2}\right)\ln 2 - \frac{1}{2}\ln 2\pi N \\
&\quad - \left(N_\uparrow + \frac{1}{2}\right)\left(m - \frac{1}{2}m^2\right) \\
&\quad - \left(N_\downarrow + \frac{1}{2}\right)\left(-m - \frac{1}{2}m^2\right) \\
&= (N+1)\ln 2 - \frac{1}{2}\ln 2\pi N + m(N_\downarrow - N_\uparrow) + \frac{1}{2}m^2(N+1) \\
&= (N+1)\ln 2 - \frac{1}{2}\ln 2\pi N - Nm^2 + \frac{1}{2}m^2(N+1) \\
&\approx (N+1)\ln 2 - \frac{1}{2}\ln 2\pi N - \frac{1}{2}m^2 N
\end{aligned}
\tag{4.136}
$$

This gives us for large N

$$
g(N,m) \approx 2^N \sqrt{\frac{2}{\pi N}} e^{-m^2 N/2}
\tag{4.137}
$$

For $N = 20$ this approximation and the exact expression are plotted in fig. 4.14.

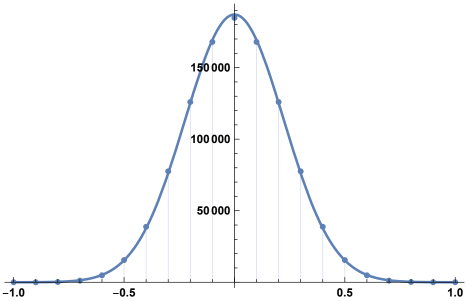


Figure 4.14: Distribution of number of configurations for $N = 20$ magnets as a function of magnetization.

With the large scales of this extremely peaked function, no visible difference can be seen. That difference does exist, and is plotted in fig. 4.15.

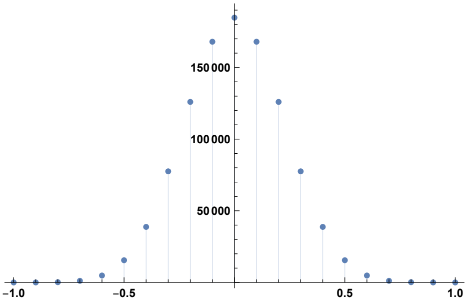


Figure 4.15: $N = 20$ differences between the exact binomial expression and the Gaussian approximation.

Exercise 4.5 3N SHO particle phase space volume

Calculate the phase space volume calculate for $3N$ classical SHO particles.

Answer for Exercise 4.5

Our Hamiltonian is

$$\begin{aligned} H &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} m \omega^2 \mathbf{r}_i^2 \\ &= \sum_{i \in [1,N], \alpha \in \{1,2,3\}} \frac{p_{i_\alpha}^2}{2m} + \frac{1}{2} m \omega^2 x_{i_\alpha}^2 . \end{aligned} \tag{4.138}$$

Let's calculate the phase space volume for the shell in $[E - \Delta/2, E + \Delta/2]$ (as in the midterm for the 1D SHO). That is

$$\begin{aligned}
&\int_{E-\frac{\Delta}{2} \le H \le E+\frac{\Delta}{2} \le H} d^{3N} x d^{3N} p \\
&= \int_{E-\frac{\Delta}{2} \le \sum_{i\alpha} \left(\frac{p_{i\alpha}^2}{2m} + \frac{1}{2} m\omega^2 x_{i\alpha}^2 \right) \le E+\frac{\Delta}{2} \le H} d^{3N} x d^{3N} p \\
&= \int_{2m\left(E-\frac{\Delta}{2}\right) \le \sum_{i\alpha} \left(p_{i\alpha}^2 + m^2\omega^2 x_{i\alpha}^2 \right) \le 2m\left(E+\frac{\Delta}{2}\right)} d^{3N} x d^{3N} p.
\end{aligned} \tag{4.139}$$

Now change variables $\tilde{x}_{i_\alpha} = m\omega x_{i_\alpha}$. This gives us

$$\begin{aligned}
&\int_{E-\frac{\Delta}{2} \le H \le E+\frac{\Delta}{2} \le H} d^{3N} x d^{3N} p \\
&= \frac{1}{(m\omega)^{3N}} \int_{2m\left(E-\frac{\Delta}{2}\right) \le \sum_{i\alpha} \left(p_{i\alpha}^2 + \tilde{x}_{i\alpha}^2 \right) \le 2m\left(E+\frac{\Delta}{2}\right)} d^{3N} \tilde{x} d^{3N} p.
\end{aligned} \tag{4.140}$$

This integral is now the volume of a $6N$ dimensional spherical shell, giving

$$\int_{E-\frac{\Delta}{2} \le H \le E+\frac{\Delta}{2} \le H} d^{3N} x d^{3N} p = \frac{1}{(m\omega)^{3N}} \frac{\pi^{6N/2}}{(6N/2)!} r^{6N} \Big|_{\sqrt{2m\left(E-\frac{\Delta}{2}\right)}}^{\sqrt{2m\left(E+\frac{\Delta}{2}\right)}}. \tag{4.141}$$

This is

$$\boxed{\int_{E-\frac{\Delta}{2} \le H \le E+\frac{\Delta}{2} \le H} d^{3N} x d^{3N} p = \left(\frac{2\pi\Delta}{\omega} \right)^{3N}} \tag{4.142}$$

Exercise 4.6 Bohr-Somerfelt quantization condition ([13], pr. 2.5)

Show that

$$\oint p dq = \left(n + \frac{1}{2} \right) h, \tag{4.143}$$

provided the particle's potential is such that

$$m\hbar \left| \frac{dV}{dq} \right| \ll (m(E - V))^{3/2}. \tag{4.144}$$

Answer for Exercise 4.6

I took a guess that this was actually the WKB condition

$$\frac{k'}{k^2} \ll 1, \tag{4.145}$$

where the WKB solution was of the form

$$k^2(q) = 2m(E - V(q))/\hbar^2 \tag{4.146a}$$

$$\psi(q) = \frac{1}{\sqrt{k}} e^{\pm i \int k(q) dq}. \tag{4.146b}$$

The WKB validity condition is

$$1 \gg \frac{-2mV'}{\hbar} \frac{1}{2} \frac{1}{\sqrt{2m(E-V)}} \frac{\hbar^2}{2m(E-V)}, \tag{4.147}$$

or

$$m\hbar \left| V' \right| \ll (2m(E-V))^{3/2}. \tag{4.148}$$

This differs by a factor of $2\sqrt{2}$ from the constraint specified in the problem, but I'm guessing that constant factors of that sort have just been dropped.

Even after figuring out that this question was referring to WKB, I didn't know what to make of the oriented integral $\int pdq$. With p being an operator in the QM context, what did this even mean. I found the answer in [4] §12.12. Here p just means

$$p(q) = \hbar k(q), \tag{4.149}$$

where $k(q)$ is given by eq. (4.146a). The rest of the problem can also be found there and relies on the WKB connection formulas, which aren't derived in any text that I own. Quoting results based on other results that I don't know the origin of it's worthwhile, so that's as far as I'll attempt this question (but do plan to eventually look up and understand those WKB connection formulas, and then see how they can be applied in a problem like this).

Exercise 4.7 Small angle pendulum phase space ([13] *pr. 2.6*)

Analyze the (presumably small angle) pendulum problem in phase space. Also show that the phase space area A contained in the trajectory relates the energy and period of the system.

Answer for Exercise 4.7

With coordinates as in fig. 4.16, our Lagrangian is

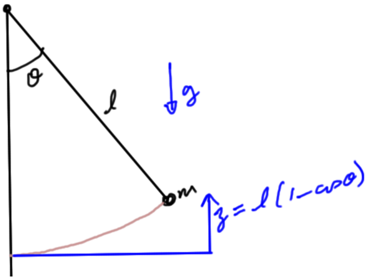


Figure 4.16: 1d pendulum.

$$\mathcal{L} = \frac{1}{2} m l^2 \dot{\theta}^2 - g m l (1 - \cos\theta). \tag{4.150}$$

As a sign check we find for small θ from the Euler-Lagrange equations $\ddot{\theta} = -(g/l)\theta$ as expected. For the Hamiltonian, we need the canonical momentum

$$p_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = m l^2 \dot{\theta}. \tag{4.151}$$

Observe that this canonical momentum does not have dimensions of momentum, but that of angular momentum ($m l \dot{\theta} \times l$). Our Hamiltonian is

$$H = \frac{1}{2 m l^2} p_\theta^2 + g m l (1 - \cos\theta). \tag{4.152}$$

Hamilton's equations for this system, in matrix form are

$$\frac{d}{dt} \begin{bmatrix} \theta \\ p_\theta \end{bmatrix} = \begin{bmatrix} \frac{\partial H}{\partial p_\theta} \\ -\frac{\partial H}{\partial \theta} \end{bmatrix} = \begin{bmatrix} p_\theta / m l^2 \\ -g m l \sin\theta \end{bmatrix} \tag{4.153}$$

With $\omega = g/l$, it is convenient to non-dimensionalize this

$$\frac{d}{dt} \begin{bmatrix} \theta \\ p_\theta / \omega m l^2 \end{bmatrix} = \omega \begin{bmatrix} p_\theta / \omega m l^2 \\ -\sin\theta \end{bmatrix}. \tag{4.154}$$

Now we can make the small angle approximation. Writing

$$\mathbf{u} = \begin{bmatrix} \theta \\ p_\theta/\omega m l^2 \end{bmatrix} \tag{4.155a}$$

$$i = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}. \tag{4.155b}$$

Our pendulum equation is reduced to

$$\mathbf{u}' = i\omega\mathbf{u}, \tag{4.156}$$

With a solution that we can read off by inspection

$$\mathbf{u} = e^{i\omega t}\mathbf{u}_0 = \begin{bmatrix} \cos\omega t & \sin\omega t \\ -\sin\omega t & \cos\omega t \end{bmatrix} \mathbf{u}_0. \tag{4.157}$$

Let's put the initial phase space point into polar form

$$\begin{aligned} \mathbf{u}_0^2 &= \theta_0^2 + \frac{p_0^2}{\omega^2 m^2 l^4} \\ &= \frac{2}{\omega^2 m l^2}\left(\frac{p_0^2}{2ml^2} + \frac{1}{2}\omega^2 m l^2 \theta_0^2\right) \\ &= \frac{2}{gml}\left(\frac{p_0^2}{2ml^2} + \frac{1}{2} gml\theta_0^2\right). \end{aligned} \tag{4.158}$$

This doesn't appear to be an exact match for eq. (4.152), but we can write for small θ_0

$$\begin{aligned} 1 - \cos\theta_0 &= 2\sin^2\left(\frac{\theta_0}{2}\right) \\ &\approx 2\left(\frac{\theta_0}{2}\right)^2 \\ &= \frac{\theta_0^2}{2}. \end{aligned} \tag{4.159}$$

This shows that we can rewrite our initial conditions as

$$\mathbf{u}_0 = \sqrt{\frac{2E}{gml}} e^{i\phi} \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \tag{4.160}$$

where

$$\tan\phi = \left(\omega m l^2 \theta_0 / p_0\right) . \tag{4.161}$$

Our time evolution in phase space is given by

$$\begin{bmatrix} \theta(t) \\ p_\theta(t) \end{bmatrix} = \sqrt{\frac{2E}{gml}} \begin{bmatrix} \cos(\omega t + \phi) \\ -\omega m l^2 \sin(\omega t + \phi) \end{bmatrix} , \tag{4.162}$$

or

$$\boxed{\begin{bmatrix} \theta(t) \\ p_\theta(t) \end{bmatrix} = \frac{1}{\omega l}\sqrt{\frac{2E}{m}} \begin{bmatrix} \cos(\omega t + \phi) \\ -\omega m l^2 \sin(\omega t + \phi) \end{bmatrix} .} \tag{4.163}$$

This is plotted in fig. 4.17.

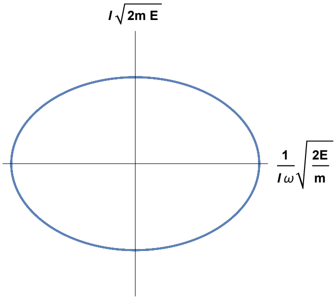


Figure 4.17: Phase space trajectory for small angle pendulum.

The area of this ellipse is

$$A = \pi \frac{1}{\omega^2 l^2} \frac{2E}{m} \omega m l^2 = \frac{2\pi}{\omega} E. \tag{4.164}$$

With τ for the period of the trajectory, this is

$$A = \tau E. \tag{4.165}$$

As a final note, observe that the oriented integral from problem 2.5 of the text $\oint p_\theta d\theta$, is also this area. This is a general property, which can be seen geometrically in fig. 4.18, where we see that the counterclockwise oriented integral of $\oint p dq$ would give the negative area. The integrals along the c_4, c_1 paths give the area under the blob, whereas the integrals along the other paths where the sense is opposite, give the complete area under the top boundary. Since they are oppositely sensed, adding them gives just the area of the blob.

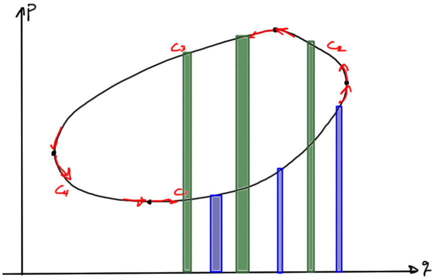


Figure 4.18: Area from oriented integral along path.

Let's do this $\oint p_\theta d\theta$ integral for the pendulum phase trajectories. With

$$\theta = \frac{1}{\omega l}\sqrt{\frac{2E}{m}}\cos(\omega t + \phi) \tag{4.166a}$$

$$p_\theta = -ml\sqrt{\frac{2E}{m}}\sin(\omega t + \phi). \tag{4.166b}$$

We have

$$\begin{aligned}\oint p_\theta d\theta &= \frac{ml}{\omega l}\frac{2E}{m}\int_0^{2\pi/\omega} \sin^2(\omega t + \phi)\omega dt \\ &= 2E\int_0^{2\pi/\omega} \frac{1 - \cos\left(2(\omega t + \phi)\right)}{2} dt \\ &= E\frac{2\pi}{\omega} \\ &= E\tau.\end{aligned} \tag{4.167}$$

THERMODYNAMICS. 5

Let's move on to discuss some concepts of thermodynamics

5.1 FIRST LAW OF THERMODYNAMICS.

This is the law of energy conservation! [1]

$$dE = \text{đ}W + \text{đ}Q, \tag{5.1}$$

where dE is the change in energy, $\text{đ}W$ is the work done on the system, and $\text{đ}Q$ is the heat supplied to the system, and the đ differentials indicate that the change is path dependent. For example the number of times a piston is moved back and forth can be significant, even given a specific change in the total differential change in the piston position. The total change of energy in such a change is not path dependent.

Consider a piston setup compressing some gas taking the position of the piston from $X \rightarrow X + dX$ as in fig. 5.1.

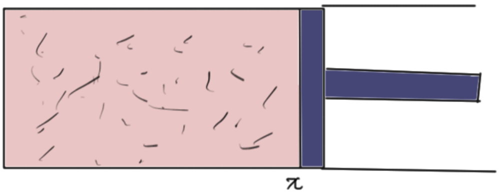


Figure 5.1: Piston and gas.

$$\text{đ}W = \sum_i \underbrace{\boxed{f_i}}_{\text{Generated force}} \overbrace{\boxed{dX_i}}^{\text{Controllable macroscopic coordinate}}. \tag{5.2}$$

---

[1] This requires some corrections if relativistic systems are studied.

What is $đQ$? These are the microscopic, and uncontrollable changes in energy.

5.2 ADIABATIC AND OTHER PROCESSES.

- Change $X_i \rightarrow X_i + dX_i$
- Change $đQ$

Adiabatic process These are those that are thermally isolated, or

$$đQ = 0. \tag{5.3}$$

The only way to change energy is to change the macroscopic X_i, so the change in energy is given by

$$dE = đW = \sum_i f_i dX_i. \tag{5.4}$$

These are what we are used to thinking about as conservative systems. Imagine, for example, a force applied to a spring, slowly so that there is no heat loss, we can figure out the total change in energy by summing differential changes to the spring.

We can imagine that there is some way to change the position that results in a change of energy. This is of course just the force as in fig. 5.2.

$$-\frac{dE}{dx_i} \sim \text{force}. \tag{5.5}$$

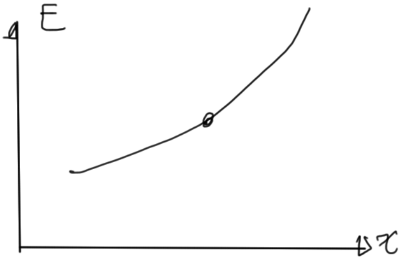


Figure 5.2: A possible energy position relationship.

We can imagine that we started with an initially thermally isolated system, with the macroscopic parameter unchanged, but somebody sneaks in and heats the system, before re-thermally isolating it. We'd then have a system that perhaps looks like fig. 5.3.

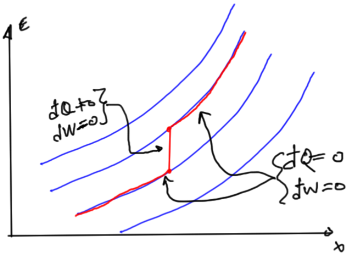


Figure 5.3: Level curves for adiabatic and non-adiabatic changes to the system.

The jumps from one curve from another is the product of the sneaky heat suppliers.

Now, if we think about this in a higher dimensional space, we'd instead have level surfaces.

5.3 FIRST LAW.

Energy conservation.

1. Work. Macroscopic control
2. heat. Uncontrollable (microscopically)

This is summarized by the differential relationship

$$dE = đW + đQ. \tag{5.6}$$

5.4 EXAMPLES OF WORK.

We have many types of work (in contrast to only one type of heat). Examples

- $-PdV = đW$

- $q\mathbf{E} \cdot dl$
- $kxdx$
- Hdm

Homework: verify the signs of these.
We put these into a general form, to first order, of

$$đW_i = f_i dx_i, \tag{5.7}$$

where we assume that higher order terms are not significant.

$$đW = \sum_i đW_i = \sum_i f_i dx_i. \tag{5.8}$$

5.5 HEAT.

We have only one type of heat, which we loosely describe as something imbued by contact with a "hotter" system, as in fig. 5.4.

Figure 5.4: System in contact with heat source.

5.6 ADIABATIC PROCESSES.

This is defined as the condition where we have no heat exchange with the environment, or

$$đQ = 0. \tag{5.9}$$

We contrast this with heating processes for which we have

$$đW = 0. \tag{5.10}$$

Since we have N coordinates ($đW = \sum_{i=1}^{N} f_i dx_i$). We can think about an $n+1$ dimensional space, where

- N-dimensions are x_i
- 1 dimension that characterizes heat exchange.

Example 5.1: $n = 1$

Given work on gas

$$đW = -P dV. \tag{5.11}$$

We have a coordinate, not yet precisely defined, for which fixed levels indicate that there is no heat exchange occurring, as in fig. 5.5.

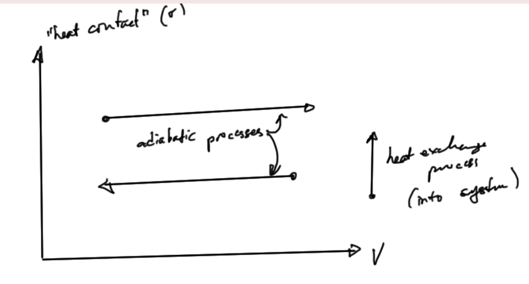


Figure 5.5: Adiabatic and heat exchange processes.

We'll call this axis σ, the thermodynamic entropy.

We've been introduced to statistical entropy

$$S = k_B \ln \Omega. \tag{5.12}$$

We'll assume for now that these are not related and will eventually figure out the connection between these two concepts.

Example 5.2: $n = 2$

A representation of a adiabatic, or constant σ-hypersurface process is given in fig. 5.6, a heating/cooling process with transition between σ-hypersurfaces in fig. 5.7, and a cyclic process, in fig. 5.8.

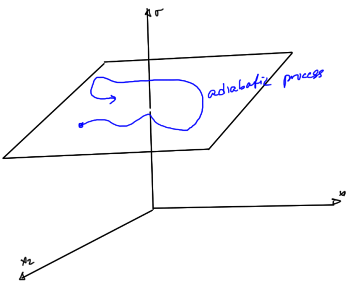


Figure 5.6: Adiabatic process.

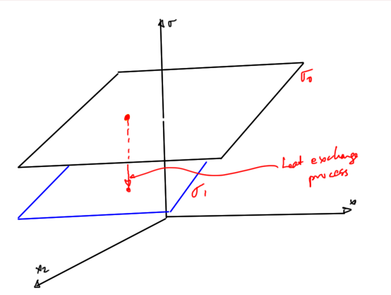


Figure 5.7: Heat exchange process.

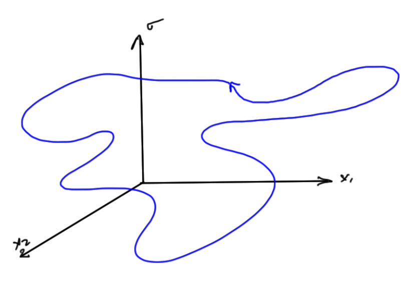


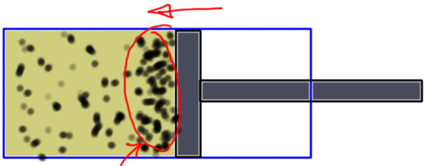
Figure 5.8: Cyclic process.

The cyclic process is one for which $dE = đW + đQ = 0$, however, this does not imply $đW = 0$ and $đQ = 0$ since we only require that the sum of the two is zero. In this whole process, we can have for example a net change in heat. Example: the engine of a car. Work is done, and heat is generated, but a car that was initially stopped and returns to its final destination, stops and cools down again, has still had significant internal action in the process.

5.7 REVERSIBLE PROCESSES.

What do we mean by reversible? We mean that any of the changes in the system have been done so slowly that we could reverse the direction of the processes at any point, and should we do so, both the system and the environment will be returned to its initial state. This is an idealization that is, most of the time, a good approximation, but gives us an excellent idea of the limits of what we can theoretically describe.

Question : Why does the speed of the process make a difference? If we are making changes to the system quickly, imagine that we are compressing a gas as in fig. 5.9.



only subset of system reacts to the change

Figure 5.9: Fast gas compression by a piston.

Doing work slowly means that the whole system can react to the change imposed. If we compressed the gas quickly, then changes to the system start only at the contact point with the piston. This can't be reversed. If we pull the piston out at this point, none of the non-front gas particles will be able to react. The system will not be in thermal equilibrium for fast changes.

We have energy conservation split into two types of energy

$$dE = \underbrace{\boxed{\text{đ}W}}_{\text{Organized macroscopic variable } X} + \overbrace{\boxed{\text{đ}Q}}^{\text{disorganized}}. \tag{5.13}$$

In fig. 5.10 we plot changes that are adiabatic processes ($\text{đ}Q = 0$) and heating and cooling processes (with $\text{đ}W = 0$).

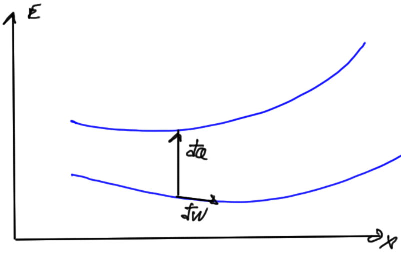


Figure 5.10: Adiabatic and heating processes.

Given a dimensionality of $d_w + 1$, a cyclic change is that for which we have

$$\{X_{\text{initial}}\} \rightarrow \{X_{\text{final}}\} \tag{5.14a}$$

$$E_{\text{initial}} \rightarrow E_{\text{final}} \tag{5.14b}$$

$$\Delta W \neq 0 \tag{5.14c}$$

$$\Delta Q \neq 0 \tag{5.14d}$$

$$\Delta E = 0 \tag{5.14e}$$

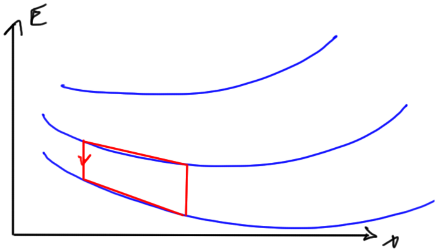


Figure 5.11: Cyclic process.

Such a cyclic process could be represented as in fig. 5.11.

Here we've labeled the level curves with a parameter σ, as yet undefined. We call σ the thermodynamic entropy, and say that

$$(\sigma, \{x_i\}), \tag{5.15}$$

specifies the state of the system.

Example: Pushing a block against a surface with friction.

5.8 EQUILIBRIUM.

Considering two systems in contact as in fig. 5.12.

Figure 5.12: Two systems in contact.

We require

1. Mechanical equilibrium.

requires balance of the forces f_i

$$\frac{\partial E}{\partial x_i} = f_i, \tag{5.16}$$

and[2]

$$\frac{\partial E_1}{\partial x_i} = \frac{\partial E_2}{\partial x_i}. \tag{5.17}$$

2. Thermal stability

$$\frac{\partial E_1}{\partial \sigma} = \frac{\partial E_2}{\partial \sigma}. \tag{5.18}$$

We must have some quantity that characterizes the state of the system in a non-macroscopic fashion. The identity eq. (5.18) is a statement that we have equal temperatures.

We define temperature as

$$T \equiv \frac{\partial E}{\partial \sigma}. \tag{5.19}$$

We could potentially define different sorts of temperature, for example, perhaps $T^3 \equiv \partial E/\partial \sigma$. Should we do this, we effectively also define σ in a specific way. The definition eq. (5.19) effectively defines this non-macroscopic parameter σ (the entropy) in the simplest possible way.

5.9 CYCLIC STATE VARIABLE VERSES NON-STATE VARIABLES.

$$\{x_i\}, \sigma \rightarrow \text{“state variable”} \tag{5.20}$$

A non-cyclic process changes these, whereas a cyclic process takes $\sigma, \{x_i\}$ back to the initial values. This is characterized by

$$\oint d\sigma = 0 \tag{5.21a}$$

$$\oint dx_i = 0. \tag{5.21b}$$

---

[2] Note the neglect of the sign here, the direction of the force isn’t really of interest.

This doesn't mean that the closed loop integral of other qualities, such as temperature are necessarily zero

$$\oint T d\sigma = \oint \text{đ}Q \neq 0 \tag{5.22a}$$

$$\oint f_i dx_i = \oint \text{đ}W \neq 0. \tag{5.22b}$$

Note that the identification of $\text{đ}Q = T d\sigma$ follows from our definition

$$\left(\frac{\partial E}{\partial \sigma}\right)_x = T, \tag{5.23}$$

so that with $\text{đ}W = 0$ we have

$$dE = T \text{đ}\sigma. \tag{5.24}$$

Graphically we have for a cyclic process fig. 5.13.

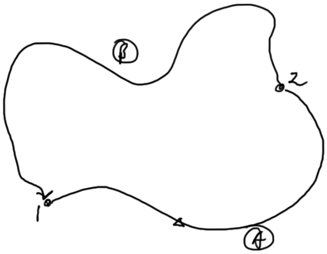


Figure 5.13: Cyclic process.

We have

$$\text{đ}W_{\rightarrow} = -\text{đ}W_{\leftarrow} \tag{5.25a}$$

$$\text{đ}Q_{\rightarrow} = -\text{đ}Q_{\leftarrow}, \tag{5.25b}$$

so that

$$\Delta Q_{12}^{(\mathrm{A})} + \Delta Q_{21}^{(\mathrm{B})} \neq 0, \tag{5.26}$$

or

$$\Delta Q_{12}^{(\mathrm{A})} \neq \Delta Q_{12}^{(\mathrm{B})}. \tag{5.27}$$

5.10 IRREVERSIBLE AND REVERSIBLE PROCESSES.

Reversible means that an undoing of the macroscopic quantities brings us back to the initial state. A counter example is a block on a spring as illustrated in fig. 5.14.

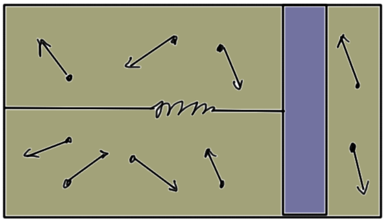


Figure 5.14: Heat loss and irreversibility.

In such a system the block will hit gas atoms as it moves. It's hard to imagine that such gas particles will somehow spontaneously reorganize itself so that they return to their initial positions and velocities. This is the jist of the second law of thermodynamics. Real processes introduce a degree of irreversibility with

$$\text{Energy}_1 \rightarrow \text{Energy}_2 \tag{5.28a}$$

$$\text{Work} \rightarrow \text{Heat}, \tag{5.28b}$$

but not all

$$\text{Heat} \rightarrow \text{Work}. \tag{5.29}$$

5.11 PROBLEMS.

Exercise 5.1 Sackur-Tetrode entropy of an Ideal Gas ([14] 2.35)

The entropy of an ideal gas is given by

$$S = N k_{\mathrm{B}} \left(\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right). \tag{5.30}$$

Find the temperature of this gas via $(\partial S/\partial E)_{V,N} = 1/T$. Find the energy per particle at which the entropy becomes negative. Is there any meaning to this temperature?

Answer for Exercise 5.1

Taking derivatives we find

$$\begin{aligned}\frac{1}{T} &= \frac{\partial}{\partial E}\left(\cancel{N k_B \ln \frac{V}{N}} + N k_B \frac{3}{2} \ln\left(\frac{4\pi m E}{3 N h^2}\right) + \cancel{N k_B \frac{5}{2}}\right) \\ &= \frac{3}{2} N k_B \frac{1}{E}\end{aligned} \tag{5.31}$$

or

$$\boxed{T = \frac{2}{3}\frac{E}{N k_B}.} \tag{5.32}$$

The energies for which the entropy is negative are given by

$$\left(\frac{4\pi m E}{3 N h^2}\right)^{3/2} \le \frac{N}{V} e^{-5/2}, \tag{5.33}$$

or

$$E \le \frac{3 N h^2}{4\pi m}\left(\frac{N}{V e^{5/2}}\right)^{2/3} = \frac{3 h^2 N^{5/3}}{4\pi m V^{2/3} e^{5/2}}. \tag{5.34}$$

In terms of the temperature T this negative entropy condition is given by

$$\frac{3\cancel{N}}{\cancel{2}} k_B T \le \frac{3\cancel{N}}{\cancel{2}}\left(\frac{N}{V}\right)^{2/3} \frac{h^2}{e^{5/2}}, \tag{5.35}$$

or

$$\boxed{\frac{\sqrt{2\pi m k_B T}}{h} \le \left(\frac{N}{V}\right)^{1/3} \frac{1}{e^{5/4}}.} \tag{5.36}$$

There will be a particle density V/N for which this distance $h/\sqrt{2\pi m k_B T}$ will start approaching the distance between atoms. This distance constrains the validity of the ideal gas law entropy equation. Putting this quantity back into the entropy eq. (5.30) we have

$$\frac{S}{Nk_\mathrm{B}} = \ln \frac{V}{N} \left(\frac{\sqrt{2\pi m k_\mathrm{B} T}}{h} \right)^3 + \frac{5}{2}. \tag{5.37}$$

We see that a positive entropy requirement puts a bound on this distance (as a function of temperature) since we must also have

$$\frac{h}{\sqrt{2\pi m k_\mathrm{B} T}} \ll \left(\frac{V}{N} \right)^{1/3}, \tag{5.38}$$

for the gas to be in the classical domain. I'd actually expect a gas to liquefy before this transition point, making such a low temperature nonphysical. To get a feel for whether this is likely the case, we should expect that the logarithm argument to be

$$\frac{V}{N} \left(\frac{\sqrt{2\pi m k_\mathrm{B} T}}{h} \right)^3, \tag{5.39}$$

at the point where gasses liquefy (at which point we assume the ideal gas law is no longer accurate) to be well above unity. Checking this for 1 liter of a gas with $10^2 3$ atoms for hydrogen, helium, and neon respectively we find the values for 5.39 are

$$173.682, 130.462, 23993. \tag{5.40}$$

At least for these first few cases we see that the ideal gas law has lost its meaning well before the temperatures below which the entropy would become negative.

Exercise 5.2 Ideal gas thermodynamics ([14] 1.33)

An ideal gas starts at (V_0, P_0) in the pressure-volume diagram (x-axis = V, y-axis = P), then moves at constant pressure to a larger volume (V_1, P_0), then moves to a larger pressure at constant volume to (V_1, P_1), and finally returns to (V_0, P_0), thus undergoing a cyclic process (forming a triangle in $P - V$ plane). For each step, find the work done on the gas, the change in energy content, and heat added to the gas. Find the total work/energy/heat change over the entire cycle.

Answer for Exercise 5.2

Our process is illustrated in fig. 5.15.

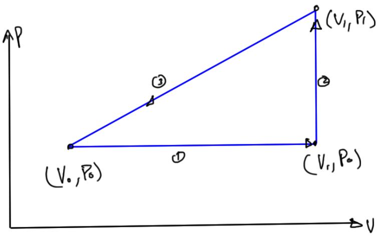


Figure 5.15: Cyclic pressure volume process.

Step 1 This problem is somewhat underspecified. From the ideal gas law, regardless of how the gas got from the initial to the final states, we have

$$P_0 V_0 = N_0 k_B T_0 \tag{5.41a}$$

$$P_0 V_1 = N_1 k_B T_1, \tag{5.41b}$$

so a volume increase with fixed P implies that there is a corresponding increase in NT. We could have for example, an increase in the number of particles, as in the evaporation process illustrated of fig. 5.16, where a piston held down by (fixed) atmospheric pressure is pushed up as the additional gas boils off.

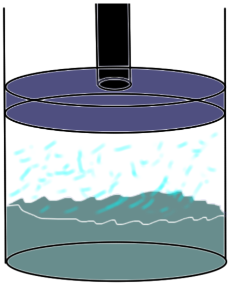


Figure 5.16: Evaporation process under (fixed) atmospheric pressure.

Alternately, we could have a system such as that of fig. 5.17, with a fixed amount of gas is in contact with a heat source that supplies the energy required to induce the required increase in temperature.

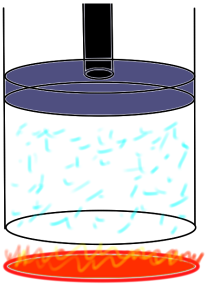


Figure 5.17: Gas of fixed mass absorbing heat.

Regardless of the source of the energy that accounts for the increase in volume the work done <u>on</u> the gas (a negation of the positive work the gas is performing on the system, perhaps a piston as in the picture) is

$$đW_1 = -\int_{V_0}^{V_1} p dV = -P_0(V_1 - V_0). \tag{5.42}$$

Let's now assume that we have the second sort of configuration above, where the total amount of gas is held fixed. From the ideal gas relations of eq. (5.41), and with $\Delta V = V_1 - V_0$, $\Delta T = T_1 - T_0$, and $N_1 = N_0 = N$, we have

$$P_0 \Delta V = N k_B \Delta T. \tag{5.43}$$

The change in energy of the ideal gas, assuming three degrees of freedom, is

$$dU = \frac{3}{2} N k_B \Delta T = \frac{3}{2} P_0 \Delta V. \tag{5.44}$$

The energy balance then requires that the total heat absorbed by the gas must include that portion that has done work on the system, plus the excess kinetic energy of the gas. That is

$$đQ_1 = \frac{3}{2} P_0 \Delta V + P_0 \Delta V = \frac{5}{2} P_0 \Delta V. \tag{5.45}$$

Step 2 For this leg of the cycle we have no work done on the gas

$$\text{đ}W_2 = -\int_{V_1}^{V_1} P dV = 0. \tag{5.46}$$

We do, however have a change in energy. The energy of the gas is

$$U = \frac{3}{2} N k_\text{B} T = \frac{3}{2} P V. \tag{5.47}$$

With $\Delta P = P_1 - P_0$, the change of energy of the gas, the total heat absorbed by the gas, is

$$dU_2 = \text{đ}Q_2 = \frac{3}{2} V_1 \Delta P. \tag{5.48}$$

Step 3 For the final leg of the cycle, the work done on the gas is

$$\begin{aligned} \text{đ}W_3 &= -\int_{V_1}^{V_0} P dV \\ &= \int_{V_0}^{V_1} P dV \\ &= \Delta V \frac{P_0 + P_1}{2}. \end{aligned} \tag{5.49}$$

This is positive this time Unlike the first part of the cycle, the work done on the gas is positive this time (work is being done on the gas to both compress it). The change in energy of the gas, however, is negative, with the difference between final and initial energy being

$$\begin{aligned} dU_3 &= \frac{3}{2}(P_0 V_0 - P_1 V_1) \\ &= -\frac{3}{2}(P_1 V_1 - P_0 V_0) \\ &< 0. \end{aligned} \tag{5.50}$$

The simultaneous compression and the pressure reduction require energy to be removed from the gas. We must have a negative change in heat $\text{đ}Q < 0$, with heat emitted in this phase of the cycle. This can be verified explicitly

$$\begin{aligned} \text{đ}Q_3 &= dU - \text{đ}W \\ &= -\frac{3}{2}(P_1 V_1 - P_0 V_0) - \frac{1}{2}\Delta V (P_1 + P_0) \\ &< 0. \end{aligned} \tag{5.51}$$

Changes over the complete cycle. Summarizing the results from each of the phases, we have

$$đW_1 = -P_0 \Delta V \tag{5.52a}$$

$$đQ_1 = \frac{5}{2} P_0 \Delta V \tag{5.52b}$$

$$dU_1 = \frac{3}{2} P_0 \Delta V \tag{5.52c}$$

$$đW_2 = 0 \tag{5.53a}$$

$$đQ_2 = \frac{3}{2} V_1 \Delta P \tag{5.53b}$$

$$dU_2 = \frac{3}{2} V_1 \Delta P \tag{5.53c}$$

$$đW_3 = \Delta V \frac{P_0 + P_1}{2} \tag{5.54a}$$

$$đQ_3 = -\frac{1}{2}(3(P_1 V_1 - P_0 V_0) + \Delta V (P_1 + P_0)) \tag{5.54b}$$

$$dU_3 = -\frac{3}{2}(P_1 V_1 - P_0 V_0). \tag{5.54c}$$

Summing the changes in the work we have

$$\sum_{i=1}^{3} đW_i = \frac{1}{2} \Delta V \Delta P > 0. \tag{5.55}$$

This is the area of the triangle, as expected. Since it is positive, there is net work done on the gas.

We expect the energy changes to sum to zero, and this can be verified explicitly finding

$$\sum_{i=1}^{3} dU_i = \frac{3}{2} P_0 \Delta V - \frac{3}{2}(P_1 V_1 - P_0 V_0) = 0. \tag{5.56}$$

With net work done on the gas and no change in energy, there should be no net heat absorption by the gas, with a total change in heat that should equal, in amplitude, the total work done on the gas. This is confirmed by summation

$$\begin{aligned}\sum_{i=1}^{3} đQ_i &= \frac{5}{2} P_0 \Delta V + \frac{3}{2} V_1 \Delta P - \frac{1}{2}(3(P_1 V_1 - P_0 V_0) + \Delta V (P_1 + P_0)) \\ &= -\frac{1}{2} \Delta P \Delta V.\end{aligned} \tag{5.57}$$

Exercise 5.3 Adiabatic process for an Ideal Gas ([14] *1.40(a)*)

Show that when an ideal monoatomic gas expands adiabatically, the temperature and pressure are related by

$$\frac{dT}{dP} = \frac{2}{5}\frac{T}{P}. \tag{5.58}$$

Answer for Exercise 5.3

From (3.34b) of [11], we find that the Adiabatic condition can be expressed algebraically as

$$0 = đQ = T dS = dU + P dV. \tag{5.59}$$

With

$$U = \frac{3}{2} N k_{\mathrm{B}} T = \frac{3}{2} P V, \tag{5.60}$$

this is

$$\begin{aligned}0 &= \frac{3}{2} V dP + \frac{3}{2} P dV + P dV \\ &= \frac{3}{2} V dP + \frac{5}{2} P dV.\end{aligned} \tag{5.61}$$

Dividing through by PV, this becomes a perfect differential, and we can integrate

$$\begin{aligned}0 &= 3\int \frac{dP}{P} + 5\int \frac{dV}{V} \\ &= 3\ln P + 5\ln V + \ln C \\ &= 3\ln PV + 2\ln V + \ln C \\ &= \ln(Nk_\mathrm{B}T)^3 + \ln\left(\frac{Nk_\mathrm{B}T}{P}\right)^2 + \ln C.\end{aligned} \tag{5.62}$$

Exponentiating yields

$$T^5 = C'P^2. \tag{5.63}$$

The desired relation follows by taking derivatives

$$\begin{aligned}2C'P &= 5T^4\frac{dT}{dP} \\ &= 5C'\frac{P^2}{T}\frac{dT}{dP},\end{aligned} \tag{5.64}$$

or

$$\frac{dT}{dP} = \frac{2}{5}\frac{T}{P}, \tag{5.65}$$

as desired.

STATISTICAL AND THERMODYNAMIC CONNECTION.

6

6.1 CONNECTIONS BETWEEN STATISTICAL AND THERMODYNAMIC VIEWS.

1. "Heat". Disorganized energy.
2. $S_{\text{Statistical entropy}}$. This is the thermodynamic entropy introduced by Boltzmann (microscopic).

6.2 IDEAL GAS.

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{6.1}$$

$$\Omega(E) = \frac{1}{h^{3N} N!} \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N \delta(E - H). \tag{6.2}$$

Let's isolate the contribution of the Hamiltonian from a single particle and all the rest

$$H = \frac{\mathbf{p}_1^2}{2m} + \sum_{i \neq 1}^{N} \frac{\mathbf{p}_i^2}{2m} = \frac{\mathbf{p}_1^2}{2m} + H', \tag{6.3}$$

so that the number of states in the phase space volume in the phase space region associated with the energy is

$$\begin{aligned}
&\Omega(N, E) \\
&= \frac{V^N}{h^{3N} N!} \int d\mathbf{p}_1 \int d\mathbf{p}_2 d\mathbf{p}_3 \cdots d\mathbf{p}_N \delta(E - H' - H_1) \\
&= \frac{V^{N-1}}{h^{3(N-1)} (N-1)!} \frac{V}{h^3 N} \int d\mathbf{p}_1 \int d\mathbf{p}_2 d\mathbf{p}_3 \cdots d\mathbf{p}_N \delta(E - H' - H_1) \\
&= \frac{V}{h^3 N} \int d\mathbf{p}_1 \Omega(N - 1, E - H_1).
\end{aligned} \tag{6.4}$$

With entropy defined by

$$S = k_{\mathrm{B}} \ln \Omega, \tag{6.5}$$

we have

$$\Omega(N-1, E-H_1) = \exp\left(\frac{1}{k_{\mathrm{B}}} S\left(N-1, E-\frac{\mathbf{p}_1^2}{2m}\right)\right), \tag{6.6}$$

so that

$$\Omega(N, E) = \frac{V}{h^3 N} \int d\mathbf{p}_1 \exp\left(\frac{1}{k_{\mathrm{B}}} S\left(N-1, E-\frac{\mathbf{p}_1^2}{2m}\right)\right). \tag{6.7}$$

For $N \gg 1$ and $E \gg \mathbf{p}_1^2/2m$, the exponential can be approximated by

$$\begin{aligned} &\exp\left(\frac{1}{k_{\mathrm{B}}} S\left(N-1, E-\frac{\mathbf{p}_1^2}{2m}\right)\right) \\ &\quad = \exp\left(\frac{1}{k_{\mathrm{B}}}\left(S(N,E) - \left(\frac{\partial S}{\partial N}\right)_{E,V} - \frac{\mathbf{p}_1^2}{2m}\left(\frac{\partial S}{\partial E}\right)_{N,V}\right)\right), \end{aligned} \tag{6.8}$$

so that

$$\Omega(N, E) = \int d\mathbf{p}_1 \overset{B}{\boxed{\frac{V}{h^3 N} e^{\frac{S}{k_{\mathrm{B}}}(N,E)} e^{-\frac{1}{k_{\mathrm{B}}}\left(\frac{\partial S}{\partial N}\right)_{E,V}}}} e^{-\frac{\mathbf{p}_1^2}{2mk_{\mathrm{B}}}\left(\frac{\partial S}{\partial E}\right)_{N,V}}, \tag{6.9}$$

or

$$\Omega(N, E) = B \int d\mathbf{p}_1 e^{-\frac{\mathbf{p}_1^2}{2mk_{\mathrm{B}}}\left(\frac{\partial S}{\partial E}\right)_{N,V}}. \tag{6.10}$$

$$\mathcal{P}(\mathbf{p}_1) \propto e^{-\frac{\mathbf{p}_1^2}{2mk_{\mathrm{B}}T}}. \tag{6.11}$$

This is the Maxwell distribution.

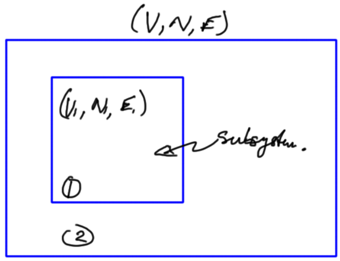


Figure 6.1: Partitioning out a subset of a larger system.

6.3 NON-IDEAL GAS. GENERAL CLASSICAL SYSTEM.

Breaking the system into a subsystem 1 and the reservoir 2 so that with

$$H = H_1 + H_2, \tag{6.12}$$

we have

$$\begin{aligned}\Omega(N, V, E) &= \int d\{x_1\}d\{p_1\}d\{x_2\}d\{p_2\}\times \\ &\qquad \delta(E - H_1 - H_2)\frac{1}{h^{3N_1}N_1!\,h^{3N_2}N_2!} \\ &\propto \int d\{x_1\}d\{p_1\}e^{\frac{1}{k_\mathrm{B}}S(E-H_1,N-N_1)}.\end{aligned} \tag{6.13}$$

$$\Omega(N, V, E) \sim \int d\{x_1\}d\{p_1\}\overset{\text{“environment”, or “heat bath”}}{\boxed{e^{\frac{1}{k_\mathrm{B}}S(E,N)}e^{-\frac{N_1}{k_\mathrm{B}}\left(\frac{\partial S}{\partial N}\right)_{E,V}}}}e^{-\frac{H_1}{k_\mathrm{B}}\left(\frac{\partial S}{\partial E}\right)_{N,V}}. \tag{6.14}$$

$$H_1 = \sum_{i\in 1}\frac{\mathbf{p}_i}{2m} + \sum_{i\in j} V(\mathbf{x}_i - \mathbf{x}_j) + \sum_{i\in 1}\Phi(\mathbf{x}_i). \tag{6.15}$$

$$\mathcal{P} \propto e^{-\frac{H(\{x_1\}\{p_1\})}{k_\mathrm{B}T}}, \tag{6.16}$$

and for the subsystem

$$\mathcal{P}_1 = \frac{e^{-\frac{H_1}{k_\mathrm{B}T}}}{\int d\{x_1\}d\{p_1\}e^{-\frac{H_1}{k_\mathrm{B}T}}}. \tag{6.17}$$

6.4 CANONICAL ENSEMBLE.

Can we use results for this subvolume, can we use this to infer results for the entire system? Suppose we break the system into a number of smaller subsystems as in fig. 6.2.

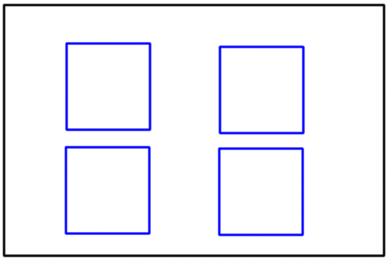


Figure 6.2: Larger system partitioned into many small subsystems.

$$\overset{\text{microcanonical}}{\boxed{(N, V, E)}} \rightarrow (N, V, T) \tag{6.18}$$

We'd have to understand how large the differences between the energy fluctuations of the different subsystems are. We've already assumed that we have minimal long range interactions since we've treated the subsystem 1 above in isolation. With $\beta = 1/(k_\mathrm{B} T)$ the average energy is

$$\langle E \rangle = \frac{\int d\{x_1\} d\{p_1\} H e^{-\beta H}}{\int d\{x_1\} d\{p_1\} e^{-\beta H}} \tag{6.19}$$

$$\left\langle E^2 \right\rangle = \frac{\int d\{x_1\} d\{p_1\} H^2 e^{-\beta H}}{\int d\{x_1\} d\{p_1\} e^{-\beta H}}. \tag{6.20}$$

We define the partition function

$$\boxed{Z \equiv \frac{1}{h^{3N} N!} \int d\{x_1\} d\{p_1\} e^{-\beta H}.} \tag{6.21}$$

Observe that the derivative of Z is

$$\frac{\partial Z}{\partial \beta} = -\frac{1}{h^{3N} N!} \int d\{x_1\} d\{p_1\} H e^{-\beta H}, \tag{6.22}$$

allowing us to express the average energy compactly in terms of the partition function

$$\boxed{\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}.} \tag{6.23}$$

Taking second derivatives we find the variance of the energy

$$\begin{aligned}\frac{\partial^2 \ln Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta}\frac{\int d\{x_1\}d\{p_1\}(-H)e^{-\beta H}}{\int d\{x_1\}d\{p_1\}e^{-\beta H}} \\ &= \frac{\int d\{x_1\}d\{p_1\}(-H)^2 e^{-\beta H}}{\int d\{x_1\}d\{p_1\}e^{-\beta H}} - \frac{\left(\int d\{x_1\}d\{p_1\}(-H)e^{-\beta H}\right)^2}{\left(\int d\{x_1\}d\{p_1\}e^{-\beta H}\right)^2}.\end{aligned} \tag{6.24}$$

We have a second thermodynamic result directly obtained from the partition function

$$\boxed{\sigma_{\mathrm{E}}^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}} \tag{6.25}$$

We also have

$$\begin{aligned}\sigma_{\mathrm{E}}^2 &= -\frac{\partial \langle E \rangle}{\partial \beta} \\ &= \frac{\partial \langle E \rangle}{\partial T}\frac{\partial T}{\partial \beta} \\ &= -\frac{\partial \langle E \rangle}{\partial T}\frac{\partial}{\partial \beta}\frac{1}{k_{\mathrm{B}}\beta} \\ &= \frac{\partial \langle E \rangle}{\partial T}\frac{1}{k_{\mathrm{B}}\beta^2} \\ &= k_{\mathrm{B}}T^2\frac{\partial \langle E \rangle}{\partial T}.\end{aligned} \tag{6.26}$$

Recalling that the heat capacity was defined by

$$C_{\mathrm{V}} = \frac{\partial \langle E \rangle}{\partial T}, \tag{6.27}$$

we have

$$\sigma_{\mathrm{E}}^2 = k_{\mathrm{B}}T^2 C_{\mathrm{V}} \propto N \tag{6.28}$$

$$\frac{\sigma_{\mathrm{E}}}{\langle E \rangle} \propto \frac{1}{\sqrt{N}}. \tag{6.29}$$

Question: What is this N proportionality?

The specific heat is the total energy change in response to a small change in temperature. This specific heat $\sim N$ since the energy change $\sim N$. So $\sigma_E^2 \sim N$. This is just the extensivity of the energy for any system with short range interactions. Doubling the size doubles the energy content.

6.5 CANONICAL PARTITION AND HELMHOLTZ FREE ENERGY.

We found

$$\frac{\sigma_{\mathrm{E}}}{E} \propto \frac{T\sqrt{C_{\mathrm{V}}}}{E} k_{\mathrm{B}}^2 \tag{6.30a}$$

$$Z = \sum_{\{c\}} e^{-\beta E(c)} \tag{6.30b}$$

$$C_{\mathrm{V}} \sim N \tag{6.30c}$$

$$E \sim N, \tag{6.30d}$$

where the partition function acts as a probability distribution so that we can define an average as

$$\langle A \rangle = \frac{\sum_{\{c\}} A(c) e^{-\beta E(c)}}{Z}. \tag{6.31}$$

If we suppose that the energy is typically close to the average energy as in fig. 6.3. , then we can approximate the partition function as

$$\begin{aligned} Z &\approx e^{-\beta \langle E \rangle} \sum_{\{c\}} \delta_{E,\bar{E}} \\ &= e^{-\beta \langle E \rangle} e^{S/k_{\mathrm{B}}}, \end{aligned} \tag{6.32}$$

where we've used $S = k_{\mathrm{B}} \ln \Omega$ to express the number of states where the energy matches the average energy $\Omega = \sum \delta_{E,\bar{E}}$.

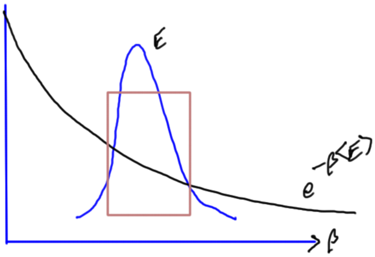


Figure 6.3: Peaked energy distribution.

This gives us

$$\begin{aligned}Z &= e^{-\beta(\langle E\rangle - k_{\mathrm{B}} T S/k_{\mathrm{B}})} \\ &= e^{-\beta(\langle E\rangle - TS)},\end{aligned} \tag{6.33}$$

or

$$\boxed{Z = e^{-\beta F},} \tag{6.34}$$

where we define the Helmholtz free energy F as

$$\boxed{F = \langle E\rangle - TS.} \tag{6.35}$$

Equivalently, the log of the partition function provides us with the partition function

$$F = -k_{\mathrm{B}} T \ln Z. \tag{6.36}$$

Recalling our expression for the average energy, we can now write that in terms of the free energy

$$\begin{aligned}\langle E\rangle &= \frac{\sum_{\{c\}} E(c) e^{-\beta E(c)}}{\sum_{\{c\}} e^{-\beta E(c)}} \\ &= -\frac{\partial}{\partial \beta} \ln Z \\ &= \frac{\partial(\beta F)}{\partial \beta}.\end{aligned} \tag{6.37}$$

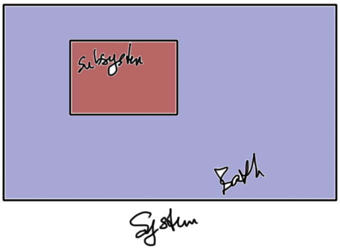


Figure 6.4: subsystem in heat bath.

6.6 QUANTUM MECHANICAL PICTURE.

Consider a subsystem as in fig. 6.4 where we have states of the form

$$\left|\Psi_{\text{full}}\right\rangle = \left|\chi_{\text{subsystem}}\right\rangle \left|\phi_{\text{bath}}\right\rangle, \tag{6.38}$$

and a total Hamiltonian operator of the form

$$H_{\text{full}} = H_{\text{subsystem}} + H_{\text{bath}} (+H_{\text{coupling}}), \tag{6.39}$$

where the total energy of the state, given energy eigenvalues $\mathcal{E}_n$ and λ_n for the states $\left|\chi_{\text{subsystem}}\right\rangle$ and $\left|\phi_{\text{bath}}\right\rangle$ respectively, is given by the sum

$$E = \mathcal{E}_m + \lambda_n. \tag{6.40}$$

Here $\mathcal{E}_m, \lambda_n$ are many body energies, so that $\delta E \sim \# e^{-\# N}$. We can now write the total number of states as

$$\begin{aligned}
\Omega(E) &= \overset{\text{subsystem}}{\boxed{\sum_m}} \underset{\text{bath}}{\boxed{\sum_n}} \delta(E - \mathcal{E}_m - \lambda_n) \\
&= \sum_m e^{\frac{1}{k_{\text{B}}} S(E - \mathcal{E}_m)} \\
&\approx \sum_m e^{\frac{1}{k_{\text{B}}} S(E)} e^{-\beta \mathcal{E}_m}
\end{aligned} \tag{6.41}$$

$$\begin{aligned} Z &= \sum_m e^{-\beta \mathcal{E}_m} \\ &= \operatorname{tr}\left(e^{-\beta \hat{H}_{\text{subsystem}}} \right). \end{aligned} \tag{6.42}$$

We've ignored the coupling term in eq. (6.39). This is actually a problem in quantum mechanics since we require this coupling to introduce state changes.

Example 6.1: Spins

Given N spin $1/2$ objects $\uparrow, \downarrow$, satisfying

$$S_z = \pm \frac{1}{2} \hbar, \tag{6.43}$$

where S_z is the magnitude of the spin operator

$$\hat{S}_z = \pm \frac{1}{2} \hbar \hat{\sigma}_z, \tag{6.44}$$

and $\hat{\sigma}_z$ is the Pauli matrix. Dropping $\hbar$ we have

$$S_z \rightarrow \pm \frac{1}{2} \sigma. \tag{6.45}$$

Our system has a state $\left| \sigma_1, \sigma_2, \cdots \sigma_N \right\rangle$ where $\sigma_i = \pm 1$. The total number of states is 2^N.

Recall from [5] §6.6 that $\hat{H} = (\sigma \cdot \mathbf{B})^2/2m$ and a gauge transformation $\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}/c$ results in an interaction term $-e\hbar \mathbf{S} \cdot \mathbf{B}/mc$. With $e = \hbar = c = 1$ and $\mathbf{B} = B\hat{\mathbf{z}}$, the portion of the Hamiltonian for just that spin interaction is

$$\hat{H} = -B \sum_i \hat{S}_{z_i}. \tag{6.46}$$

This is the associated with the Zeeman effect, where states can be split by a magnetic field, as in fig. 6.5.

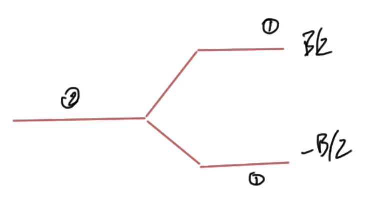


Figure 6.5: Zeeman splitting.

Our minimum and maximum energies are

$$E_{\text{min}} = -\frac{B}{2}\sum_{i=1}^{N}(+1) = -\frac{B}{2}N \tag{6.47a}$$

$$E_{\text{max}} = \frac{B}{2}\sum_{i=1}^{N}(-1) = \frac{B}{2}N. \tag{6.47b}$$

The total energy difference is

$$\Delta E = BN, \tag{6.48}$$

and the energy differences are

$$\delta E \sim \frac{BN}{2^N} \sim \# e^{-\# N}. \tag{6.49}$$

FIXME: where did this exponential come from?

This is a measure of the average energy difference between two adjacent energy levels. In a real system we cannot assume that we have non-interacting spins. Any weak interaction will split our degenerate energy levels as in fig. 6.6.

Figure 6.6: Interaction splitting.

We can now express the partition function

$$
\begin{aligned}
Z &= \sum_{\{\sigma\}} e^{-\beta\left(-\frac{B}{2}\sum_i \sigma_i\right)} \\
&= \boxed{\left(\sum_{\sigma_1\in\{-1,1\}} \exp\left(-\frac{\beta B}{2}\sigma_1\right)\right)\overset{N\text{ times.}}{\left(\sum_{\sigma_2\in\{-1,1\}} \exp\left(-\frac{\beta B}{2}\sigma_2\right)\right)}\cdots} \\
&= \left(\exp\left(-\frac{\beta B}{2}(1)\right) + \exp\left(-\frac{\beta B}{2}(-1)\right)\right)^N \\
&= \left(2\cosh\left(\frac{B}{2k_\mathrm{B}T}\right)\right)^N .
\end{aligned}
\tag{6.50}
$$

Our free energy is

$$
F = -k_\mathrm{B} T N \ln\left(2\cosh\left(\frac{B}{2k_\mathrm{B}T}\right)\right). \tag{6.51}
$$

For the expected value of the spin we find

$$
\langle S_z \rangle = \sum_i \langle S_{z_i} \rangle , \tag{6.52}
$$

where the expectation for a single particle's operator is

$$\begin{aligned}\langle S_{z_i} \rangle &= \frac{\sum_\sigma \frac{\sigma}{2} e^{\beta B \sigma/2}}{\sum_\sigma e^{\beta B \sigma/2}} \\ &= \frac{1}{2} \frac{2 \sinh\left(\beta B \sigma/2\right)}{2 \cosh\left(\beta B \sigma/2\right)} \\ &= \frac{1}{2} \tanh\left(\frac{B}{2 k_B T}\right).\end{aligned} \tag{6.53}$$

Example 6.2: Spin entropy in zero magnetic field

In [11] §6, is stated

Consider an atomic of spin I, where I may represent both electronic and nuclear spins. The internal partition function associated with the spin alone is:

$$Z_{\text{int}} = 2I + 1. \tag{6.54}$$

My question reading this: If I is the magnitude of the spin, then how would it also show up like this in the partition function (with no temperature or energy dependence?)

Prof Paramekanti's answer: At zero magnetic field, all spin states have exactly the same energy, which can be arbitrarily be chosen to be zero. The partition function then simply counts the number of configurations (since $\exp(-\beta H) = 1$, the trace is just a sum of "ones"). For a spin-I,the number of states is just $(2I + 1)$.

6.7 INTERACTING SPIN.

For this section

$$\boxed{\hbar = k_B = 1.}$$

This lecture requires concepts from phy456 [10].

We'll look at pairs of spins as a toy model of interacting spins as depicted in fig. 6.7.

Figure 6.7: Pairs of interacting spins.

Example: Simple atomic system, with the nucleus and the electron can interact with each other (hyper-fine interaction).

Consider two interacting spin 1/2 operators $\mathbf{S}$ each with components $\hat{S}^x$, $\hat{S}^y$, $\hat{S}^z$

$$H = J\mathbf{S}_1 \cdot \mathbf{S}_2 - B(\hat{S}_1^z + \hat{S}_2^z) \tag{6.55}$$

$$\hat{S}_1^z + \hat{S}_2^z \propto \text{magnetization along } \hat{\mathbf{z}}. \tag{6.56}$$

We rewrite the dot product term of the Hamiltonian in terms of just the squares of the spin operators

$$H = J\frac{(\mathbf{S}_1 + \mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2}{2} - B(\hat{S}_1^z + \hat{S}_2^z). \tag{6.57}$$

The squares $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, $(\mathbf{S}_1 + \mathbf{S}_2)^2$ can be thought of as "length"s of the respective angular momentum vectors. We write

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \tag{6.58}$$

for the total angular momentum. We recall that we have

$$\hat{S}_2^z = \hat{S}_1^z = S(S+1), \tag{6.59}$$

where $S = 1/2$, and $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ implies that $S_{\text{total}} \in \{0, 2\}$.

$S_{\text{total}} = 0$ state, $m = 0$ (singlet state) For this case the energy eigenvalue of H is

$$J\frac{0 - 3/4 - 3/4}{2} - B(0) = -\frac{3}{4}J. \tag{6.60}$$

This happens to be the eigenvalue corresponding to the eigenvector

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right), \tag{6.61}$$

but that isn't actually required for the stat mech problem.

$S_{\text{total}} = 1$ state, $m = 1$ As above we can compute the energy eigenvalue

$$J\frac{2 - \frac{3}{4} - \frac{3}{4}}{2} - B = \frac{J}{4} - B. \tag{6.62}$$

It can be shown that the eigenvector for this state is

$$\frac{1}{\sqrt{2}}\left(\uparrow\uparrow\right). \tag{6.63}$$

$S_{\text{total}} = 1$ state, $m = 0$ Our energy eigenvalue is

$$J\frac{2 - \frac{3}{4} - \frac{3}{4}}{2} - (0)B = \frac{J}{4}. \tag{6.64}$$

For which the corresponding state is

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right). \tag{6.65}$$

$S_{\text{total}} = 1$ state, $m = -1$ Our energy eigenvalue is

$$J\frac{2 - \frac{3}{4} - \frac{3}{4}}{2} - (-1)B = \frac{J}{4} + B. \tag{6.66}$$

With corresponding state

$$\frac{1}{\sqrt{2}}\left(\downarrow\downarrow\right). \tag{6.67}$$

The energy eigenvalues for the singlet and these last three (triplet) states are illustrated schematically in fig. 6.8.

Our single pair partition function is

$$Z_1 = e^{+\beta 3J/4} + e^{-\beta(J/4 - B)} + e^{-\beta 3J/4} + e^{-\beta(J/4 + B)}. \tag{6.68}$$

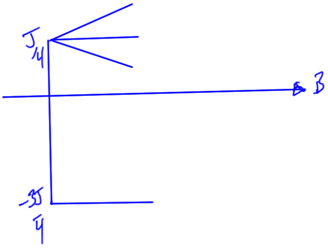


Figure 6.8: Energy levels for two interacting spins as a function of magnetic field.

For N pairs our partition function is

$$Z = Z_1^N = \left(e^{+\beta 3J/4} + e^{-\beta(J/4-B)} + e^{-\beta J/4} + e^{-\beta(J/4+B)} \right)^N . \tag{6.69}$$

Our free energy is

$$\begin{aligned} F &= -T \ln Z \\ &= -TN \ln Z_1 \\ &= -TN \ln \left(e^{+\beta 3J/4} + e^{-\beta(J/4-B)} + e^{-\beta J/4} + e^{-\beta(J/4+B)} \right) . \end{aligned} \tag{6.70}$$

We can use this to find the average energy

$$\begin{aligned} \langle H \rangle &= -\frac{\partial (\beta F)}{\partial \beta} \\ &= -N \frac{\partial}{\partial \beta} \ln Z_1 \\ &= -\frac{N}{Z_1} \frac{\partial Z_1}{\partial \beta} . \end{aligned} \tag{6.71}$$

The partition function derivative is

$$\begin{aligned}
&\frac{\partial Z_1}{\partial \beta} \\
&= \frac{\partial}{\partial \beta}\left(e^{+\beta 3J/4} + e^{-\beta(J/4-B)} + e^{-\beta J/4} + e^{-\beta(J/4+B)} \right) \\
&= \left(3\frac{J}{4} e^{+\beta 3J/4} - \left(\frac{J}{4} - B\right) e^{-\beta(J/4-B)} - \frac{J}{4} e^{-\beta J/4} - \left(\frac{J}{4} + B\right) e^{-\beta(J/4+B)} \right) \\
&= e^{-\beta J/4}\left(3\frac{J}{4} e^{\beta J} - \left(\frac{J}{4} - B\right) e^{\beta B} - \frac{J}{4} - \left(\frac{J}{4} + B\right) e^{-\beta B} \right) \\
&= \frac{N}{Z_1} e^{-\beta J/4}\left(\frac{J}{4}\left(3e^{\beta J} - e^{\beta B} - 1 - e^{-\beta B} \right) + B\left(e^{\beta B} - e^{-\beta B} \right) \right) \\
&= e^{-\beta J/4}\left(\frac{J}{4}\left(3e^{\beta J} - 1 - 2\cosh(\beta B) \right) + 2B\sinh(\beta B) \right).
\end{aligned} \tag{6.72}$$

So that the average energy is

$$\langle H \rangle = -\frac{N}{Z_1} e^{-\beta J/4}\left(\frac{J}{4}\left(3e^{\beta J} - 1 - 2\cosh(\beta B) \right) + 2B\sinh(\beta B) \right). \tag{6.73}$$

We could use this to calculate the specific heat directly, but let's express the specific heat first in terms of β derivatives of Z_1.

$$\begin{aligned}
C_{\mathrm{V}} &= \frac{\partial \langle H \rangle}{\partial T} \\
&= -\frac{1}{T^2}\frac{\partial \langle H \rangle}{\partial \beta} \\
&= -\beta^2 \frac{\partial}{\partial \beta}\left(-\frac{N}{Z_1}\frac{\partial Z_1}{\partial \beta} \right) \\
&= \beta^2 N \left(-\frac{1}{Z_1^2}\left(\frac{\partial Z_1}{\partial \beta}\right)^2 + \frac{1}{Z_1}\frac{\partial^2 Z_1}{\partial \beta^2} \right) \\
&= \frac{N\beta^2}{Z_1^2}\left(\frac{\partial^2 Z_1}{\partial \beta^2} - \left(\frac{\partial Z_1}{\partial \beta}\right)^2 \right).
\end{aligned} \tag{6.74}$$

After a bit of work, we find for the second partial of the partition function

$$\frac{\partial^2 Z_1}{\partial \beta^2} = e^{-\beta J/4} \times \\ \left(\left(\frac{3J}{4}\right)^2 e^{\beta J} + 2\cosh(\beta B) \left(\left(\frac{J}{4}\right)^2 + B^2 \right) - JB\sinh(\beta B) + \left(\frac{J}{4}\right)^2 \right). \tag{6.75}$$

That gives us the specific heat, but it's a messy expression, and not particularly illuminating.

Our magnetization μ is

$$\begin{aligned} \mu &= \frac{\partial F}{\partial B} \\ &= \frac{TN}{Z_1} \left(\beta e^{-\beta(J/4-B)} - \beta e^{-\beta(J/4+B)} \right) \\ &= \frac{\cancel{T\beta} N}{Z_1} e^{-\beta J/4} \left(e^{\beta B} - e^{-\beta B} \right) \\ &= \frac{2N}{Z_1} e^{-\beta J/4} \sinh(\beta B). \end{aligned} \tag{6.76}$$

The moment per particle, is

$$m = \frac{\mu}{N} = 2\frac{e^{-\beta J/4}}{Z_1} \sinh\left(\frac{B}{T}\right). \tag{6.77}$$

Low temperatures, small B ($T \ll J, B \ll J$) The $e^{3\beta J/4}$ term will dominate.

$$Z_1 \approx e^{3J\beta/4} \tag{6.78}$$

$$m \approx 2e^{-\beta J} \sinh\left(\frac{B}{T}\right). \tag{6.79}$$

The specific heat has a similar behavior

$$C_V \sim e^{-\beta J}. \tag{6.80}$$

Considering a single spin $1/2$ system, we have energies as illustrated in fig. 6.10.

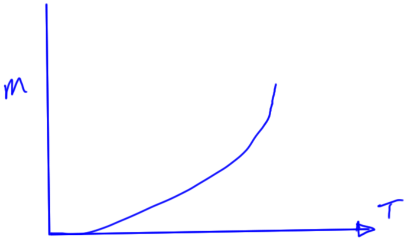


Figure 6.9: magnetic moment.

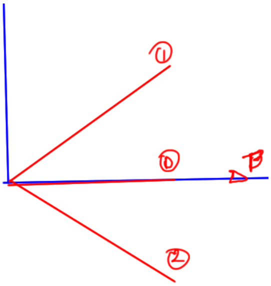


Figure 6.10: Single particle spin energies as a function of magnetic field.

At zero temperatures we have a finite non-zero magnetization as illustrated in fig. 6.11, but as we heat the system up, the state of the system will randomly switch between the 1, and 2 states. The partition function democratically averages over all such possible states.

Once the system heats up, the spins are democratically populated within the entire set of possible states.

We contrast this to this interacting spins problem which has a magnetization of the form fig. 6.12.

For the single particle specific heat we have specific heat of the form fig. 6.13.

We'll see the same kind of specific heat distribution with temperature for the interacting spins problem, but the peak will be found at an energy that's given by the difference in energies of the two states as illustrated in fig. 6.14.

$$\Delta E = \frac{J}{4} - \frac{-3J}{4} = J. \tag{6.81}$$

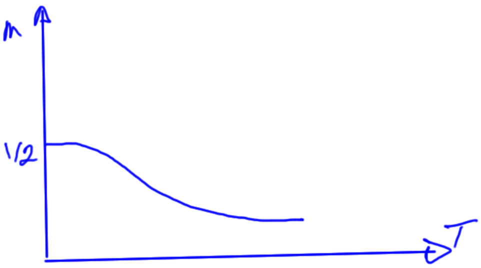


Figure 6.11: Single spin magnetization.

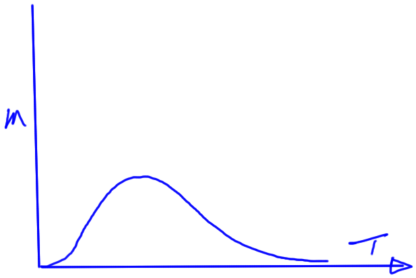


Figure 6.12: Interacting spin magnetization.

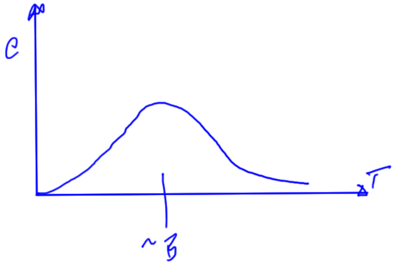


Figure 6.13: Single particle specific heat.

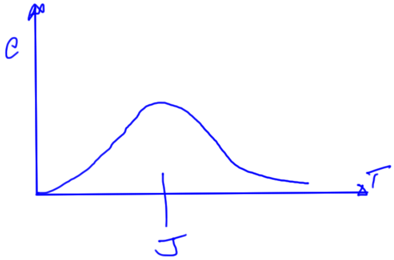


Figure 6.14: Magnetization for interacting spins.

6.8 PROBLEMS.

Exercise 6.1 Polymer stretching - entropic force. (*2013 ps5, p1*)

Consider a toy model of a polymer in one dimension which is made of N steps (amino acids) of unit length, going left or right like a random walk. Let one end of this polymer be at the origin and the other end be at a point $X = \sqrt{N}$ (viz. the rms size of the polymer), so $1 \ll X \ll N$. We have previously calculated the number of configurations corresponding to this condition (approximate the binomial distribution by a Gaussian).

a. Using this, find the entropy of this polymer as $S = k_{\mathrm{B}} \ln \Omega$. The free energy of this polymer, even in the absence of any other interactions, thus has an entropic contribution, $F = -TS$. If we stretch this polymer, we expect to have fewer available configurations, and thus a smaller entropy and a higher free energy.

b. Find the change in free energy of this polymer if we stretch this polymer from its end being at X to a larger distance $X + \Delta X$.

c. Show that the change in free energy is linear in the displacement for small ΔX, and hence find the temperature dependent "entropic spring constant" of this polymer. (This "entropic force" is important to overcome for packing DNA into the nucleus, and in many biological processes.)

Typo correction (via email): You need to show that the change in free energy is quadratic in the displacement ΔX, not linear in ΔX. The force is linear in ΔX. (Exactly as for a "spring".)

Answer for Exercise 6.1

Part a. Entropy. In lecture 2 probabilities for the sums of fair coin tosses were considered. Assigning ± 1 to the events Y_k for heads and tails coin tosses respectively, a random variable $Y = \sum_k Y_k$ for the total of N such events was found to have the form

$$P_N(Y) = \begin{cases} \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N-Y}{2}\right)!\left(\frac{N+Y}{2}\right)!} & \text{if } Y \text{ and } N \text{ have same parity} \\ 0 & \text{otherwise} \end{cases} \tag{6.82}$$

For an individual coin tosses we have averages $\left\langle Y_1 \right\rangle = 0$, and $\left\langle Y_1^2 \right\rangle = 1$, so the central limit theorem provides us with a large N Gaussian approximation for this distribution

$$P_N(Y) \approx \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{Y^2}{2N}\right). \tag{6.83}$$

This fair coin toss problem can also be thought of as describing the coordinate of the end point of a one dimensional polymer with the beginning point of the polymer is fixed at the origin. Writing $\Omega(N, Y)$ for the total number of configurations that have an end point at coordinate Y we have

$$P_N(Y) = \frac{\Omega(N, Y)}{2^N}, \tag{6.84}$$

From this, the total number of configurations that have, say, length $X = |Y|$, in the large N Gaussian approximation, is

$$\Omega(N, X) = 2^N \left(P_N(+X) + P_N(-X)\right) = \frac{2^{N+2}}{\sqrt{2\pi N}} \exp\left(-\frac{X^2}{2N}\right). \tag{6.85}$$

The entropy associated with a one dimensional polymer of length X is therefore

$$S_N(X) = -k_\mathrm{B} \frac{X^2}{2N} + k_\mathrm{B} \ln \frac{2^{N+2}}{\sqrt{2\pi N}} = -k_\mathrm{B} \frac{X^2}{2N} + \text{constant}. \tag{6.86}$$

Writing S_0 for this constant the free energy is

$$\boxed{F = U - TS = U + k_B T \frac{X^2}{2N} + S_0 T.} \tag{6.87}$$

Part b. Change in free energy. At constant temperature, stretching the polymer from its end being at X to a larger distance $X + \Delta X$, results in a free energy change of

$$\begin{aligned}
\Delta F &= F(X + \Delta X) - F(X) \\
&= \frac{k_B T}{2N} \left((X + \Delta X)^2 - X^2 \right) \\
&= \frac{k_B T}{2N} \left(2X\Delta X + (\Delta X)^2 \right).
\end{aligned} \tag{6.88}$$

If ΔX is assumed small, our constant temperature change in free energy $\Delta F \approx (\partial F/\partial X)_T \Delta X$ is

$$\boxed{\Delta F = \frac{k_B T}{N} X \Delta X.} \tag{6.89}$$

Part c. Temperature dependent spring constant. I found the statement and subsequent correction of the problem statement somewhat confusing. To figure this all out, I thought it was reasonable to step back and relate free energy to the entropic force explicitly.

Consider temporarily a general thermodynamic system, for which we have by definition free energy and thermodynamic identity respectively

$$F = U - TS, \tag{6.90a}$$

$$dU = TdS - PdV. \tag{6.90b}$$

The differential of the free energy is

$$\begin{aligned}
dF &= dU - TdS - SdT \\
&= -PdV - SdT \\
&= \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV.
\end{aligned} \tag{6.91}$$

Forming the wedge product with dT, we arrive at the two form

$$\begin{aligned} 0 &= \left(\left(P + \left(\frac{\partial F}{\partial V} \right)_T \right) dV + \left(S + \left(\frac{\partial F}{\partial T} \right)_V \right) dT \right) \wedge dT \\ &= \left(P + \left(\frac{\partial F}{\partial V} \right)_T \right) dV \wedge dT, \end{aligned} \tag{6.92}$$

This provides the relation between free energy and the “pressure” for the system

$$P = -\left(\frac{\partial F}{\partial V} \right)_T. \tag{6.93}$$

For a system with a constant cross section ΔA, $dV = \Delta A dX$, so the force associated with the system is

$$f = P \Delta A = -\frac{1}{\Delta A} \left(\frac{\partial F}{\partial X} \right)_T \Delta A, \tag{6.94}$$

or

$$f = -\left(\frac{\partial F}{\partial X} \right)_T. \tag{6.95}$$

Okay, now we have a relation between the force and the rate of change of the free energy

$$f(X) = -\frac{k_{\mathrm{B}} T}{N} X. \tag{6.96}$$

Our temperature dependent “entropic spring constant” in analogy with $f = -kX$, is therefore

$$\boxed{k = \frac{k_{\mathrm{B}} T}{N}.} \tag{6.97}$$

Exercise 6.2 **Independent 1D harmonic oscillators (*2013 ps5, p2*)**

Consider a set of N independent classical harmonic oscillators, each having a frequency ω.

a. Find the canonical partition at a temperature T for this system of oscillators keeping track of correction factors of Planck constant. (Note that the oscillators are distinguishable, and we do not need $1/N!$ correction factor.)

b. Using this, derive the mean energy and the specific heat at temperature T.

c. For quantum oscillators, the partition function of each oscillator is simply $\sum_n e^{-\beta E_n}$ where E_n are the (discrete) energy levels given by $(n+1/2)\hbar\omega$, with $n = 0, 1, 2, \cdots$. Hence, find the canonical partition function for N independent distinguishable quantum oscillators, and find the mean energy and specific heat at temperature T.

d. Show that the quantum results go over into the classical results at high temperature $k_B T \gg \hbar\omega$, and comment on why this makes sense.

e. Also find the low temperature behavior of the specific heat in both classical and quantum cases when $k_B T \ll \hbar\omega$.

Answer for Exercise 6.2

Part a. Classical partition function For a single particle in one dimension our partition function is

$$Z_1 = \frac{1}{h} \int dp dq e^{-\beta\left(\frac{1}{2m} p^2 + \frac{1}{2} m\omega^2 q^2\right)}, \tag{6.98}$$

with

$$a = \sqrt{\frac{\beta}{2m}} p \tag{6.99a}$$

$$b = \sqrt{\frac{\beta m}{2}} \omega q, \tag{6.99b}$$

we have

$$\begin{aligned} Z_1 &= \frac{1}{h\omega} \sqrt{\frac{2m}{\beta}} \sqrt{\frac{2}{\beta m}} \int da db e^{-a^2 - b^2} \\ &= \frac{2}{\beta h\omega} 2\pi \int_0^\infty r e^{-r^2} \\ &= \frac{2\pi}{\beta h\omega} \\ &= \frac{1}{\beta\hbar\omega}. \end{aligned} \tag{6.100}$$

So for N distinguishable classical one dimensional harmonic oscillators we have

$$\boxed{Z_N(T) = Z_1^N = \left(\frac{k_\mathrm{B} T}{\hbar\omega}\right)^N.} \tag{6.101}$$

Part b. Classical mean energy and heat capacity From the free energy

$$F = -k_\mathrm{B} T \ln Z_N = N k_\mathrm{B} T \ln(\beta\hbar\omega), \tag{6.102}$$

we can compute the mean energy

$$\begin{aligned} U &= \frac{1}{k_\mathrm{B}} \frac{\partial}{\partial\beta} \left(\frac{F}{T}\right) \\ &= N \frac{\partial}{\partial\beta} \ln(\beta\hbar\omega) \\ &= \frac{N}{\beta}, \end{aligned} \tag{6.103}$$

or

$$\boxed{U = N k_\mathrm{B} T.} \tag{6.104}$$

The specific heat follows immediately

$$\boxed{C_\mathrm{V} = \frac{\partial U}{\partial T} = N k_\mathrm{B}.} \tag{6.105}$$

Part c. Quantum partition function, mean energy and heat capacity For a single one dimensional quantum oscillator, our partition function is

$$\begin{aligned} Z_1 &= \sum_{n=0}^\infty e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \\ &= e^{-\beta\hbar\omega/2} \sum_{n=0}^\infty e^{-\beta\hbar\omega n} \\ &= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} \\ &= \frac{1}{\sinh(\beta\hbar\omega/2)}. \end{aligned} \tag{6.106}$$

Assuming distinguishable quantum oscillators, our N particle partition function is

$$\boxed{Z_N(\beta) = \frac{1}{\sinh^N(\beta \hbar\omega/2)}.} \tag{6.107}$$

This time we don't add the $1/\hbar$ correction factor, nor the $N!$ indistinguishability correction factor.

Our free energy is

$$F = N k_{\mathrm{B}} T \ln \sinh(\beta \hbar\omega/2), \tag{6.108}$$

our mean energy is

$$\begin{aligned} U &= \frac{1}{k_{\mathrm{B}}} \frac{\partial}{\partial\beta} \frac{F}{T} \\ &= N \frac{\partial}{\partial\beta} \ln \sinh(\beta\hbar\omega/2) \\ &= N \frac{\cosh(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)} \frac{\hbar\omega}{2}, \end{aligned} \tag{6.109}$$

or

$$\boxed{U(T) = \frac{N\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right).} \tag{6.110}$$

This is plotted in fig. 6.15.

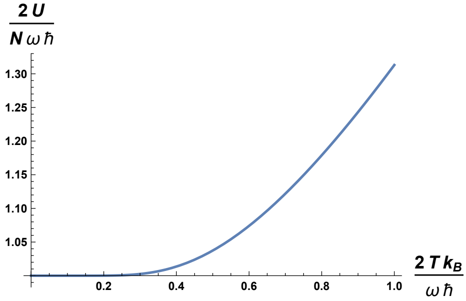


Figure 6.15: Mean energy for N one dimensional quantum harmonic oscillators.

With $\coth'(x) = -1/\sinh^2(x)$, our specific heat is

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{N\hbar\omega}{2} \frac{-1}{\sinh^2\left(\frac{\hbar\omega}{2k_B T}\right)} \frac{\hbar\omega}{2k_B} \left(\frac{-1}{T^2}\right), \end{aligned} \tag{6.111}$$

or

$$\boxed{C_V = N k_B \left(\frac{\hbar\omega}{2k_B T \sinh\left(\frac{\hbar\omega}{2k_B T}\right)}\right)^2.} \tag{6.112}$$

Part d. Classical limits In the high temperature limit $1 \gg \hbar\omega/k_B T$, we have

$$\cosh\left(\frac{\hbar\omega}{2k_B T}\right) \approx 1 \tag{6.113}$$

$$\sinh\left(\frac{\hbar\omega}{2k_B T}\right) \approx \frac{\hbar\omega}{2k_B T}, \tag{6.114}$$

so

$$U \approx N \frac{\cancel{\hbar\omega}}{\cancel{2}} \frac{\cancel{2} k_B T}{\cancel{\hbar\omega}}, \tag{6.115}$$

or

$$U(T) \approx N k_B T, \tag{6.116}$$

matching the classical result of eq. (6.104). Similarly from the quantum specific heat result of eq. (6.112), we have

$$C_V(T) \approx N k_B \left(\frac{\hbar\omega}{2k_B T \left(\frac{\hbar\omega}{2k_B T}\right)}\right)^2 = N k_B. \tag{6.117}$$

This matches our classical result from eq. (6.105). We expect this equivalence at high temperatures since our quantum harmonic partition function eq. (6.107) is approximately

$$Z_N \approx \frac{2}{\beta\hbar\omega}, \tag{6.118}$$

This differs from the classical partition function only by this factor of 2. While this alters the free energy by $k_B T \ln 2$, it doesn't change the mean energy since $\partial(k_B \ln 2)/\partial\beta = 0$. At high temperatures the mean energy are large enough that the quantum nature of the system has no significant effect.

Part e. Low temperature limits For the classical case the heat capacity was constant ($C_V = N k_B$), all the way down to zero. For the quantum case the heat capacity drops to zero for low temperatures. We can see that via L'hopitals rule. With $x = \hbar\omega\beta/2$ the low temperature limit is

$$\begin{aligned}
\lim_{T\rightarrow 0} C_V &= N k_B \lim_{x\rightarrow\infty} \frac{x^2}{\sinh^2 x} \\
&= N k_B \lim_{x\rightarrow\infty} \frac{2x}{2\sinh x \cosh x} \\
&= N k_B \lim_{x\rightarrow\infty} \frac{1}{\cosh^2 x + \sinh^2 x} \\
&= N k_B \lim_{x\rightarrow\infty} \frac{1}{\cosh(2x)} \\
&= 0.
\end{aligned} \tag{6.119}$$

We also see this in the plot of fig. 6.16.

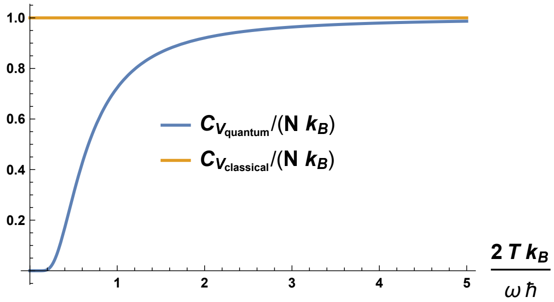


Figure 6.16: Specific heat for N quantum oscillators.

Exercise 6.3 Quantum electric dipole (*2013 ps5, p3*)

A quantum electric dipole at a fixed space point has its energy determined by two parts - a part which comes from its angular motion and a part coming from its interaction with an applied electric field $\mathcal{E}$. This leads to a quantum Hamiltonian

$$H = \frac{\mathbf{L} \cdot \mathbf{L}}{2I} - \mu \mathcal{E} L_z, \tag{6.120}$$

where I is the moment of inertia, and we have assumed an electric field $\mathcal{E} = \mathcal{E}\hat{\mathbf{z}}$. This Hamiltonian has eigenstates described by spherical harmonics $Y_{l,m}(\theta, \phi)$, with m taking on $2l+1$ possible integral values, $m = -l, -l+1, \cdots, l-1, l$. The corresponding eigenvalues are

$$\lambda_{l,m} = \frac{l(l+1)\hbar^2}{2I} - \mu \mathcal{E} m \hbar. \tag{6.121}$$

(Recall that l is the total angular momentum eigenvalue, while m is the eigenvalue corresponding to L_z.)

a. Schematically sketch these eigenvalues as a function of $\mathcal{E}$ for $l = 0, 1, 2$.
b. Find the quantum partition function, assuming only $l = 0$ and $l = 1$ contribute to the sum.
c. Using this partition function, find the average dipole moment $\mu \left\langle L_z \right\rangle$ as a function of the electric field and temperature for small electric fields, commenting on its behavior at very high temperature and very low temperature.
d. Estimate the temperature above which discarding higher angular momentum states, with $l \geq 2$, is not a good approximation.

Answer for Exercise 6.3

Part a. Sketch the energy eigenvalues Let's summarize the values of the energy eigenvalues $\lambda_{l,m}$ for $l = 0, 1, 2$ before attempting to plot them.

$l = 0$ For $l = 0$, the azimuthal quantum number can only take the value $m = 0$, so we have

$$\lambda_{0,0} = 0. \tag{6.122}$$

$l = 1$ For $l = 1$ we have

$$\frac{l(l+1)}{2} = 1(2)/2 = 1, \tag{6.123}$$

so we have

$$\lambda_{1,0} = \frac{\hbar^2}{I} \tag{6.124a}$$

$$\lambda_{1,\pm 1} = \frac{\hbar^2}{I} \mp \mu \mathcal{E} \hbar. \tag{6.124b}$$

$l = 2$ For $l = 2$ we have

$$\frac{l(l+1)}{2} = 2(3)/2 = 3, \tag{6.125}$$

so we have

$$\lambda_{2,0} = \frac{3\hbar^2}{I} \tag{6.126a}$$

$$\lambda_{2,\pm 1} = \frac{3\hbar^2}{I} \mp \mu \mathcal{E} \hbar \tag{6.126b}$$

$$\lambda_{2,\pm 2} = \frac{3\hbar^2}{I} \mp 2\mu \mathcal{E} \hbar. \tag{6.126c}$$

These are sketched as a function of $\mathcal{E}$ in fig. 6.17.

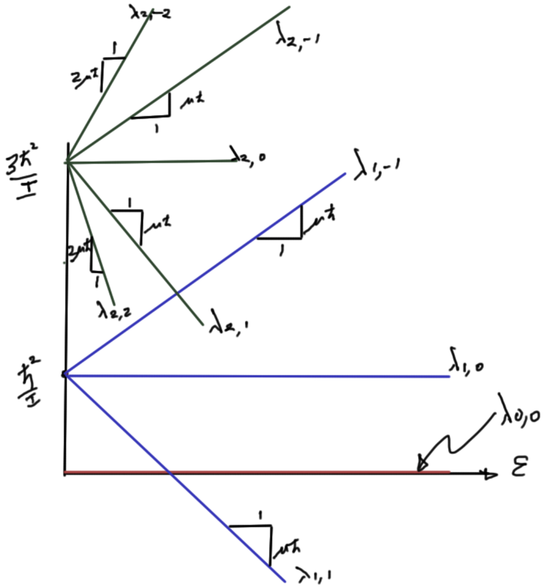


Figure 6.17: Energy eigenvalues for $l = 0, 1, 2$.

Part b. Partition function Our partition function, in general, is

$$
\begin{aligned}
Z &= \sum_{l=0}^{\infty} \sum_{m=-l}^{l} e^{-\lambda_{l,m}\beta} \\
&= \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I} \right) \sum_{m=-l}^{l} e^{m\mu\hbar\mathcal{E}\beta}.
\end{aligned}
\tag{6.127}
$$

Dropping all but $l = 0, 1$ terms this is

$$
Z \approx 1 + e^{-\hbar^2\beta/I} \left(1 + e^{-\mu\hbar\mathcal{E}\beta} + e^{\mu\hbar\mathcal{E}\beta} \right),
\tag{6.128}
$$

or

$$
\boxed{Z \approx 1 + e^{-\hbar^2\beta/I}(1 + 2\cosh(\mu\hbar\mathcal{E}\beta)).}
\tag{6.129}
$$

Part c. Average dipole moment For the average dipole moment, averaging over both the states and the partitions, we have

$$\begin{aligned}
Z \left\langle \mu L_z \right\rangle &= \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left\langle lm \right| \mu L_z \left| lm \right\rangle e^{-\beta \lambda_{l,m}} \\
&= \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mu \left\langle lm \right| m \hbar \left| lm \right\rangle e^{-\beta \lambda_{l,m}} \\
&= \mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \sum_{m=-l}^{l} m e^{\mu m \hbar \mathcal{E} \beta} \\
&= \mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \sum_{m=1}^{l} m \left(e^{\mu m \hbar \mathcal{E} \beta} - e^{-\mu m \hbar \mathcal{E} \beta} \right) \\
&= 2\mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \sum_{m=1}^{l} m \sinh(\mu m \hbar \mathcal{E} \beta).
\end{aligned} \tag{6.130}$$

For the cap of $l = 1$ we have

$$\begin{aligned}
\left\langle \mu L_z \right\rangle &\approx \frac{2\mu\hbar}{Z} \left(1(0) + e^{-\hbar^2 \beta / I} \sinh(\mu \hbar \mathcal{E} \beta) \right) \\
&\approx 2\mu\hbar \frac{e^{-\hbar^2 \beta / I} \sinh(\mu \hbar \mathcal{E} \beta)}{1 + e^{-\hbar^2 \beta / I} \left(1 + 2\cosh(\mu \hbar \mathcal{E} \beta) \right)},
\end{aligned} \tag{6.131}$$

or

$$\boxed{\left\langle \mu L_z \right\rangle \approx \frac{2\mu\hbar \sinh(\mu \hbar \mathcal{E} \beta)}{e^{\hbar^2 \beta / I} + 1 + 2\cosh(\mu \hbar \mathcal{E} \beta)}.} \tag{6.132}$$

This is plotted in fig. 6.18.

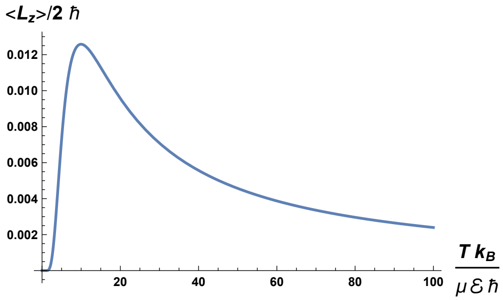


Figure 6.18: Dipole moment.

For high temperatures $\mu \hbar \mathcal{E} \beta \ll 1$ or $k_B T \gg \mu \hbar \mathcal{E}$, expanding the hyperbolic sine and cosines to first and second order respectively and the exponential to first order we have

$$
\begin{aligned}
\langle \mu L_z \rangle &\approx 2\mu \hbar \frac{\frac{\mu \hbar \mathcal{E}}{k_B T}}{4 + \frac{\hbar^2}{I k_B T} + \left(\frac{\mu \hbar \mathcal{E}}{k_B T} \right)^2} \\
&= \frac{2(\mu \hbar)^2 \mathcal{E} k_B T}{4(k_B T)^2 + \hbar^2 k_B T/I + (\mu \hbar \mathcal{E})^2} \\
&\approx \frac{(\mu \hbar)^2 \mathcal{E}}{4 k_B T}.
\end{aligned}
\tag{6.133}
$$

Our dipole moment tends to zero approximately inversely proportional to temperature. These last two respective approximations are plotted along with the all temperature range result in fig. 6.19.

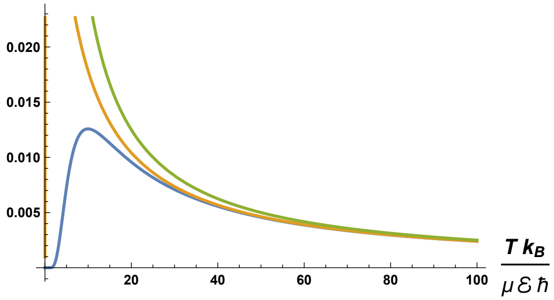


Figure 6.19: High temperature approximations to dipole moments.

For low temperatures $k_B T \ll \mu \hbar \mathcal{E}$, where $\mu \hbar \mathcal{E} \beta \gg 1$ we have

$$
\begin{aligned}
\langle \mu L_z \rangle &\approx \frac{2\mu \hbar e^{\mu \hbar \mathcal{E} \beta}}{e^{\hbar^2 \beta/I} + e^{\mu \hbar \mathcal{E} \beta}} \\
&= \frac{2\mu \hbar}{1 + e^{(\hbar^2 \beta/I - \mu \hbar \mathcal{E})/k_B T}}.
\end{aligned}
\tag{6.134}
$$

Provided the electric field is small enough (which means here that $\mathcal{E} < \hbar/\mu I$) this will look something like fig. 6.20.

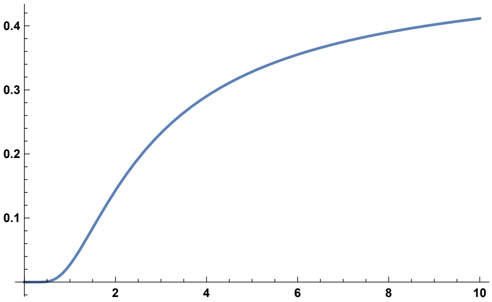


Figure 6.20: Low temperature dipole moment behavior.

Part d. Approximation validation In order to validate the approximation, let's first put the partition function and the numerator of the dipole moment into a tidier closed form, evaluating the sums over the radial indices l. First let's sum the exponentials for the partition function, making an $n = m + l$

$$\begin{aligned}\sum_{m=-l}^{l} a^m &= a^{-l} \sum_{n=0}^{2l} a^n \\ &= a^{-l} \frac{a^{2l+1} - 1}{a - 1} \\ &= \frac{a^{l+1} - a^{-l}}{a - 1} \\ &= \frac{a^{l+1/2} - a^{-(l+1/2)}}{a^{1/2} - a^{-1/2}}.\end{aligned} \tag{6.135}$$

With a substitution of $a = e^b$, we have

$$\boxed{\sum_{m=-l}^{l} e^{bm} = \frac{\sinh(b(l + 1/2))}{\sinh(b/2)}.} \tag{6.136}$$

Now we can sum the azimuthal exponentials for the dipole moment. This sum is of the form

$$\begin{aligned}\sum_{m=-l}^{l} m a^m &= a \left(\sum_{m=1}^{l} + \sum_{m=-l}^{-1} \right) m a^{m-1} \\ &= a \frac{d}{da} \sum_{m=1}^{l} \left(a^m + a^{-m} \right) \\ &= a \frac{d}{da} \left(\sum_{m=-l}^{l} a^m - \not{1} \right) \\ &= a \frac{d}{da} \left(\frac{a^{l+1/2} - a^{-(l+1/2)}}{a^{1/2} - a^{-1/2}} \right).\end{aligned} \tag{6.137}$$

With $a = e^b$, and $1 = a db/da$, we have

$$a \frac{d}{da} = a \frac{db}{da} \frac{d}{db} = \frac{d}{db}, \tag{6.138}$$

we have

$$\sum_{m=-l}^{l} m e^{bm} = \frac{d}{db} \left(\frac{\sinh(b(l+1/2))}{\sinh(b/2)} \right). \tag{6.139}$$

With a little help from Mathematica to simplify that result we have

$$\boxed{\sum_{m=-l}^{l} m e^{bm} = \frac{l \sinh(b(l+1)) - (l+1) \sinh(bl)}{2 \sinh^2(b/2)}.} \tag{6.140}$$

We can now express the average dipole moment with only sums over radial indices l

$$\begin{aligned}\langle \mu L_z \rangle &= \mu \hbar \frac{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \sum_{m=-l}^{l} m e^{\mu m \hbar \mathcal{E} \beta}}{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \sum_{m=-l}^{l} e^{m \mu \hbar \mathcal{E} \beta}} \\ &= \mu \hbar \frac{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \frac{l \sinh(\mu \hbar \mathcal{E} \beta (l+1)) - (l+1) \sinh(\mu \hbar \mathcal{E} \beta l)}{2 \sinh^2(\mu \hbar \mathcal{E} \beta/2)}}{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I} \right) \frac{\sinh(\mu \hbar \mathcal{E} \beta (l+1/2))}{\sinh(\mu \hbar \mathcal{E} \beta/2)}}.\end{aligned} \tag{6.141}$$

So our average dipole moment, with $x = \mu \hbar \mathcal{E} \beta$, is

$$\boxed{\langle \mu L_z \rangle = \frac{\mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right)\left(l \sinh(x(l+1)) - (l+1)\sinh(xl)\right)}{2\sinh(x/2)\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right)\sinh(x(l+1/2))}.} \tag{6.142}$$

The hyperbolic sine in the denominator from the partition function and the difference of hyperbolic sines in the numerator both grow fast. This is illustrated in fig. 6.21.

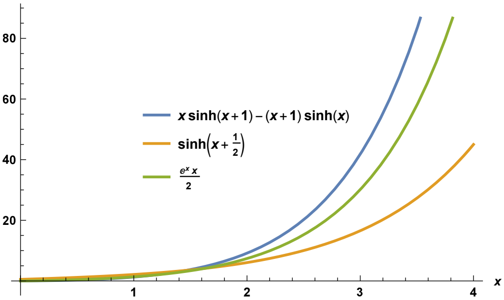


Figure 6.21: Hyperbolic sine plots for dipole moment.

Let's look at the order of these hyperbolic sines for large arguments. For the numerator we have a difference of the form

$$\begin{aligned} x\sinh(x+1) - (x+1)\sinh(x) &= \frac{1}{2}\Big(x\left(e^{x+1} - e^{-x-1}\right) \\ &\qquad - (x+1)\left(e^x - e^{-x}\right)\Big) \\ &\approx \frac{1}{2}\left(xe^{x+1} - (x+1)e^x\right) \\ &= \frac{1}{2}\left(xe^x(e-1) - e^x\right) \\ &= O(xe^x). \end{aligned} \tag{6.143}$$

For the hyperbolic sine from the partition function we have for large x

$$\sinh(x+1/2) = \frac{1}{2}\left(e^{x+1/2} - e^{-x-1/2}\right) \approx \frac{\sqrt{e}}{2}e^x = O(e^x). \tag{6.144}$$

While these hyperbolic sines increase without bound as l increases, we have a negative quadratic dependence on l in the $\mathbf{L}^2$ contribution to these sums, provided that is small enough we can neglect the linear growth of the hyperbolic sines. We wish for that factor to be large enough that it dominates for all l. That is

$$\frac{l(l+1)\hbar^2}{2Ik_\mathrm{B}T} \gg 1, \tag{6.145}$$

or

$$T \ll \frac{l(l+1)\hbar^2}{2Ik_\mathrm{B}T}. \tag{6.146}$$

Observe that the RHS of this inequality, for $l = 1, 2, 3, 4, \cdots$ satisfies

$$\frac{\hbar^2}{Ik_\mathrm{B}} < \frac{3\hbar^2}{Ik_\mathrm{B}} < \frac{6\hbar^2}{Ik_\mathrm{B}} < \frac{10\hbar^2}{Ik_\mathrm{B}} < \cdots \tag{6.147}$$

So, for small electric fields, our approximation should be valid provided our temperature is constrained by

$$\boxed{T \ll \frac{\hbar^2}{Ik_\mathrm{B}}.} \tag{6.148}$$

Exercise 6.4 Energy and temperature ([11] *pr. 2.1*)

Suppose $g(U) = CU^{3N/2}$, where C is a constant and N is the number of particles. This form of $g(U)$ actually applies to an ideal gas.

a. Show that $U = 3N\tau/2$

b. Show that $(\partial^2\sigma/\partial U^2)_N$ is negative.

Answer for Exercise 6.4

Part a. Temperature We've got

$$\begin{aligned}\frac{1}{\tau} &= \frac{\partial \sigma}{\partial U} \\ &= \frac{\partial}{\partial U}\left(\ln C + \frac{3N}{2}\ln U\right) \\ &= \frac{3N}{2}\frac{1}{U},\end{aligned} \tag{6.149}$$

or

$$U = \frac{3N}{2}\tau. \tag{6.150}$$

Part b. Second derivative of entropy From above

$$\frac{\partial^2\sigma}{\partial U^2} = -\frac{3N}{2}\frac{1}{U^2}. \tag{6.151}$$

This doesn't seem particularly surprising if we look at the plots. For example for $C = 1$ and $3N/2 = 1$ we have fig. 6.22.

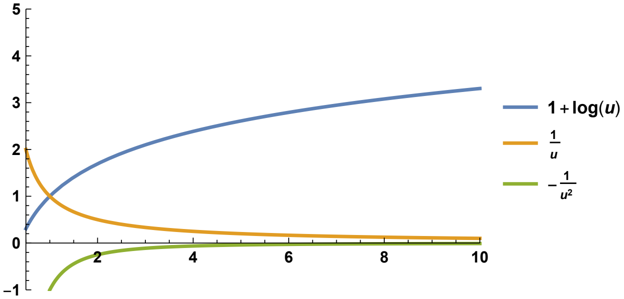


Figure 6.22: Plots of entropy and its derivatives for this multiplicity function.

The rate of change of entropy with energy decreases monotonically and is always positive, but always has a negative slope.

Exercise 6.5 Paramagnetism ([11] *pr. 2.2*)

Find the equilibrium value at temperature τ of the fractional magnetization

$$\frac{M}{Nm} = \frac{2\langle s\rangle}{N}, \tag{6.152}$$

of the system of N spins each of magnetic moment m in a magnetic field B. The spin excess is $2s$. Take the entropy as the logarithm of the multiplicity $g(N, s)$ as given in (1.35):

$$\sigma(s) \approx \ln g(N,0) - \frac{2s^2}{N}, \tag{6.153}$$

for $|s| \ll N$. Hint: Show that in this approximation

$$\sigma(U) = \sigma_0 - \frac{U^2}{2m^2B^2N}, \tag{6.154}$$

with $\sigma_0 = \ln g(N, 0)$. Further, show that $1/\tau = -U/(m^2B^2N)$, where U denotes $\langle U \rangle$, the thermal average energy.

Answer for Exercise 6.5

I found this problem very hard to interpret. What exactly is being asked for? Equation (1.35) in the text was

$$g(N,s) \approx g(N,0)e^{-\frac{2s^2}{N}} \tag{6.155a}$$

$$g(N,0) \approx \sqrt{\frac{2}{\pi N}}2^N, \tag{6.155b}$$

from which we find the entropy eq. (6.153) directly after taking logarithms. The temperature is found directly

The magnetization, for a system that has spin excess $2s$ was defined as

$$U = -2smB \equiv -MB, \tag{6.156}$$

and we can substitute that for s

$$\sigma(U) = \sigma_0 - \frac{U^2}{2m^2B^2N}, \tag{6.157}$$

and take derivatives for the temperature

$$\begin{aligned} \frac{1}{\tau} &= \frac{\partial \sigma}{\partial U} \\ &= \frac{\partial}{\partial U}\left(\sigma_0 - \frac{U^2}{2m^2B^2N}\right) \\ &= -\frac{U}{m^2B^2N}. \end{aligned} \tag{6.158}$$

This gives us a relation between temperature and the energy of the system with spin excess $2s$, and we could write

$$\frac{M}{Nm} = -\frac{U}{BNm} = \frac{mB}{\tau}. \tag{6.159}$$

Is this the relation that this problem was asking for?

Two things I don't understand from this problem:

1. Where does $2\langle s\rangle/N$ come from? If we calculate the expectation of the spin excess, we find that it is zero

$$\begin{aligned}\langle 2s\rangle &= \frac{\sqrt{\frac{2}{\pi N}}2^N \int_{-\infty}^{\infty} ds 2s e^{-\frac{2s^2}{N}}}{2^N} \\ &= 0.\end{aligned} \tag{6.160}$$

2. If $2\langle s\rangle$ has a non-zero value, then doesn't that make $\langle U\rangle$ also zero? It seems to me that U in eq. (6.158) is the energy of a system with spin excess s, and not any sort of average energy?

Exercise 6.6 Quantum harmonic oscillator ([11] *pr. 2.3*)

a. Entropy. Find the entropy of a set of N oscillators of frequency ω as a function of the total quantum number n. Use the multiplicity function (1.55) and make the Stirling approximation $\ln N! \approx N\ln N - N$. Replace $N-1$ by N.

b. Planck Energy. Let U denote the total energy $n\hbar\omega$ of the oscillators. Express the entropy as $\sigma(U,N)$. Show that the total energy at temperature τ is

$$U = \frac{N\hbar\omega}{\exp\left(\hbar\omega/\tau\right)-1}. \tag{6.161}$$

This is the Planck result; it is derived again in Chapter 4 by a powerful method that does not require us to find the multiplicity function.

Answer for Exercise 6.6

Part a. Entropy The multiplicity was found in the text to be

$$g(N,n) = \frac{(N+n-1)!}{n!\,(N-1)!} \tag{6.162}$$

I wasn't actually able to follow the argument in the text, and found the purely combinatoric wikipedia argument [17] much clearer. A similar diagram and argument can also be found in [13] §3.8.

Taking logarithms and applying the Stirling approximation, our entropy is

$$
\begin{aligned}
\sigma &= \ln g \\
&= \ln(N+n-1)! - \ln(N-1)! - \ln n! \\
&\approx (N+n-1)\ln(N+n-1) - (N+n-1) \\
&\quad - (N-1)\ln(N-1) + (N-1) - n\ln n + n \\
&= (N-1)\ln\frac{N+n-1}{N-1} + n\ln\frac{N+n-1}{n}.
\end{aligned}
\tag{6.163}
$$

Part b. Planck Energy Now we make the $N-1 \rightarrow N$ replacement suggested in the problem (ie. assuming $N \gg 1$), for

$$
\begin{aligned}
\sigma &\approx N\ln\frac{N+n}{N} + n\ln\frac{N+n}{n} \\
&= (N+n)\ln(N+n) - N\ln N - n\ln n \\
&= \left(N + \frac{U}{\hbar\omega}\right)\ln\left(N + \frac{U}{\hbar\omega}\right) - N\ln N - \frac{U}{\hbar\omega}\ln\frac{U}{\hbar\omega}.
\end{aligned}
\tag{6.164}
$$

With $(x\ln x)' = \ln x + 1$, we have

$$
\begin{aligned}
\frac{1}{\tau} &= \frac{\partial\sigma}{\partial U} \\
&= \frac{1}{\hbar\omega}\left(\ln\left(N + \frac{U}{\hbar\omega}\right) - 1 - \ln\frac{U}{\hbar\omega} + 1\right),
\end{aligned}
\tag{6.165}
$$

or

$$
Ue^{\frac{\hbar\omega}{\tau}} = N\hbar\omega + U.
\tag{6.166}
$$

A final rearrangement gives us the Planck result eq. (6.161).

Exercise 6.7 Classical gas partition function

[11] expresses the classical gas partition function (3.77) as

$$
Z_1 \propto \int \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2M\tau}\right) dp_x dp_y dp_z.
\tag{6.167}
$$

Show that this leads to the expected $3\tau/2$ result for the thermal average energy.

Answer for Exercise 6.7

Let's use the adjustment technique from the text for the N partition case and write

$$Z_N = \frac{1}{N!} Z_1^N, \tag{6.168}$$

with Z_1 as above. This gives us

$$\begin{aligned}
U &= \tau^2 \frac{\partial}{\partial \tau} \ln Z_N \\
&= \tau^2 \frac{\partial}{\partial \tau} \left(N \ln Z_1 - \ln N! \right) \\
&= N\tau^2 \frac{\partial \ln Z_1}{\partial \tau} \\
&= N\tau^2 \frac{\partial}{\partial \tau} \sum_{k=1}^{3} \ln \int \exp\left(-\frac{p_k^2}{2M\tau} \right) dp_k \\
&= N\tau^2 \sum_{k=1}^{3} \frac{\frac{\partial}{\partial \tau} \int \exp\left(-\frac{p_k^2}{2M\tau} \right) dp_k}{\int \exp\left(-\frac{p_k^2}{2M\tau} \right) dp_k} \\
&= N\tau^2 \sum_{k=1}^{3} \frac{\frac{\partial}{\partial \tau} \sqrt{2\pi M\tau}}{\sqrt{2\pi M\tau}} \\
&= 3N\tau^2 \frac{\frac{1}{2}\tau^{-1/2}}{\sqrt{\tau}} \\
&= \frac{3}{2} N\tau \\
&= \frac{3}{2} N k_{\mathrm{B}} T.
\end{aligned} \tag{6.169}$$

Exercise 6.8 Two state system ([11] *pr. 3.1*)

Find an expression for the free energy as a function of τ of a system with two states, one at energy 0 and one at energy ϵ. From the free energy, find expressions for the energy and entropy of the system.

Answer for Exercise 6.8

Our partition function is

$$Z = 1 + e^{-\epsilon/\tau}. \tag{6.170}$$

The free energy is just

$$\begin{aligned} F &= -\tau \ln Z \\ &= -\tau \ln(1 + e^{-\epsilon/\tau}). \end{aligned} \tag{6.171}$$

The entropy follows immediately

$$\begin{aligned} \sigma &= -\frac{\partial F}{\partial \tau} \\ &= \frac{\partial}{\partial \tau}\left(\tau \ln\left(1 + e^{-\epsilon/\tau}\right)\right) \\ &= \ln\left(1 + e^{-\epsilon/\tau}\right) - \tau\epsilon\frac{-1}{\tau^2}\frac{1}{1 + e^{-\epsilon/\tau}} \\ &= \ln\left(1 + e^{-\epsilon/\tau}\right) + \frac{\epsilon}{\tau}\frac{e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}}. \end{aligned} \tag{6.172}$$

The energy is

$$\begin{aligned} U &= F + \tau\sigma \\ &= -\tau \ln(1 + e^{-\epsilon/\tau}) + \tau\sigma \\ &= \tau\left(\cancel{\ln\left(1 + e^{-\epsilon/\tau}\right)} + \frac{\epsilon}{\tau}\frac{e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} - \cancel{\ln(1 + e^{-\epsilon/\tau})}\right). \end{aligned} \tag{6.173}$$

This is

$$U = \frac{\epsilon e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} = \frac{\epsilon}{1 + e^{\epsilon/\tau}}. \tag{6.174}$$

These are all plotted in fig. 6.23.

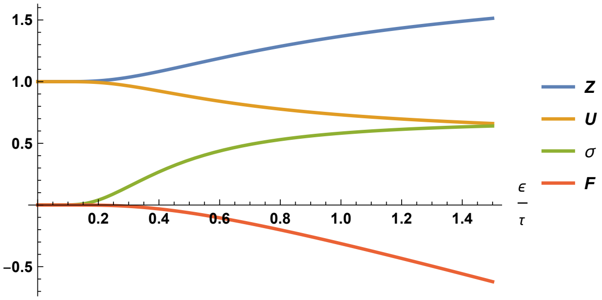


Figure 6.23: Plots for two state system.

Exercise 6.9 Magnetic susceptibility ([11] pr. 3.2)

Use the partition function to find an exact expression for the magnetization M and the susceptibility $\chi = dM/dB$ as a function of temperature and magnetic field for the model system of magnetic moments in a magnetic field. The result for the magnetization, found by other means, was $M = nm \tanh(mB/\tau)$, where n is the particle concentration. Find the free energy and express the result as a function only of τ and the parameter $x = M/nm$. Show that the susceptibility is $\chi = nm^2/\tau$ in the limit $mB \ll \tau$.

Answer for Exercise 6.9

Our partition function for a unit volume containing n spins is

$$Z = \frac{\left(e^{-mB/\tau} + e^{mB/\tau}\right)^n}{n!} = 2\frac{\left(\cosh\left(mB/\tau\right)\right)^n}{n!}, \tag{6.175}$$

so that the Free energy is

$$F = -\tau\left(\ln 2 - \ln n! + n \ln\cosh\left(mB/\tau\right)\right). \tag{6.176}$$

The energy, magnetization and magnetic field were interrelated by

$$\begin{aligned} -MB &= U \\ &= \tau^2 \frac{\partial}{\partial \tau}\left(-\frac{F}{\tau}\right) \\ &= \tau^2 n \frac{\partial}{\partial \tau} \ln\cosh\left(mB/\tau\right) \\ &= \tau^2 n \frac{-mB/\tau^2 \sinh\left(mB/\tau\right)}{\cosh\left(mB/\tau\right)} \\ &= -mBn \tanh\left(mB/\tau\right). \end{aligned} \tag{6.177}$$

This gives us

$$M = mn \tanh\left(mB/\tau\right), \tag{6.178}$$

so that

$$\chi = \frac{dM}{dB} = \frac{m^2 n}{\tau \cosh^2\left(mB/\tau\right)}. \tag{6.179}$$

For $mB/\tau \ll 1$, the cosh term goes to unity, so we have

$$\chi \approx = \frac{m^2 n}{\tau}, \tag{6.180}$$

as desired.

With $x = M/nm$, or $m = M/nx$, the free energy is

$$F = -\tau \left(\ln 2/n! + n \ln \cosh \left(\frac{MB}{nx\tau} \right) \right) \tag{6.181}$$

That last expression isn't particularly illuminating. What was the point of that substitution?

Exercise 6.10 Free energy of a harmonic oscillator (*[11] pr. 3.3*)

A one dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $\epsilon_s = s\hbar\omega$, where s is a positive integer or zero, and ω is the classical frequency of the oscillator. We have chosen the zero of energy at the state $s = 0$. Show that for a harmonic oscillator the free energy is

$$F = \tau \ln \left(1 - e^{-\hbar\omega/\tau} \right). \tag{6.182}$$

Note that at high temperatures such that $\tau \gg \hbar\omega$ we may expand the argument of the logarithm to obtain $F \approx \tau \ln(\hbar\omega/\tau)$. From eq. (6.182) show that the entropy is

$$\sigma = \frac{\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} - \ln \left(1 - e^{-\hbar\omega/\tau} \right). \tag{6.183}$$

Answer for Exercise 6.10

I found it curious that this problem dropped the factor of $\hbar\omega/2$ from the energy. Including it we have

$$\epsilon_s = \left(s + \frac{1}{2} \right) \hbar\omega, \tag{6.184}$$

So that the partition function is

$$Z = \sum_{s=0}^{\infty} e^{-\left(s+\frac{1}{2}\right)\hbar\omega/\tau} = e^{-\hbar\omega/2\tau} \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}. \tag{6.185}$$

The free energy is

$$\begin{aligned}
F &= -\tau \ln Z \\
&= -\tau \left(-\frac{\hbar\omega}{2\tau} + \ln \left(\sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} \right) \right) \\
&= \frac{\hbar\omega}{2} + \ln \left(\sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} \right).
\end{aligned} \tag{6.186}$$

We see that the contribution of the $\hbar\omega/2$ in the energy of each state just adds a constant factor to the free energy. This will drop out when we compute the entropy. Dropping that factor now that we know why it doesn't contribute, we can complete the summation, so have, by inspection

$$F = -\tau \ln Z = \tau \ln \left(1 - e^{-\hbar\omega/\tau} \right). \tag{6.187}$$

Taking derivatives for the entropy we have

$$\begin{aligned}
\sigma &= -\frac{\partial F}{\partial \tau} \\
&= -\ln \left(1 - e^{-\hbar\omega/\tau} \right) + \tau \frac{\hbar\omega}{\tau^2} \frac{e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} \\
&= -\ln \left(1 - e^{-\hbar\omega/\tau} \right) + \frac{\frac{\hbar\omega}{\tau}}{e^{\hbar\omega/\tau} - 1}.
\end{aligned} \tag{6.188}$$

Exercise 6.11 Energy fluctuation ([11] pr. 3.4)

Consider a system of fixed volume in thermal contact with a reservoir. Show that the mean square fluctuation in the energy of the system is

$$\left\langle (\epsilon - \langle \epsilon \rangle)^2 \right\rangle = \tau^2 \left(\frac{\partial U}{\partial \tau} \right)_V. \tag{6.189}$$

Here U is the conventional symbol for $\langle \epsilon \rangle$. Hint: Use the partition function Z to relate $\partial U/\partial t$ to the mean square fluctuation. Also, multiply out the term $(\cdots)^2$.

Answer for Exercise 6.11

With a probability of finding the system in state s of

$$P_s = \frac{e^{-\epsilon_s/\tau}}{Z}, \tag{6.190}$$

the average energy is

$$\begin{aligned} U &= \langle \epsilon \rangle \\ &= \sum_s P_s \epsilon_s \\ &= \sum_s \epsilon_s \frac{e^{-\epsilon_s/\tau}}{Z} \\ &= \frac{1}{Z} \sum_s \epsilon_s e^{-\epsilon_s/\tau}. \end{aligned} \tag{6.191}$$

So we have

$$\begin{aligned} \tau^2 \frac{\partial U}{\partial \tau} &= -\frac{\tau^2}{Z^2} \frac{dZ}{d\tau} \sum_s \epsilon_s e^{-\epsilon_s/\tau} + \frac{\tau^2}{Z} \sum_s \frac{\epsilon_s^2}{\tau^2} e^{-\epsilon_s/\tau} \\ &= -\frac{\tau^2}{Z^2} \frac{dZ}{d\tau} \sum_s \epsilon_s e^{-\epsilon_s/\tau} + \frac{1}{Z} \sum_s \epsilon_s^2 e^{-\epsilon_s/\tau}. \end{aligned} \tag{6.192}$$

But

$$\begin{aligned} \frac{dZ}{d\tau} &= \frac{d}{d\tau} \sum_s e^{-\epsilon_s/\tau} \\ &= \sum_s \frac{\epsilon_s}{\tau^2} e^{-\epsilon_s/\tau}, \end{aligned} \tag{6.193}$$

giving

$$\begin{aligned} \tau^2 \frac{\partial U}{\partial \tau} &= \frac{1}{Z^2} \sum_s \epsilon_s e^{-\epsilon_s/\tau} \sum_s \epsilon_s e^{-\epsilon_s/\tau} + \frac{1}{Z} \sum_s \epsilon_s^2 e^{-\epsilon_s/\tau} \\ &= - \langle \epsilon \rangle^2 + \left\langle \epsilon^2 \right\rangle, \end{aligned} \tag{6.194}$$

which shows eq. (6.189) as desired.

Exercise 6.12 Rotation of diatomic molecules (*[11] pr. 3.6*)

In our first look at the ideal gas we considered only the translational energy of the particles. But molecules can rotate, with kinetic energy. The rotation motion is quantized; and the energy levels of a diatomic molecule are of the form

$$\epsilon(j) = j(j+1)\epsilon_0, \tag{6.195}$$

where j is any positive integer including zero: $j = 0, 1, 2, \cdots$. The multiplicity of each rotation level is $g(j) = 2j + 1$.

a. Find the partition function $Z_R(\tau)$ for the rotational states of one molecule. Remember that Z is a sum over all states, not over all levels – this makes a difference.
b. Evaluate $Z_R(\tau)$ approximately for $\tau \gg \epsilon_0$, by converting the sum to an integral.
c. Do the same for $\tau \ll \epsilon_0$, by truncating the sum after the second term.
d. Give expressions for the energy U and the heat capacity C, as functions of τ, in both limits. Observe that the rotational contribution to the heat capacity of a diatomic molecule approaches 1 (or, in conventional units, k_B) when $\tau \gg \epsilon_0$.
e. Sketch the behavior of $U(\tau)$ and $C(\tau)$, showing the limiting behaviors for $\tau \to \infty$ and $\tau \to 0$.

Answer for Exercise 6.12

Part a. Partition function $Z_R(\tau)$ To understand the reference to multiplicity recall (§4.13 [5]) that the rotational Hamiltonian was of the form

$$H = \frac{\mathbf{L}^2}{2Mr^2}, \tag{6.196}$$

where the $\mathbf{L}^2$ eigenvectors satisfied

$$\mathbf{L}^2 \left| lm \right\rangle = l(l+1)\hbar^2 \left| lm \right\rangle \tag{6.197a}$$

$$L_z \left| lm \right\rangle = m\hbar \left| lm \right\rangle, \tag{6.197b}$$

and $-l \leq m \leq l$, where $l \geq 0$ is a positive integer. We see that ϵ_0 is of the form

$$\epsilon_0 = \frac{\hbar^2}{2MR_l(r)}, \tag{6.198}$$

and our partition function is

$$Z_R(\tau) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} e^{-l(l+1)\epsilon_0/\tau} = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\epsilon_0/\tau}. \tag{6.199}$$

We have no dependence on m in the sum, and just have to sum terms like fig. 6.24, and are able to sum over m trivially, which is where the multiplicity comes from.

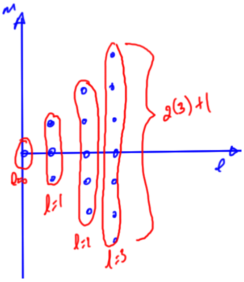


Figure 6.24: Summation over m.

To get a feel for how many terms are significant in these sums, we refer to the plot of fig. 6.25. We plot the partition function itself in, truncation at $l = 30$ terms in fig. 6.26.

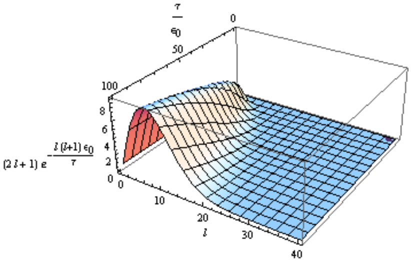


Figure 6.25: Plotting the partition function summand.

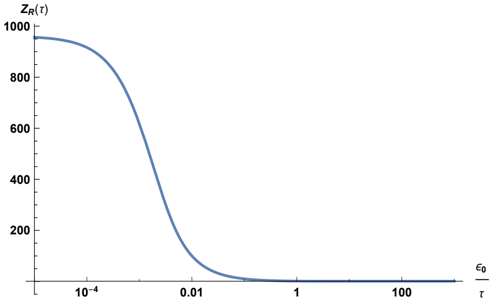


Figure 6.26: $Z_R(\tau)$ truncated after 30 terms in log plot.

Part b. Evaluate partition function for large temperatures If $\tau \gg \epsilon_0$, so that $\epsilon_0/\tau \ll 1$, all our exponentials are close to unity. Employing an integral approximation of the partition function, we can somewhat miraculously integrate this directly

$$\begin{aligned} Z_R(\tau) &\approx \int_0^\infty dl (2l+1) e^{-l(l+1)\epsilon_0/\tau} \\ &= \int_0^\infty dl \frac{d}{dl} \left(-\frac{\tau}{\epsilon_0} e^{-l(l+1)\epsilon_0/\tau} \right) \\ &= \frac{\tau}{\epsilon_0}. \end{aligned} \tag{6.200}$$

Part c. Evaluate partition function for small temperatures When $\tau \ll \epsilon_0$, so that $\epsilon_0/\tau \gg 1$, all our exponentials are increasingly close to zero as l increases. Dropping all the second and higher order terms we have

$$Z_R(\tau) \approx 1 + 3e^{-2\epsilon_0/\tau}. \tag{6.201}$$

Part d. Energy and heat capacity In the large ϵ_0/τ domain (small temperatures) we have

$$\begin{aligned} U &= \tau^2 \frac{\partial}{\partial \tau} \ln Z \\ &= \tau^2 \frac{\partial}{\partial \tau} \ln \left(1 + 3e^{-2\epsilon_0/\tau} \right) \\ &= \tau^2 \frac{3(-2\epsilon_0)(-1/\tau^2)}{1 + 3e^{-2\epsilon_0/\tau}} \\ &= \frac{6\epsilon_0}{1 + 3e^{-2\epsilon_0/\tau}} \\ &\approx 6\epsilon_0. \end{aligned} \tag{6.202}$$

The specific heat [1] in this domain is

$$
\begin{aligned}
C_V &= \frac{\partial U}{\partial \tau} \\
&= \left(\frac{6\epsilon_0/\tau}{1 + 3e^{-2\epsilon_0/\tau}} \right)^2 \\
&\approx \left(\frac{6\epsilon_0}{\tau} \right)^2 .
\end{aligned}
\tag{6.203}
$$

For the small ϵ_0/τ (large temperatures) case we have

$$
\begin{aligned}
U &= \tau^2 \frac{\partial}{\partial \tau} \ln Z \\
&= \tau^2 \frac{\partial}{\partial \tau} \ln \frac{\tau}{\epsilon_0} \\
&= \tau^2 \frac{1}{\tau} \\
&= \tau .
\end{aligned}
\tag{6.204}
$$

The heat capacity in this large temperature region is

$$
C_V = \frac{\partial U}{\partial \tau} = 1,
\tag{6.205}
$$

which is unity as described in the problem.

Part e. Sketch The energy and heat capacities are roughly sketched in fig. 6.27.

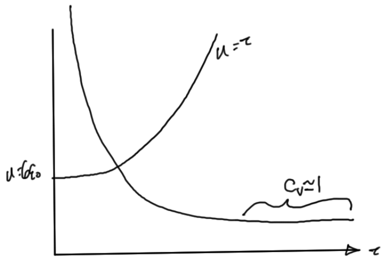


Figure 6.27: Energy and heat capacity.

---

[1] This is a dimensionless specific heat, whereas in traditional units $C_V = \partial U/\partial T$

It's somewhat odd seeming that we have a zero point energy at zero temperature. Plotting the energy (truncating the sums to 30 terms) in fig. 6.28, we don't see such a zero point energy.

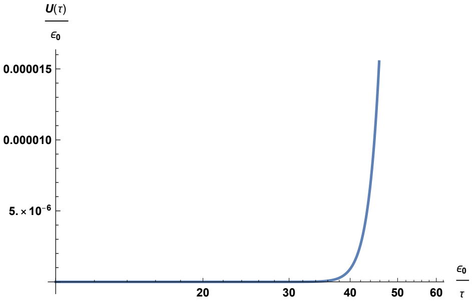


Figure 6.28: Exact plot of the energy for a range of temperatures (30 terms of the sums retained).

That plotted energy is as follows, computed without first dropping any terms of the partition function

$$
\begin{aligned}
U &= \tau^2 \frac{\partial}{\partial \tau} \ln \left(\sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\epsilon_0/\tau} \right) \\
&= \epsilon_0 \frac{\left(\sum_{l=1}^{\infty} l(l+1)(2l+1) e^{-l(l+1)\epsilon_0/\tau} \right)}{\left(\sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\epsilon_0/\tau} \right)} \\
&= \epsilon_0 \frac{\left(\sum_{l=1}^{\infty} l(l+1)(2l+1) e^{-l(l+1)\epsilon_0/\tau} \right)}{Z}.
\end{aligned}
\tag{6.206}
$$

To avoid the zero point energy, we have to use this and not the truncated partition function to do the integral approximation. Doing that calculation (which isn't as convenient but can be done in software kittelRotationalPartition.nb). We obtain

$$
\begin{aligned}
U &\approx \frac{\int_1^{\infty} l(l+1)(2l+1) e^{-l(l+1)\epsilon_0/\tau}}{\int_0^{\infty} (2l+1) e^{-l(l+1)\epsilon_0/\tau}} \\
&= \epsilon_0 e^{2\epsilon_0/\tau} \left(2 + \frac{\tau}{\epsilon_0} \right).
\end{aligned}
\tag{6.207}
$$

This approximation, which has taken the sums to infinity, is plotted in fig. 6.29.

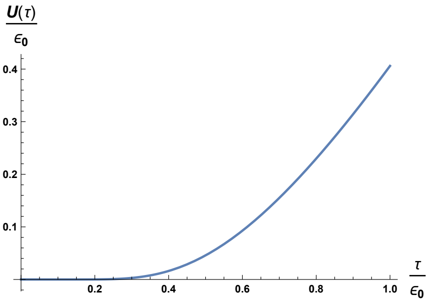


Figure 6.29: Low temperature approximation of the energy.

From eq. (6.206), we can take one more derivative to calculate the exact specific heat

$$
\begin{aligned}
C_{\mathrm{V}} &= \epsilon_0 \frac{\partial}{\partial \tau} \left(\frac{\left(\sum_{l=1}^{\infty} l(l+1)(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)}{\left(\sum_{l=0}^{\infty}(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)} \right) \\
&= \left(\frac{\epsilon_0}{\tau}\right)^2 \left(\frac{\left(\sum_{l=1}^{\infty} l^2(l+1)^2(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)}{\left(\sum_{l=0}^{\infty}(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)} \right. \\
&\qquad \left. + \frac{\left(\sum_{l=1}^{\infty} l(l+1)(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)^2}{\left(\sum_{l=0}^{\infty}(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)^2} \right) \\
&= \left(\frac{\epsilon_0}{\tau}\right)^2 \left(\frac{\left(\sum_{l=1}^{\infty} l^2(l+1)^2(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)}{Z} + \frac{U^2}{\epsilon_0^2} \right) \\
&= \frac{U^2}{\epsilon_0^2} + \left(\frac{\epsilon_0}{\tau}\right)^2 \frac{\left(\sum_{l=1}^{\infty} l^2(l+1)^2(2l+1) e^{-l(l+1)\epsilon_0/\tau}\right)}{Z}.
\end{aligned}
\tag{6.208}
$$

This is plotted to 30 terms in fig. 6.30.

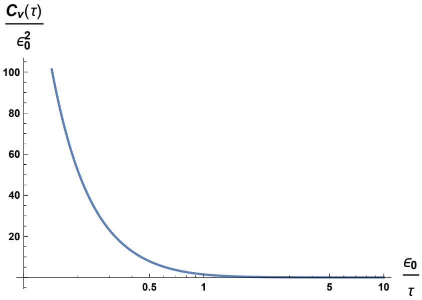


Figure 6.30: Specific heat to 30 terms.

Exercise 6.13 Zipper problem ([11] *pr. 3.7*)

A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ϵ. we require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \cdots, s-1)$ are already open.

a. Find (and sum) the partition function.
b. In the low temperature limit $k_B T \ll \epsilon$, find the average number of open links. The model is a very simplified model of the unwinding of two-stranded DNA molecules.

Answer for Exercise 6.13

The system is depicted in fig. 6.31, in the $E = 0$ and $E = \epsilon$ states.

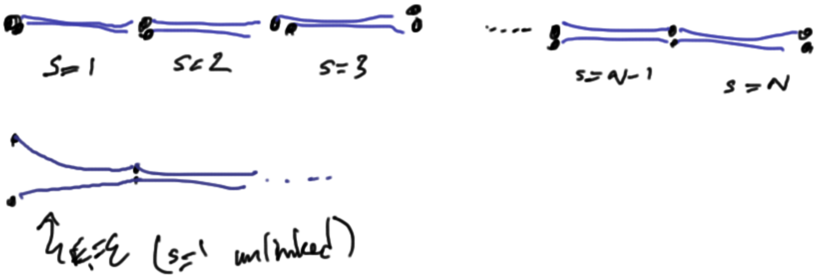


Figure 6.31: Zipper molecule model in first two states.

The left opening only constraint simplifies the combinatorics, since this restricts the available energies for the complete molecule to $0, \epsilon, 2\epsilon, \cdots, N\epsilon$.

The probability of finding the molecule with s links open is then

$$P_s = \frac{e^{-\beta s \epsilon}}{Z}, \tag{6.209}$$

with

$$Z = \sum_{s=0}^{N} e^{-\beta s \epsilon}. \tag{6.210}$$

Part a. We can sum this geometric series immediately

$$\boxed{Z = \frac{e^{-\beta(N+1)\epsilon} - 1}{e^{-\beta\epsilon} - 1}.} \tag{6.211}$$

Part b. The expectation value for the number of links is

$$\begin{aligned}
\langle s \rangle &= \sum_{s=0}^{N} s P_s \\
&= \frac{1}{Z} \sum_{s=1}^{N} s e^{-\beta s \epsilon} \\
&= -\frac{1}{Z} \frac{\partial}{\partial(\beta\epsilon)} \sum_{s=1}^{N} e^{-\beta s \epsilon}.
\end{aligned} \tag{6.212}$$

Let's write

$$a = e^{-\beta\epsilon}, \tag{6.213}$$

and make a change of variables

$$\begin{aligned}
-\frac{\partial}{\partial(\beta\epsilon)} &= \frac{\partial}{\partial \ln a} \\
&= \frac{\partial a}{\partial \ln a} \frac{\partial}{\partial a} \\
&= \frac{\partial e^{-\beta\epsilon}}{\partial(-\beta\epsilon)} \frac{\partial}{\partial a} \\
&= a \frac{\partial}{\partial a},
\end{aligned} \tag{6.214}$$

so that

$$\begin{aligned}
-\frac{\partial}{\partial \ln a} \sum_{s=1}^{N} a^s &= a \frac{d}{da} \left(\frac{a^{N+1} - a}{a - 1} \right) \\
&= a \left(\frac{(N+1)a^N - 1}{a - 1} - \frac{a^{N+1} - a}{(a-1)^2} \right) \\
&= \frac{a}{(a-1)^2} \left(\left((N+1)a^N - 1 \right)(a - 1) - a^{N+1} + a \right) \\
&= \frac{a}{(a-1)^2} \left(N a^{N+1} - (N+1)a^N + 1 \right) \\
&= \frac{a}{(a-1)^2} \left(a^N (N(a-1) - 1) + 1 \right).
\end{aligned} \tag{6.215}$$

The average number of links is thus

$$\langle k \rangle = \frac{a-1}{a^{N+1}-1} \frac{a}{(a-1)^2} \left(a^N (N(a-1)-1) + 1 \right), \tag{6.216}$$

or

$$\boxed{\langle k \rangle = \frac{1}{1-e^{-\beta\epsilon(N+1)}} \frac{1}{e^{\beta\epsilon}-1} \left(e^{-\beta\epsilon N} (N(e^{-\beta\epsilon}-1)-1) + 1 \right).} \tag{6.217}$$

In the very low temperature limit where $\beta\epsilon \gg 1$ (small T, big β), we have

$$\begin{aligned} \langle k \rangle &\approx \frac{1}{e^{\beta\epsilon}} \\ &= e^{-\beta\epsilon}, \end{aligned} \tag{6.218}$$

showing that on average no links are open at such low temperatures. An exact plot of $\langle s \rangle$ for a few small N values is in fig. 6.32.

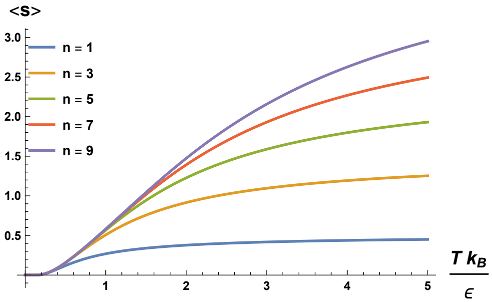


Figure 6.32: Average number of open links.

Exercise 6.14 Magnetic spin level splitting (*2013 midterm II p1*)

A particle with spin S has $2S+1$ states $-S, -S+1, \cdots S-1, S$. When exposed to a magnetic field, state splitting results in energy $E_m = \hbar m B$. Calculate the partition function, and use this to find the temperature specific magnetization. A “sum the geometric series” hint was given.

Answer for Exercise 6.14

Our partition function is

$$\begin{aligned} Z &= \sum_{m=-S}^{S} e^{-\hbar\beta m B} \\ &= e^{-\hbar\beta S B} \sum_{m=-S}^{S} e^{-\hbar\beta(m+S)B} \\ &= e^{\hbar\beta S B} \sum_{n=0}^{2S} e^{-\hbar\beta n B}. \end{aligned} \tag{6.219}$$

Writing

$$a = e^{-\hbar\beta B}, \tag{6.220}$$

that is

$$\begin{aligned} Z &= a^{-S} \sum_{n=0}^{2S} a^n \\ &= a^{-S} \frac{a^{2S+1} - 1}{a - 1} \\ &= \frac{a^{S+1} - a^{-S}}{a - 1} \\ &= \frac{a^{S+1/2} - a^{-S-1/2}}{a^{1/2} - a^{-1/2}}. \end{aligned} \tag{6.221}$$

Substitution of a gives us

$$\boxed{Z = \frac{\sinh(\hbar\beta B(S+1/2))}{\sinh(\hbar\beta B/2)}.} \tag{6.222}$$

To calculate the magnetization M, I used

$$M = -\langle H \rangle / B. \tag{6.223}$$

As [11] defines magnetization for a spin system. It was pointed out to me after the test that magnetization was defined differently in class as

$$\mu = \frac{\partial F}{\partial B}. \tag{6.224}$$

These are, up to a sign, identical, at least in this case, since we have β and B traveling together in the partition function.

In terms of the average energy

$$\begin{aligned}
M &= -\frac{\langle H \rangle}{B} \\
&= \frac{1}{B}\frac{\partial}{\partial \beta} \ln Z(\beta B) \\
&= \frac{1}{ZB}\frac{\partial}{\partial \beta} Z(\beta B) \\
&= \frac{1}{Z}\frac{\partial}{\partial(\beta B)} Z(\beta B).
\end{aligned} \tag{6.225}$$

Compare this to the in-class definition of magnetization

$$\begin{aligned}
\mu &= \frac{\partial F}{\partial B} \\
&= \frac{\partial}{\partial B}\left(-k_{\mathrm{B}} T \ln Z(\beta B)\right) \\
&= -\frac{\partial}{\partial B}\frac{\ln Z(\beta B)}{\beta} \\
&= -\frac{1}{\beta Z}\frac{\partial}{\partial B} Z(\beta B) \\
&= -\frac{1}{Z}\frac{\partial}{\partial(\beta B)} Z(\beta B).
\end{aligned} \tag{6.226}$$

Defining the magnetic moment in either of these fashions is really a cheat, because it's done without any connection to physics of the situation. In §3.9 of [13] is a much better seeming approach, where the moment is defined as $M_z = -\left\langle \boldsymbol{\mu} \cdot \mathbf{H} \right\rangle / H$, but this is then shown to have the form eq. (6.226).

Calculating it For this derivative we have

$$\begin{aligned}
\frac{\partial}{\partial(\beta B)} \ln Z &= \frac{\partial}{\partial(\beta B)} \ln \frac{\sinh(\hbar\beta B(S+1/2))}{\sinh(\hbar\beta B/2)} \\
&= \frac{\partial}{\partial(\beta B)}\left(\ln\sinh(\hbar\beta B(S+1/2)) - \ln\sinh(\hbar\beta B/2)\right) \\
&= \frac{\hbar}{2}\left((2S+1)\coth(\hbar\beta B(S+1/2)) - \coth(\hbar\beta B/2)\right).
\end{aligned} \tag{6.227}$$

This gives us

$$\mu = -\frac{1}{Z}\frac{\hbar}{2}\left((2S+1)\coth(\hbar\beta B(S+1/2)) - \coth(\hbar\beta B/2)\right) \tag{6.228}$$

$$= -\frac{\sinh(\hbar\beta B/2)}{\sinh(\hbar\beta B(S+1/2))}\frac{\hbar}{2}\left((2S+1)\coth(\hbar\beta B(S+1/2)) - \coth(\hbar\beta B/2)\right).$$

After some simplification (midtermTwoQ1FinalSimplificationMu.nb) we get

$$\boxed{\mu = \hbar\frac{(s+1)\sinh(\hbar\beta Bs) - s\sinh(\hbar\beta B(s+1))}{\cosh(\hbar\beta B(2s+1)) - 1}.} \tag{6.229}$$

I got something like this on the midterm, but recall doing it somehow much differently (after getting my marked paper back, saw that was because I'd made an error, and everything after that got messed up).

Exercise 6.15 Perturbation of classical SHO (*2013 midterm II p2*)

Consider a single particle perturbation of a classical simple harmonic oscillator Hamiltonian

$$H = \frac{1}{2}m\omega^2\left(x^2 + y^2\right) + \frac{1}{2m}\left(p_x^2 + p_y^2\right) + ax^4 + by^6. \tag{6.230}$$

Calculate the canonical partition function, mean energy and specific heat of this system.

a. This problem can be attempted in two ways, the first of which was how I did it on the midterm, differentiating under the integral sign, leaving the integrals in exact form, but not evaluated explicitly in any way.

b. By Taylor expanding around $c = 0$ and $d = 0$ with those as the variables in the Taylor expansion (as now done in the Pathria 3.29 problem), we can form a solution in short order (this was the desired approach).

Answer for Exercise 6.15

The canonical partition function is

$$Z = \int dx dy dp_x dp_y e^{-\beta H} \tag{6.231}$$

$$= \int dx e^{-\beta\left(\frac{1}{2}m\omega^2 x^2 + ax^4\right)} \int dy e^{-\beta\left(\frac{1}{2}m\omega^2 y^2 + by^6\right)} \int dp_x dp_y e^{-\beta p_x^2/2m} e^{-\beta p_y^2/2m}.$$

With

$$u = \sqrt{\frac{\beta}{2m}} p_x \tag{6.232a}$$

$$v = \sqrt{\frac{\beta}{2m}} p_y, \tag{6.232b}$$

the momentum integrals are

$$\begin{aligned}
\int dp_x dp_y e^{-\beta p_x^2/2m} e^{-\beta p_y^2/2m} &= \frac{2m}{\beta} \int du du e^{-u^2 - v^2} \\
&= \frac{m}{\beta} 2\pi \int 2r dr e^{-r^2} \\
&= \frac{2\pi m}{\beta}.
\end{aligned} \tag{6.233}$$

Writing

$$f(x) = \frac{1}{2} m\omega^2 x^2 + a x^4 \tag{6.234a}$$

$$g(x) = \frac{1}{2} m\omega^2 y^2 + b y^6, \tag{6.234b}$$

we have

$$\boxed{Z = \frac{2\pi m}{\beta} \int dx e^{-\beta f(x)} \int dy e^{-\beta g(y)}.} \tag{6.235}$$

Part a. Attempt 1: differentiation under the integral sign The mean energy is

$$\begin{aligned}
\langle H \rangle &= \frac{\int H e^{-\beta H}}{\int e^{-\beta H}} \\
&= -\frac{\partial}{\partial \beta} \ln \int e^{-\beta H} \\
&= \frac{\partial}{\partial \beta} \left(\ln \beta - \ln \int dx e^{-\beta f(x)} - \ln \int dy e^{-\beta g(y)} \right) \\
&= \frac{1}{\beta} + \frac{\int dx f(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} + \frac{\int dy g(y) e^{-\beta g(y)}}{\int dy e^{-\beta g(y)}}.
\end{aligned} \tag{6.236}$$

The specific heat follows by differentiating once more

$$\begin{aligned} C_\mathrm{V} &= \frac{\partial \langle H \rangle}{\partial T} \\ &= \frac{\partial \beta}{\partial T} \frac{\partial \langle H \rangle}{\partial \beta} \\ &= -\frac{1}{k_\mathrm{B} T^2} \frac{\partial \langle H \rangle}{\partial \beta} \\ &= -k_\mathrm{B} \beta^2 \frac{\partial \langle H \rangle}{\partial \beta} \\ &= -k_\mathrm{B} \beta^2 \left(-\frac{1}{\beta^2} + \frac{\partial}{\partial \beta} \left(\frac{\int dx f(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} + \frac{\int dy g(y) e^{-\beta g(y)}}{\int dy e^{-\beta g(y)}} \right) \right). \end{aligned} \tag{6.237}$$

Differentiating the integral terms we have, for example,

$$\frac{\partial}{\partial \beta} \frac{\int dx f(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} = -\frac{\int dx f^2(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} + \left(\frac{\int dx f(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} \right)^2, \tag{6.238}$$

so that the specific heat is

$$\boxed{\begin{aligned} C_\mathrm{V} = k_\mathrm{B} \Bigg(1 &+ \frac{\int dx f^2(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} \\ &- \left(\frac{\int dx f(x) e^{-\beta f(x)}}{\int dx e^{-\beta f(x)}} \right)^2 + \frac{\int dy g^2(y) e^{-\beta g(y)}}{\int dy e^{-\beta g(y)}} - \left(\frac{\int dy g(y) e^{-\beta g(y)}}{\int dy e^{-\beta g(y)}} \right)^2 \Bigg). \end{aligned}} \tag{6.239}$$

That's as far as I took this problem. There was a discussion after the midterm with Eric about Taylor expansion of these integrals. That's not something that I tried.

Part b. Attempt 2: Taylor expanding in c and d Performing a two variable Taylor expansion of Z, about $(c, d) = (0, 0)$ we have

$$\begin{aligned} Z &\approx \frac{2\pi m}{\beta} \int dxdy e^{-\beta m\omega^2 x^2/2} e^{-\beta m\omega^2 y^2/2} \left(1 - \beta a x^4 - \beta b y^6\right) \\ &= \frac{2\pi m}{\beta} \frac{2\pi}{\beta m\omega^2} \left(1 - \beta a \frac{3!!}{(\beta m\omega^2)^2} - \beta b \frac{5!!}{(\beta m\omega^2)^3}\right), \end{aligned} \tag{6.240}$$

or

$$\boxed{Z \approx \frac{(2\pi/\omega)^2}{\beta^2} \left(1 - \frac{3a}{\beta(m\omega^2)^2} - \frac{15b}{\beta^2(m\omega^2)^3}\right).} \tag{6.241}$$

Now we can calculate the average energy

$$\begin{aligned} \langle H \rangle &= -\frac{\partial}{\partial \beta} \ln Z \\ &= -\frac{\partial}{\partial \beta} \left(-2\ln\beta + \ln\left(1 - \frac{3a}{\beta(m\omega^2)^2} - \frac{15b}{\beta^2(m\omega^2)^3}\right)\right) \\ &= \frac{2}{\beta} - \frac{\frac{3a}{\beta^2(m\omega^2)^2} + \frac{30b}{\beta^3(m\omega^2)^3}}{1 - \frac{3a}{\beta(m\omega^2)^2} - \frac{15b}{\beta^2(m\omega^2)^3}}. \end{aligned} \tag{6.242}$$

Dropping the c, d terms of the denominator above, we have

$$\boxed{\langle H \rangle = \frac{2}{\beta} - \frac{3a}{\beta^2(m\omega^2)^2} - \frac{30b}{\beta^3(m\omega^2)^3}.} \tag{6.243}$$

The heat capacity follows immediately

$$\boxed{C_V = \frac{\partial \langle H \rangle}{\partial T} = k_B \left(2 - \frac{6ak_B T}{(m\omega^2)^2} - \frac{90k_B^2 T^2 b}{(m\omega^2)^3}.\right)} \tag{6.244}$$

Exercise 6.16 Anharmonic oscillator ([13] *pr. 3.29*)

The potential energy of a one-dimensional, anharmonic oscillator may be written as

$$V(q) = cq^2 - gq^3 - fq^4, \tag{6.245}$$

where c, g, and f are positive constant; quite generally, g and f may be assumed to be very small in value.

a. Show that the leading contribution of anharmonic terms to the heat capacity of the oscillator, assumed classical, is given by

$$\frac{3}{2}k_{\mathrm{B}}^2\left(\frac{f}{c^2}+\frac{5}{4}\frac{g^2}{c^3}\right)T, \tag{6.246}$$

b. To the same order, show that the mean value of the position coordinate q is given by

$$\frac{3}{4}\frac{gk_{\mathrm{B}}T}{c^2}. \tag{6.247}$$

Answer for Exercise 6.16

Our partition function is

$$\begin{aligned}
Z &= \int dpdqe^{-\beta p^2/2m}e^{-\beta\left(cq^2-gq^3-fq^4\right)}\\
&= \sqrt{\frac{2\pi m}{\beta}}\int dqe^{-\beta\left(cq^2-gq^3-fq^4\right)}.
\end{aligned} \tag{6.248}$$

How to expand this wasn't immediately clear to me (as it wasn't on the midterm either). We can't Taylor expand in q, because there's no single position q that is of interest to expand around (we are integrating over all q). What we can do though is Taylor expand about the values f and g, which are assumed to be small. Here's the two variable Taylor expansion of this perturbed harmonic oscillator exponential. With

$$A(f,g) = e^{-\beta\left(cq^2-gq^3-fq^4\right)} \tag{6.249}$$

The expansion to second order is

$$\begin{aligned}
A(f,g) &= A(0,0) + f\left.\frac{\partial A}{\partial f}\right|_{f=0} + g\left.\frac{\partial A}{\partial g}\right|_{g=0} + \frac{1}{2}f^2\left.\frac{\partial^2 A}{\partial f^2}\right|_{f=0}\\
&\quad + \frac{1}{2}g^2\left.\frac{\partial^2 A}{\partial g^2}\right|_{g=0} + fg\left.\frac{\partial^2 A}{\partial g\partial f}\right|_{f,g=0} + \cdots\\
&= e^{-\beta cq^2}\left(1 + g\beta q^3 + f\beta q^4 + \frac{1}{2}g^2\left(\beta q^3\right)^2 + \frac{1}{2}f^2\left(\beta q^4\right)^2\right.\\
&\qquad\qquad\left. + fg\left(\beta q^3\right)\left(\beta q^4\right) + \cdots\right)\\
&= e^{-\beta cq^2}\left(1+g\beta q^3+f\beta q^4+\frac{1}{2}g^2\beta^2q^6+fg\beta^2q^7+\frac{1}{2}f^2\beta^2q^8+\cdots\right).
\end{aligned} \tag{6.250}$$

This can now be integrated by parts, where any odd powers are killed. For even powers we have

$$\begin{aligned}\int q^{2N} e^{-aq^2} dq &= \int q^{2N-1} d\frac{e^{-aq^2}}{-2a} \\ &= \frac{2N-1}{2a} \int q^{2(N-1)} e^{-aq^2} dq \\ &= \frac{(2N-1)!!}{(2a)^N} \sqrt{\frac{\pi}{a}}.\end{aligned} \tag{6.251}$$

This gives us

$$\begin{aligned}Z &= \sqrt{\frac{\pi}{\beta c}}\sqrt{\frac{2\pi m}{\beta}} \left(1 + f\beta \frac{3!!}{(2\beta c)^2} + \frac{1}{2} g^2 \beta^2 \frac{5!!}{(2\beta c)^3} + \frac{1}{2} f^2 \beta^2 \frac{7!!}{(2\beta c)^4} + \cdots \right) \\ &= \frac{\pi}{\beta}\sqrt{\frac{2m}{c}} \left(1 + \frac{3f}{4c^2\beta} + \frac{15g^2}{16c^3\beta} + \frac{105 f^2}{32c^4\beta} + \cdots \right).\end{aligned} \tag{6.252}$$

Retaining only the first two terms of the expansion, we have

$$\boxed{Z \approx \frac{\pi}{\beta}\sqrt{\frac{2m}{c}} \left(1 + \frac{3f}{4c^2\beta} + \frac{15g^2}{16c^3\beta} \right).} \tag{6.253}$$

Part a. Specific heat. Our average energy, in this approximation

$$\begin{aligned}\langle H \rangle &= -\frac{\partial}{\partial \beta} \ln Z \\ &\approx -\frac{\partial}{\partial \beta} \left(-\ln\beta + \ln\left(1 + \frac{3f}{4c^2\beta} + \frac{15g^2}{16c^3\beta} \right) \right) \\ &= \frac{1}{\beta} + \frac{1}{\beta^2} \frac{\frac{3f}{4c^2} + \frac{15g^2}{16c^3}}{1 + \frac{1}{\beta}\left(\frac{3f}{4c^2} + \frac{15g^2}{16c^3} \right)} \\ &= k_B T + k_B^2 T^2 \left(\frac{3f}{4c^2} + \frac{15g^2}{16c^3} \right) \left(1 - k_B T \left(\frac{3f}{4c^2} + \frac{15g^2}{16c^3} \right) + \cdots \right).\end{aligned} \tag{6.254}$$

So to first order in T our specific heat is

$$\begin{aligned}C_V &= \frac{\partial \langle H \rangle}{\partial T} \\ &\approx k_B + 2k_B^2 T \left(\frac{3f}{4c^2} + \frac{15g^2}{16c^3} \right),\end{aligned} \tag{6.255}$$

or

$$\boxed{C_{\mathrm{V}} = k_{\mathrm{B}} + k_{\mathrm{B}}^2 T \left(\frac{3f}{2c^2} + \frac{15g^2}{8c^3} \right) + \cdots} \tag{6.256}$$

Part b. Coordinate expectation.

$$\begin{aligned}
\langle q \rangle &= \sqrt{\frac{2\pi m}{\beta}} \frac{1}{Z} \int q e^{-\beta\left(cq^2 - gq^3 - fq^4\right)} dq \\
&= \sqrt{\frac{2\pi m}{\beta}} \frac{\int q e^{-\beta c q^2} \left(1 + g\beta q^3 + f\beta q^4\right) dq}{\frac{\pi}{\beta}\sqrt{\frac{2m}{c}} \left(1 + \frac{3f}{4c^2\beta} + \frac{15g^2}{16c^3\beta}\right)} \\
&\approx \sqrt{\frac{\cancel{2\pi m}}{\cancel{\beta}}} g\cancel{\beta} \frac{3!!}{(2\beta c)^2} \sqrt{\frac{\cancel{\pi}}{\cancel{\beta}\cancel{c}}} \frac{1}{\frac{\cancel{\pi}}{\beta}\sqrt{\frac{\cancel{2m}}{\cancel{c}}}},
\end{aligned} \tag{6.257}$$

or

$$\boxed{\langle q \rangle \approx \frac{3 g k_{\mathrm{B}} T}{4c^2}.} \tag{6.258}$$

Compare this to the expectation of the coordinate for an unperturbed harmonic oscillator

$$\begin{aligned}
\langle q \rangle &= \frac{\int q e^{-\beta c q^2}}{\int e^{-\beta c q^2}} \\
&= 0.
\end{aligned} \tag{6.259}$$

We now have a temperature dependence to the expectation of the coordinate that we didn't have for the harmonic oscillator.

Exercise 6.17 Quantum anharmonic oscillator (*[13] pr. 3.30*)

The energy levels of a quantum-mechanical, one-dimensional, anharmonic oscillator may be approximated as

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega - x \left(n + \frac{1}{2}\right)^2 \hbar\omega \qquad n = 0, 1, 2, \cdots \tag{6.260}$$

The parameter x, usually $\ll 1$, represents the degree of anharmonicity. Show that, to the first order in x and the fourth order in

$u \equiv \hbar\omega/k_B T$, the specific heat of a system of N such oscillators is given by

$$C = N k_B \left(\left(1 - \frac{1}{12} u^2 + \frac{1}{240} u^4 \right) + 4x \left(\frac{1}{u} + \frac{1}{80} u^3 \right) \right). \tag{6.261}$$

Answer for Exercise 6.17

We can expand the partition function in a first order Taylor series about $x = 0$, then evaluate the sums

$$\begin{aligned} Z_1 &= \sum_{n=0}^{\infty} \exp\left(-\beta \left(n + \frac{1}{2} \right) \hbar\omega + \beta x \left(n + \frac{1}{2} \right)^2 \hbar\omega \right) \\ &= \sum_{n=0}^{\infty} \exp\left(- \left(n + \frac{1}{2} \right) u + x \left(n + \frac{1}{2} \right)^2 u \right) \\ &\approx \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)u} \left(1 + xu \left(n + \frac{1}{2} \right)^2 \right). \end{aligned} \tag{6.262}$$

The quadratic sum can be evaluated indirectly as it can be expressed as a derivative

$$\begin{aligned} Z_1 &= \left(1 + xu \frac{d^2}{du^2} \right) \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)u} \\ &= \left(1 + xu \frac{d^2}{du^2} \right) e^{-u/2} \sum_{n=0}^{\infty} e^{-nu} \\ &= \left(1 + xu \frac{d^2}{du^2} \right) e^{-u/2} \frac{1}{1 - e^{-u}} \\ &= \left(1 + xu \frac{d^2}{du^2} \right) \frac{1}{e^{u/2} - e^{-u/2}} \\ &= \left(1 + xu \frac{d^2}{du^2} \right) \frac{1}{2 \sinh(u/2)}. \end{aligned} \tag{6.263}$$

Finally, evaluation of the derivatives gives us

$$Z_1 = \frac{1}{\sinh(u/2)} \left(1 + xu \frac{2 \coth^2(u/2) - 1}{8} \right). \tag{6.264}$$

Now we'd like to compute the specific heat in terms of derivatives of u. First, for the average energy

$$\begin{aligned}\langle H \rangle &= -N \frac{\partial}{\partial \beta} \ln Z_1 \\ &= -N \hbar\omega \frac{\partial}{\partial u} \ln Z_1.\end{aligned} \tag{6.265}$$

The specific heat is

$$\begin{aligned}C_{\mathrm{V}} &= \frac{\partial \langle H \rangle}{\partial T} \\ &= \frac{\partial u}{\partial T} \frac{\partial \langle H \rangle}{\partial u} \\ &= \frac{\hbar\omega}{k_{\mathrm{B}}} \frac{\partial (1/T)}{\partial T} \frac{\partial \langle H \rangle}{\partial u} \\ &= -\frac{\hbar\omega}{k_{\mathrm{B}} T^2} \frac{\partial \langle H \rangle}{\partial u} \\ &= -\frac{k_{\mathrm{B}} u^2}{\hbar\omega} \frac{\partial \langle H \rangle}{\partial u},\end{aligned} \tag{6.266}$$

or

$$C_{\mathrm{V}} = N k_{\mathrm{B}} u^2 \frac{\partial^2}{\partial u^2} \ln Z_1. \tag{6.267}$$

Actually computing that is messy algebra (See pathria_3_30.nb), and the result isn't particularly interesting looking. The plot fig. 6.33 is interesting though and shows negative heat capacities near zero and a funny little jog near $C_{\mathrm{V}} = 0$.

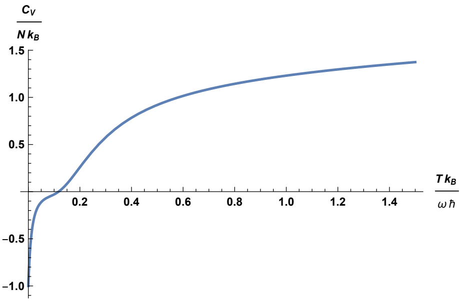


Figure 6.33: Quantum anharmonic heat capacity.

Also confirmed in the Mathematica notebook is equation 6.261, which follows by first doing a first order series expansion in x, then a subsequent series expansion in u.

GRAND CANONICAL ENSEMBLE.

7

7.1 GRAND PARTITION FUNCTION.

This lecture had a large amount of spoken content not captured in these notes. Reference to §4 [13] was made for additional details.

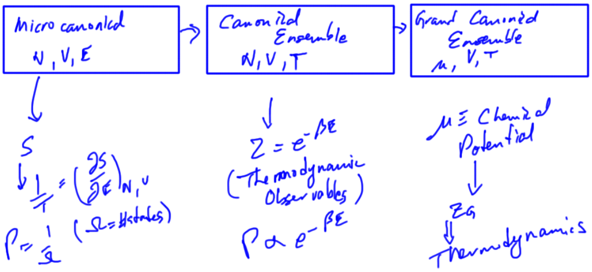


Figure 7.1: Ensemble pictures.

We are now going to allow particles to move to and from the system and the reservoir. The total number of states in the system is

$$\Omega_{\text{total}}(N, V, E) = \sum_{N_S, E_S} \Omega_S(N_S, V_S, E_S)\Omega_R(N - N_S, V_R, E - E_S), \tag{7.1}$$

so for $N_S \ll N$, and $E_S \ll E$, we have

$$\begin{aligned}
\Omega_R &= \exp\left(\frac{1}{k_B} S_R(N - N_S, V_R, E - E_S)\right) \\
&\approx \exp\left(\frac{1}{k_B} S_R(N, V_R, E) - \frac{N_S}{k_B}\left(\frac{\partial S_R}{\partial N}\right)_{V,E} - \frac{E_S}{k_B}\left(\frac{\partial S_R}{\partial E}\right)_{N,V}\right) \\
&\propto \Omega_S(N_S, V_S, E_S) e^{-\frac{\mu}{k_B T} N_S} e^{-\frac{E_S}{k_B T}},
\end{aligned} \tag{7.2}$$

where the chemical potential and temperature are defined respectively as

$$\frac{\mu}{T} = -\left(\frac{\partial S_R}{\partial N}\right)_{V,E} \tag{7.3a}$$

$$\frac{1}{T} = \left(\frac{\partial S_R}{\partial E} \right)_{N,V} . \tag{7.3b}$$

$$\mathcal{P} \propto e^{\frac{\mu}{k_\mathrm{B} T} N_S} e^{-\frac{E_S}{k_\mathrm{B} T}} . \tag{7.4}$$

With $\{c\}$ as the set of all possible configuration pairs $\{N_S, E_S\}$, we define the grand partition function

$$\Omega = \sum_{\{c\}} e^{\frac{\mu}{k_\mathrm{B} T} N_S} e^{-\frac{E_S}{k_\mathrm{B} T}} . \tag{7.5}$$

So that the probability of finding a given state with energy and particle numbers $\{E_S, N_S\}$ is

$$\mathcal{P}(E_S, N_S) = \frac{e^{\frac{\mu}{k_\mathrm{B} T} N_S} e^{-\frac{E_S}{k_\mathrm{B} T}}}{\Omega} . \tag{7.6}$$

For a classical system we have

$$\{c\} \rightarrow \{x\}\{p\}, \tag{7.7}$$

whereas in a quantum content we have

$$\{c\} \rightarrow \text{eigenstate}. \tag{7.8}$$

$$\Omega^{\mathrm{QM}} = \mathrm{tr}_{\{\text{energy},N\}} \left(e^{-\beta(\hat{H} - \mu \hat{N})} \right) . \tag{7.9}$$

We want to do this because the calculation of the number of states

$$\int_{\{x\}\{p\}} \delta \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots + mgx_1 + mgx_2 + \cdots \right) , \tag{7.10}$$

can quickly become intractable. We want to go to the canonical ensemble was because the partition function

$$Z_c = \int_{\{x\}\{p\}} e^{-\beta \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots + mgx_1 + mgx_2 + \cdots \right)} , \tag{7.11}$$

yields the same results, but can be much easier to compute. We have a similar reason to go to the grand canonical ensemble, because this computation, once we allow the number of particles to vary also becomes very hard.

We are now going to define a notion of equilibrium so that it includes

- All forces are equal (mechanical equilibrium)
- Temperatures are equal (no net heat flow)
- Chemical potentials are equal (no net particle flow)

We'll isolate a subsystem, containing a large number of particles fig. 7.2.

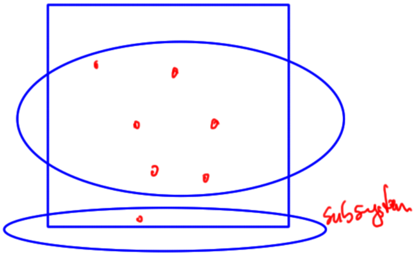


Figure 7.2: A subsystem to and from which particle motion is allowed.

When we think about Fermions we have to respect the "Pauli exclusion" principle .

Suppose we have just a one dimensional Fermion system for some potential as in fig. 7.3.

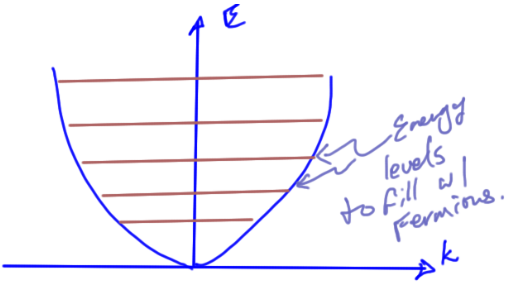


Figure 7.3: Energy level filling in a quantum system.

For every momentum k there are two possible occupation numbers $n_k \in \{0, 1\}$ our partition function is

$$Z_c = \sum_{n_k, \sum_k n_k = N} e^{-\beta \sum_k \epsilon_k n_k}. \tag{7.12}$$

We'd find that this calculation with this $\sum_k n_k = N$ constraint becomes essentially impossible.

We'll see that relaxing this constraint will allow this calculation to become tractable.

7.2 FERMIONS AND BOSONS.

Was mentioned that three dimensions confines us to looking at either Fermions or Bosons, and that two dimensions is a rich subject (interchange of two particles isn't the same as one particle cycling around the other ending up in the same place – how is that different than a particle cycling around another in a two dimensional space?)

Definitions

- Fermion. Antisymmetric under exchange. $n_k = 0, 1$.

  Paramekanti: "Fermions: basically they hate each other".

- Boson. Symmetric under exchange. $n_k = 0, 1, 2, \cdots$.

  Unlike Fermions, Bosons "love each other". You can pack as many Bosons as you want into a space. This allows Bosons to all collectively collapse into the ground state (Bose-Einstein condensation).

In either case our energies are

$$\epsilon_k = \frac{\hbar^2 k^2}{2m}. \tag{7.13}$$

For Fermions we'll have occupation filling of the form fig. 7.4, where there can be only one particle at any given site (an energy level for that value of momentum). For Bosonic systems as in fig. 7.5, we don't have a restriction of only one particle for each state, and can have any given number of particles for each value of momentum.

Our Hamiltonian is

$$H = \sum_k \hat{n}_k \epsilon_k, \tag{7.14}$$

where we have a number operator

$$N = \sum \hat{n}_k, \tag{7.15}$$

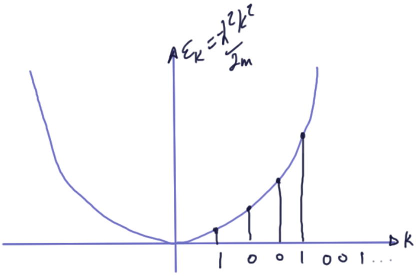


Figure 7.4: Fermionic energy level filling for free particle in a box.

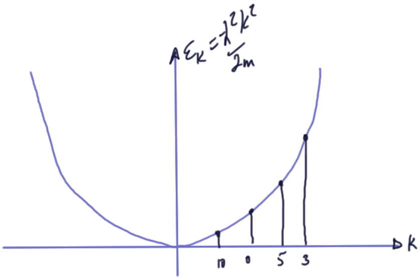


Figure 7.5: Bosonic free particle in a box energy level filling.

such that

$$[N, H] = 0. \tag{7.16}$$

$$\Omega = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{n_k, \sum n_m = N} e^{-\beta \sum_m n_m \epsilon_m}. \tag{7.17}$$

While the second sum is constrained, because we are summing over all n_k, this is essentially an unconstrained sum, so we can write

$$\begin{aligned}\Omega &= \sum_{n_k} e^{\beta\mu \sum_m n_m} e^{-\beta \sum_n n_n \epsilon_n} \\ &= \sum_{n_k} e^{-\beta \sum_m (\epsilon_m - \mu) n_m} \\ &= \sum_{n_k} \left(\prod_k e^{-\beta(\epsilon_k - \mu) n_k} \right) \\ &= \prod_k \left(\sum_{n_k} e^{-\beta(\epsilon_k - \mu) n_k} \right).\end{aligned} \tag{7.18}$$

A dumb expansion of the Fermi-Dirac grand partition function Let's make a bit more sense of some of the index manipulation done above.

There are some similarily confusing portions in §6.2 [13] where we have the following notation for the sums in the grand partition function Ω

$$\Omega = \sum_{N=0}^{\infty} z^N Q_N(V, T) \tag{7.19a}$$

$$Q_N(V, T) = {\sum_{\{n_\epsilon\}}}' e^{-\beta \sum_\epsilon n_\epsilon \epsilon}. \tag{7.19b}$$

This was shorthand notation for the canonical ensemble, subject to constraints on N and E

$$Q_N(V, T) = \sum_E e^{-\beta E} \tag{7.20a}$$

$$E = \sum_\epsilon n_\epsilon \epsilon \tag{7.20b}$$

$$N = \sum_\epsilon n_\epsilon. \tag{7.20c}$$

I found this notation pretty confusing, since the normal conventions about what is a dummy index in the various summations do not hold.

The claim of the text (and in class) is that we could write out the grand canonical partition function as

$$\Omega = \left(\sum_{n_0} \left(z e^{-\beta \epsilon_0} \right)^{n_0} \right) \left(\sum_{n_1} \left(z e^{-\beta \epsilon_1} \right)^{n_1} \right) \cdots \tag{7.21}$$

Let's verify this for a Fermi-Dirac distribution by dispensing with the notational tricks and writing out the original specification of the grand canonical partition function in long form, and compare that to the first few terms of the expansion of eq. (7.21).

Let's consider a specific value of E, namely all those values of E that apply to $N = 3$. Note that we have $n_\epsilon \in \{0, 1\}$ only for a Fermi-Dirac system, so this means we can have values of E like

$$E \in \{\epsilon_0 + \epsilon_1 + \epsilon_2, \epsilon_0 + \epsilon_3 + \epsilon_7, \epsilon_2 + \epsilon_6 + \epsilon_{11}, \cdots\} \tag{7.22}$$

Our grand canonical partition function, when written out explicitly, will have the form

$$\Omega = z^0 e^{-0} + z^1 \sum_{\epsilon_k} e^{-\beta\epsilon_k} + z^2 \sum_{\epsilon_k, \epsilon_m} e^{-\beta(\epsilon_k + \epsilon_m)} + z^3 \sum_{\epsilon_r, \epsilon_s, \epsilon_t} e^{-\beta(\epsilon_r + \epsilon_s + \epsilon_t)} + \cdots \tag{7.23}$$

Okay, that's simple enough and really what the primed notation is getting at. Now let's verify that after simplification this matches up with eq. (7.21). Expanding this out a bit we have

$$\begin{aligned}
\Omega &= \left(\sum_{n_0=0}^{1} \left(z e^{-\beta\epsilon_0}\right)^{n_0}\right) \left(\sum_{n_1=0}^{1} \left(z e^{-\beta\epsilon_1}\right)^{n_1}\right) \cdots \\
&= \left(1 + z e^{-\beta\epsilon_0}\right) \left(1 + z e^{-\beta\epsilon_1}\right) \left(1 + z e^{-\beta\epsilon_2}\right) \cdots \\
&= \left(1 + z e^{-\beta\epsilon_0} + z e^{-\beta\epsilon_1} + z e^{-\beta(\epsilon_0+\epsilon_1)}\right) \left(1 + z e^{-\beta\epsilon_2} + z e^{-\beta\epsilon_3} \right. \\
&\qquad \left. + z^2 e^{-\beta(\epsilon_2+\epsilon_3)}\right) \left(1 + z e^{-\beta\epsilon_4}\right) \cdots \\
&= \left(1 + z\left(e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}\right) + z^2 \left(e^{-\beta(\epsilon_0+\epsilon_1)} + e^{-\beta(\epsilon_0+\epsilon_2)} \right.\right. \\
&\qquad \left. + e^{-\beta(\epsilon_0+\epsilon_3)} + e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)}\right) \\
&\qquad \left. + z^3 \left(e^{-\beta(\epsilon_0+\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_0+\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_0+\epsilon_2+\epsilon_3)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}\right)\right) \left(1 \right. \\
&\qquad \left. + z e^{-\beta\epsilon_4}\right) \cdots
\end{aligned} \tag{7.24}$$

This completes the verification of the result as expected. It is definitely a brute force way of doing so, but easy to understand and I found for myself that it removed some of the notation that obfuscated what is really a simple statement.

Once we are comfortable with this Fermi-Dirac expression of the grand canonical partition function, we can then write it in the product form that leads to the sum that we want after taking logs

$$\Omega = \left(1 + z e^{-\beta\epsilon_0}\right) \left(1 + z e^{-\beta\epsilon_1}\right) \left(1 + z e^{-\beta\epsilon_2}\right) \cdots = \prod_{\epsilon} \left(1 + z e^{-\beta\epsilon}\right). \tag{7.25}$$

Fermions

$$\sum_{n_k=0}^{1} e^{-\beta(\epsilon_k-\mu)n_k} = 1 + e^{-\beta(\epsilon_k-\mu)}. \tag{7.26}$$

Bosons

$$\sum_{n_k=0}^{\infty} e^{-\beta(\epsilon_k-\mu)n_k} = \frac{1}{1 - e^{-\beta(\epsilon_k-\mu)}}. \tag{7.27}$$

Observe that we require $\epsilon_k - \mu \ge 0$. Our grand partition functions are then

$$\Omega^f = \prod_k \left(1 + e^{-\beta(\epsilon_k-\mu)}\right) \tag{7.28a}$$

$$\Omega^b = \prod_k \frac{1}{1 - e^{-\beta(\epsilon_k-\mu)}}. \tag{7.28b}$$

We can use these to compute the average number of particles

$$\begin{aligned}\left\langle n_k^f \right\rangle &= \frac{1 \times 0 + e^{-\beta(\epsilon_k-\mu)} \times 1}{1 + e^{-\beta(\epsilon_k-\mu)}} \\ &= \frac{e^{-\beta(\epsilon_k-\mu)}}{1 + e^{-\beta(\epsilon_k-\mu)}},\end{aligned} \tag{7.29}$$

or

$$\boxed{\left\langle n_k^f \right\rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)} + 1}} \tag{7.30}$$

For Bosons we have

$$\left\langle n_k^b \right\rangle = \frac{0 \times 1 + e^{-\beta(\epsilon_k-\mu)} \times 1 + e^{-2\beta(\epsilon_k-\mu)} \times 2 + \cdots}{1 + e^{-\beta(\epsilon_k-\mu)} + e^{-2\beta(\epsilon_k-\mu)} + \cdots} \tag{7.31}$$

This chemical potential over temperature exponential

$$e^{\beta\mu} \equiv z, \tag{7.32}$$

is called the fugacity. The denominator has the form

$$D = 1 + z e^{-\beta\epsilon_k} + z^2 e^{-2\beta\epsilon_k} + \cdots, \tag{7.33}$$

so we see that

$$\begin{aligned} z\frac{\partial D}{\partial z} &= ze^{-\beta\epsilon_k} + 2z^2 e^{-2\beta\epsilon_k} + 3z^3 e^{-3\beta\epsilon_k} + \cdots \\ &= e^{-\beta(\epsilon_k-\mu)} + 2e^{-2\beta(\epsilon_k-\mu)} + 3e^{-3\beta(\epsilon_k-\mu)} + \cdots, \end{aligned} \tag{7.34}$$

which is exactly the numerator, or

$$N = z\frac{\partial D}{\partial z}. \tag{7.35}$$

Proceeding

$$\begin{aligned} \left\langle n_k^b \right\rangle &= \frac{z\frac{\partial D_k}{\partial z}}{D_k} \\ &= z\frac{\partial}{\partial z}\ln D_k \\ &= -z\frac{\partial}{\partial z}\ln\left(1 - ze^{-\beta\epsilon_k}\right) \\ &= z\frac{e^{-\beta\epsilon_k}}{1 - ze^{-\beta\epsilon_k}} \\ &= \frac{1}{z^{-1}e^{\beta\epsilon_k} - 1}, \end{aligned} \tag{7.36}$$

or

$$\boxed{\left\langle n_k^b \right\rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)} - 1}.} \tag{7.37}$$

What is the density ρ? For Fermions

$$\begin{aligned} \rho &= \frac{N}{V} \\ &= \frac{1}{V}\sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} + 1}. \end{aligned} \tag{7.38}$$

The simplest such system is the "free particle in a box", with Hamiltonian

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi = \epsilon\Psi. \tag{7.39}$$

For a box with one corner fixed at the origin, and all sides of length L, we have solutions

$$\Psi = \sin\left(\frac{\pi n_x x}{L}\right)\sin\left(\frac{\pi n_y y}{L}\right)\sin\left(\frac{\pi n_z z}{L}\right), \tag{7.40}$$

and an energy quantization given by

$$\frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \epsilon. \tag{7.41}$$

With $\epsilon_{\mathbf{k}} = \hbar^2\mathbf{k}^2/2m$, we have $k_\alpha = \pi n_\alpha/L$, and can make an integral approximation of the sum

$$\begin{aligned}\frac{1}{V}\sum_{\mathbf{k}} f_{\mathbf{k}} &\approx \frac{1}{V}\frac{1}{2^3}\int dn_x dn_y dn_y f_{\mathbf{n}} \\ &= \frac{1}{V}\frac{1}{2^3}\int dk_x dk_y dk_y \left(\frac{L}{\pi}\right)^3 f_{\mathbf{k}} \\ &= \frac{L^3}{V}\int \frac{d^3\mathbf{k}}{(2\pi)^3} f_{\mathbf{k}}.\end{aligned} \tag{7.42}$$

Since $V = L^3$, the leading term cancels out. Generalizing to other (possibly lower) dimensional spaces, our Fermionic density in a d-dimensional space is approximated by

$$\boxed{\rho = \int \frac{d^d k}{(2\pi)^d}\frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} + 1}.} \tag{7.43}$$

This integral is actually difficult to evaluate. However, for $T \rightarrow 0$ ($\beta \rightarrow \infty$), we can evaluate the limit. If $\epsilon_{\mathbf{k}} - \mu(0) < 0$, the exponential term goes as $e^{-1/0}$ which tends to zero, so we have $\left\langle n_k^f \right\rangle = 1$ for $\epsilon_{\mathbf{k}} < \mu(0)$. When $\epsilon_{\mathbf{k}} - \mu(0) > 0$, the exponential term goes as $e^{1/0}$ which tends to infinity, so $\left\langle n_k^f \right\rangle \rightarrow 1$ for $\epsilon_{\mathbf{k}} > \mu(0)$. This can be summarized as

$$\left.\left\langle n_k^f \right\rangle\right|_{T=0} = \Theta(\mu(0) - \epsilon_k). \tag{7.44}$$

This is illustrated in fig. 7.6, where the smearing that occurs with increasing temperature is also indicated. [11] §7 calls ϵ_{F} as defined above the Fermi energy, the energy at which all the lowest order orbitals are exactly filled. Without any limiting assumption, a discussion of why this energy is being equated with the $T = 0$ chemical potential energy can be found in [13] §8.1 (where the exact integral is evaluated, or at least expressed). When that integral approximation of the sum is performed exactly, we see that at $T = 0$, the illustrated cutoff occurs at this $\epsilon_{\mathrm{F}} = \mu(0)$ point.

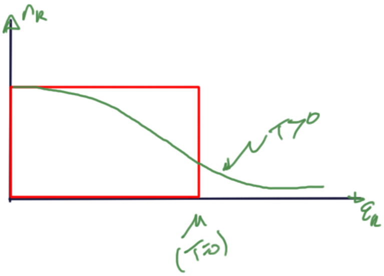


Figure 7.6: Occupation numbers for different energies.

With

$$E_{\mathrm{F}} = \mu(T = 0), \tag{7.45}$$

we want to ask what is the radius of the ball for which

$$\epsilon_k = E_{\mathrm{F}}, \tag{7.46}$$

or

$$E_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}. \tag{7.47}$$

With this definition

$$k_{\mathrm{F}} = \sqrt{\frac{2mE_{\mathrm{F}}}{\hbar^2}}, \tag{7.48}$$

so that our density where $\epsilon_k = \mu$ is

$$\begin{aligned}
\rho &= \int_{k \le k_{\mathrm{F}}} \frac{d^3k}{(2\pi)^3} \times 1 \\
&= \frac{1}{(2\pi)^3} 4\pi \int^{k_{\mathrm{F}}} k^2 dk \\
&= \frac{4\pi}{3} k_{\mathrm{F}}^3 \frac{1}{(2\pi)^3},
\end{aligned} \tag{7.49}$$

so that

$$k_F = (6\pi^2\rho)^{1/3}. \tag{7.50}$$

Our chemical potential at zero temperature is then

$$\mu(T = 0) = \frac{\hbar^2}{2m}(6\pi^2\rho)^{2/3}. \tag{7.51}$$

$$\rho^{-1/3} = \text{interparticle spacing}. \tag{7.52}$$

We can convince ourself that the chemical potential must have the form fig. 7.7.

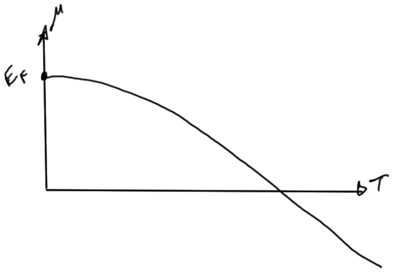


Figure 7.7: Large negative chemical potential at high temperatures.

Given large negative chemical potential at high temperatures our number distribution will have the form

$$\begin{aligned}\langle n_k \rangle &= e^{-\beta(\epsilon_k - \mu)} \\ &\propto e^{-\beta\epsilon_k}.\end{aligned} \tag{7.53}$$

We see that the classical Boltzmann distribution is recovered for high temperatures. We can also calculate the chemical potential at high temperatures. We'll find that this has the form

$$e^{\beta\mu} = \rho\lambda_T^3, \tag{7.54}$$

where this quantity λ_T is called the thermal de Broglie wavelength.

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \tag{7.55}$$

7.3 FERMI GAS THERMODYNAMICS.

Review Continuing a discussion of [13] §8.1 content. We found

$$n_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}. \tag{7.56}$$

With no spin

$$\int n_{\mathbf{k}} \times \frac{d^3k}{(2\pi)^3} = \rho. \tag{7.57}$$

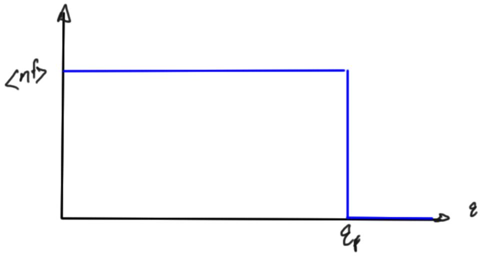


Figure 7.8: Occupancy at low temperature limit.

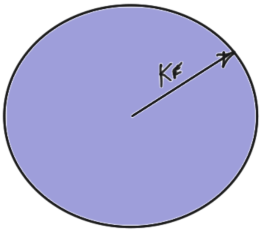


Figure 7.9: Volume integral over momentum up to Fermi energy limit.

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}, \tag{7.58}$$

gives

$$k_{\mathrm{F}} = (6\pi^2 \rho)^{1/3} \tag{7.59}$$

$$\sum_{\mathbf{k}} n_{\mathbf{k}} = N \tag{7.60}$$

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z). \tag{7.61}$$

This is for periodic boundary conditions [1], where

$$\Psi(x + L) = \Psi(x) \tag{7.62}$$

Moving on

$$\sum_{k_x} n(\mathbf{k}) = \sum_{p_x} \Delta p_x n(\mathbf{k}), \tag{7.63}$$

with

$$\Delta k_x = \frac{2\pi}{L} \Delta p_x, \tag{7.64}$$

this gives

$$\begin{aligned} \sum_{k_x} n(\mathbf{k}) &= \sum_{n_x} \frac{L}{2\pi} \Delta k_x \\ &\rightarrow \frac{L}{2\pi} \int dk_x. \end{aligned} \tag{7.65}$$

Over all dimensions

$$\begin{aligned} \sum_{\mathbf{k}} n_{\mathbf{k}} &= \left(\frac{L}{2\pi}\right)^3 \left(\int d^3\mathbf{k}\right) n(\mathbf{k}) \\ &= N, \end{aligned} \tag{7.66}$$

so that

$$\rho = \int \frac{d^3\mathbf{k}}{(2\pi)^3}. \tag{7.67}$$

Again

$$k_{\mathrm{F}} = (6\pi^2 \rho)^{1/3}. \tag{7.68}$$

---

[1] I filled in details in the last lecture using a particle in a box, whereas this periodic condition was intended. We see that both achieve the same result

Example 7.1: Spin considerations

$$\sum_{\mathbf{k},m_s} = N \tag{7.69}$$

$$\sum_{\mathbf{k},m_s} \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = (2S+1)\left(\int \frac{d^3\mathbf{k}}{(2\pi)^3} n(\mathbf{k}) \right) L^3. \tag{7.70}$$

This gives us

$$k_{\mathrm{F}} = \left(\frac{6\pi^2 \rho}{2S+1} \right)^{1/3}, \tag{7.71}$$

and again

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}. \tag{7.72}$$

High Temperatures Now we want to look at the at higher temperature range, where the occupancy may look like fig. 7.10

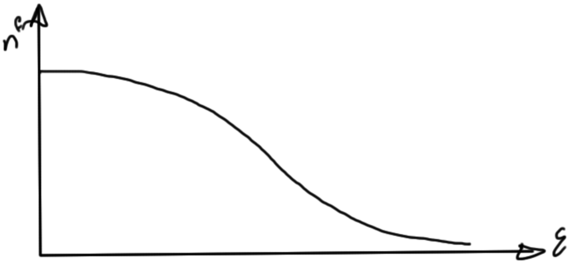


Figure 7.10: Occupancy at higher temperatures.

$$\mu(T=0) = \epsilon_{\mathrm{F}} \tag{7.73}$$

$$\mu(T \rightarrow \infty) \rightarrow -\infty, \tag{7.74}$$

so that for large T we have

$$\frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \rightarrow e^{-\beta(\epsilon_k - \mu)}. \tag{7.75}$$

$$
\begin{aligned}
\rho &= \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{\beta\mu} e^{-\beta\epsilon_k} \\
&= e^{\beta\mu} \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-\beta\epsilon_k} \\
&= e^{\beta\mu} \int dk \frac{4\pi k^2}{(2\pi)^3} e^{-\beta\hbar^2 k^2/2m}.
\end{aligned}
\tag{7.76}
$$

Mathematica (or integration by parts) tells us that

$$
\frac{1}{(2\pi)^3} \int 4\pi^2 k^2 dk e^{-ak^2} = \frac{1}{(4\pi a)^{3/2}},
\tag{7.77}
$$

so we have

$$
\begin{aligned}
\rho &= e^{\beta\mu} \left(\frac{2m}{4\pi\beta\hbar^2} \right)^{3/2} \\
&= e^{\beta\mu} \left(\frac{2mk_\mathrm{B}T4\pi^2}{4\pi h^2} \right)^{3/2} \\
&= e^{\beta\mu} \left(\frac{2mk_\mathrm{B}T\pi}{h^2} \right)^{3/2}.
\end{aligned}
\tag{7.78}
$$

Introducing λ for the thermal de Broglie wavelength, $\lambda^3 \sim T^{-3/2}$

$$
\lambda \equiv \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}},
\tag{7.79}
$$

we have

$$
\rho = e^{\beta\mu} \frac{1}{\lambda^3}.
\tag{7.80}
$$

Does it make any sense to have density as a function of temperature? An inappropriately extended to low temperatures plot of the density is found in fig. 7.11 for a few arbitrarily chosen numerical values of the chemical potential μ, where we see that it drops to zero with temperature. I suppose that makes sense if we are not holding volume constant.

We can write

$$
\boxed{e^{\beta\mu} = \left(\rho\lambda^3\right)}
\tag{7.81}
$$

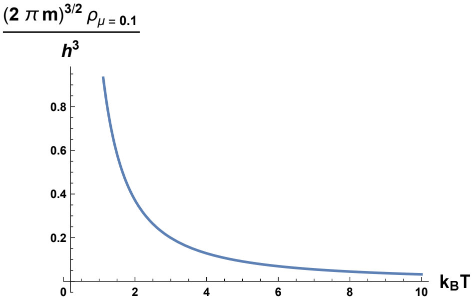


Figure 7.11: Density as a function of temperature.

$$\begin{aligned}\frac{\mu}{k_B T} &= \ln\left(\rho\lambda^3\right) \\ &\sim -\frac{3}{2}\ln T,\end{aligned} \tag{7.82}$$

or (taking ρ (and/or volume?) as a constant) we have for large temperatures

$$\mu \propto -T\ln T. \tag{7.83}$$

The chemical potential is plotted in fig. 7.12, whereas this $-k_B T \ln k_B T$ function is plotted in fig. 7.13. The contributions to μ from the $k_B T \ln(\rho h^3(2\pi m)^{-3/2})$ term are dropped for the high temperature approximation.

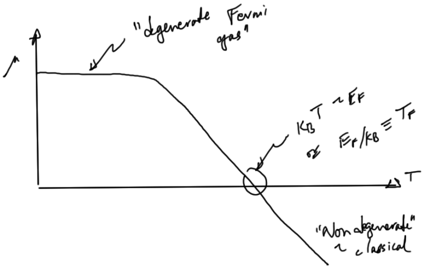


Figure 7.12: Chemical potential over degenerate to classical range.

Pressure

$$P = -\frac{\partial E}{\partial V}. \tag{7.84}$$

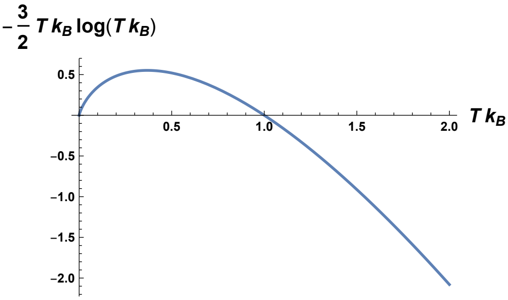


Figure 7.13: High temp approximation of chemical potential, extended back to $T = 0$.

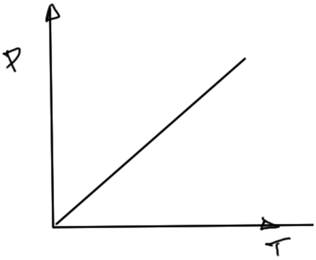


Figure 7.14: Ideal gas pressure vs volume.

For a classical ideal gas as in fig. 7.14 we have

$$P = \rho k_{\mathrm{B}} T. \tag{7.85}$$

For a Fermi gas at $T = 0$ using the low temperature approximation eq. (7.44) we have

$$\begin{aligned}
E &= \sum_{\mathbf{k}} \epsilon_k n_k \\
&= \sum_{\mathbf{k}} \epsilon_k \Theta(\mu_0 - \epsilon_k) \\
&= \frac{V}{(2\pi)^3} \int_{\epsilon_k < \mu_0} \frac{\hbar^2 \mathbf{k}^2}{2m} d^3\mathbf{k} \\
&= \frac{V}{(2\pi)^3} \int_0^{k_{\mathrm{F}}} \frac{\hbar^2 \mathbf{k}^2}{2m} d^3\mathbf{k} \\
&= \frac{V}{(2\pi)^3} \frac{\hbar^2}{2m} \int_0^{k_{\mathrm{F}}} k^2 4\pi k^2 dk \\
&\propto k_{\mathrm{F}}^5.
\end{aligned} \tag{7.86}$$

Specifically,

$$E(T=0) = V \times \frac{3}{5} \overset{\sim k_{\mathrm{F}}^2}{\boxed{\epsilon_{\mathrm{F}}}} \underset{\sim k_{\mathrm{F}}^3}{\boxed{\rho}}, \tag{7.87}$$

or

$$\frac{E}{N} = \frac{3}{5} \epsilon_{\mathrm{F}} \tag{7.88}$$

$$\begin{aligned}
E &= \frac{3}{5} N \frac{\hbar^2}{2m} \left(6\pi^2 \frac{N}{V} \right)^{2/3} \\
&= a V^{-2/3},
\end{aligned} \tag{7.89}$$

so that

$$\frac{\partial E}{\partial V} = -\frac{2}{3} a V^{-5/3}. \tag{7.90}$$

$$\begin{aligned}
P &= -\frac{\partial E}{\partial V} \\
&= \frac{2}{3}\left(aV^{-2/3}\right)V^{-1} \\
&= \frac{2}{3}\frac{E}{V} \\
&= \frac{2}{3}\left(\frac{3}{5}\epsilon_{\mathrm{F}}\rho\right) \\
&= \frac{2}{5}\epsilon_{\mathrm{F}}\rho.
\end{aligned} \tag{7.91}$$

We see that the pressure ends up deviating from the classical result at low temperatures, as sketched in fig. 7.15. This low temperature limit for the pressure $2\epsilon_{\mathrm{F}}\rho/5$ is called the degeneracy pressure.

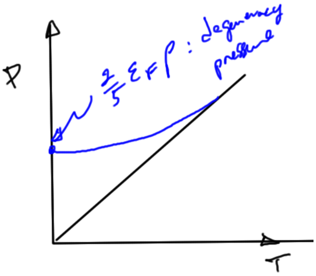


Figure 7.15: Fermi degeneracy pressure.

Review

1. Energy was found to be

$$\frac{E}{N} = \frac{3}{5}\epsilon_{\mathrm{F}} \qquad \text{where } T = 0. \tag{7.92}$$

2. Pressure was found to have the form fig. 7.16

3. The chemical potential was found to have the form fig. 7.17.

   We found that

$$e^{\beta\mu} = \rho\lambda_{\mathrm{T}}^3 \tag{7.93a}$$

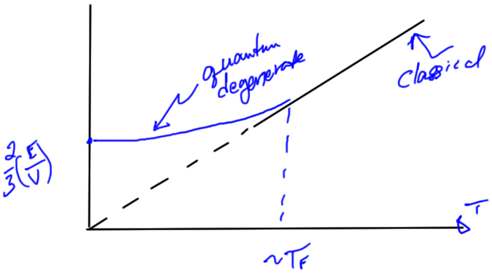


Figure 7.16: Pressure in Fermi gas.

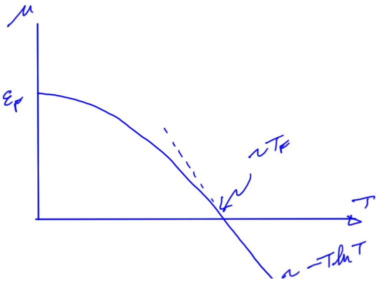


Figure 7.17: Chemical potential in Fermi gas.

$$\lambda_{\mathrm{T}} = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}, \tag{7.93b}$$

so that the zero crossing is approximately when

$$\begin{aligned} e^{\beta \times 0} &= 1 \\ &= \rho \lambda_{\mathrm{T}}^3. \end{aligned} \tag{7.94}$$

That last identification provides the relation $T \sim T_{\mathrm{F}}$. FIXME: that bit wasn't clear to me.

How about at other temperatures?

1. $\mu(T) =?$
2. $E(T) =?$
3. $C_{\mathrm{V}}(T) =?$

We had

$$\begin{aligned} N &= \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \\ &= \sum_{\mathbf{k}} n_{\mathrm{F}}(\epsilon_{\mathbf{k}}), \end{aligned} \tag{7.95}$$

and taking the average of eq. (7.14) we have

$$E(T) = \sum_k \epsilon_{\mathbf{k}} n_{\mathrm{F}}(\epsilon_{\mathbf{k}}). \tag{7.96}$$

We can define a density of states

$$\begin{aligned} \sum_{\mathbf{k}} &= \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\epsilon \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \int_{-\infty}^{\infty} d\epsilon \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}), \end{aligned} \tag{7.97}$$

where the liberty to informally switch the order of differentiation and integration has been used. This construction allows us to write a more general sum

$$\begin{aligned} \sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}}) &= \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\epsilon \delta(\epsilon - \epsilon_{\mathbf{k}}) f(\epsilon) \\ &= \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\epsilon \delta(\epsilon - \epsilon_{\mathbf{k}}) f(\epsilon) \\ &= \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \left(\sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \right). \end{aligned} \tag{7.98}$$

This sum, evaluated using a continuum approximation, is

$$\begin{aligned} N(\epsilon) &\equiv \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{V}{(2\pi)^3} \int d^3\mathbf{k} \delta \left(\epsilon - \frac{\hbar^2 k^2}{2m} \right) \\ &= \frac{V}{(2\pi)^3} 4\pi \int_0^{\infty} k^2 dk \delta \left(\epsilon - \frac{\hbar^2 k^2}{2m} \right). \end{aligned} \tag{7.99}$$

Using

$$\delta(g(x)) = \sum_{x_0} \frac{\delta(x - x_0)}{|g'(x_0)|}, \tag{7.100}$$

where the roots of $g(x)$ are x_0, we have

$$\begin{aligned} N(\epsilon) &= \frac{V}{(2\pi)^3} 4\pi \int_0^\infty k^2 dk \delta\left(k - \frac{\sqrt{2m\epsilon}}{\hbar}\right) \frac{1}{\frac{\hbar^2}{m}\frac{\sqrt{2m\epsilon}}{\hbar}} \\ &= \frac{V}{(2\pi)^3} 2\pi \frac{2m\epsilon}{\hbar^2} \frac{2m\hbar}{\hbar^2\sqrt{2m\epsilon}} \\ &= V\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2}\sqrt{\epsilon}. \end{aligned} \tag{7.101}$$

In 2D this would be

$$\begin{aligned} N(\epsilon) &\sim V \int dk k \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right) \\ &= V \frac{\sqrt{2m\epsilon}}{\hbar} \frac{m\hbar}{\hbar^2\sqrt{2m\epsilon}} \\ &\sim V, \end{aligned} \tag{7.102}$$

and in 1D

$$\begin{aligned} N(\epsilon) &\sim V \int dk \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right) \\ &= V \frac{m\hbar}{\hbar^2\sqrt{2m\epsilon}} \\ &\sim \frac{1}{\sqrt{\epsilon}}. \end{aligned} \tag{7.103}$$

Low temperature density and chemical potential

$$N = V \int_0^\infty \overset{1/(e^{\beta(\epsilon-\mu)}+1)}{\boxed{n_{\mathrm{F}}(\epsilon)}} \underset{\epsilon^{1/2}}{\boxed{N(\epsilon)}} \tag{7.104}$$

$$\begin{aligned}\rho &= \frac{N}{V} \\ &= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2} \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon}+1} \\ &= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2} (k_B T)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^{x}+1},\end{aligned} \tag{7.105}$$

where $z = e^{\beta\mu}$ as usual, and we write $x = \beta\epsilon$. For the low temperature asymptotic behavior see [13] appendix §E.15, as derived in the homework eq. (7.273). For z large it can be shown that this is

$$\int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^{x}+1} \approx \frac{2}{3} (\ln z)^{3/2} \left(1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2}\right), \tag{7.106}$$

so that

$$\begin{aligned}\rho &\approx \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2} (k_B T)^{3/2} \frac{2}{3} (\ln z)^{3/2} \left(1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2}\right) \\ &= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2} \frac{2}{3} \mu^{3/2} \left(1 + \frac{\pi^2}{8} \frac{1}{(\beta\mu)^2}\right) \\ &= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2} \frac{2}{3} \mu^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2\right) \\ &= \rho_{T=0} \left(\frac{\mu}{\epsilon_F}\right)^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2\right).\end{aligned} \tag{7.107}$$

Assuming a quadratic form for the chemical potential at low temperature as in fig. 7.18, we have

$$\begin{aligned}1 &= \left(\frac{\mu}{\epsilon_F}\right)^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2\right) \\ &= \left(\frac{\epsilon_F - aT^2}{\epsilon_F}\right)^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\epsilon_F - aT^2}\right)^2\right) \\ &\approx \left(1 - \frac{3}{2} a \frac{T^2}{\epsilon_F}\right) \left(1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\epsilon_F^2}\right) \\ &\approx 1 - \frac{3}{2} a \frac{T^2}{\epsilon_F} + \frac{\pi^2}{8} \frac{(k_B T)^2}{\epsilon_F^2},\end{aligned} \tag{7.108}$$

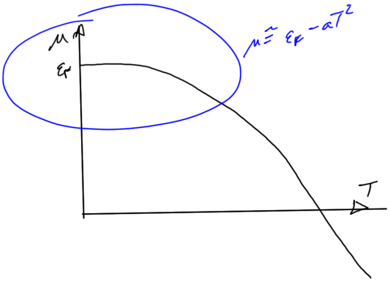


Figure 7.18: Assumed quadratic form for low temperature chemical potential.

or

$$a = \frac{\pi^2}{12}\frac{k_B^2}{\epsilon_F}, \tag{7.109}$$

We have used a Taylor expansion $(1 + x)^n \approx 1 + nx$ for small x, for an end result of

$$\mu = \epsilon_F - \frac{\pi^2}{12}\frac{(k_B T)^2}{\epsilon_F}. \tag{7.110}$$

Review Last time we found that the low temperature behavior or the chemical potential was quadratic as in fig. 7.19.

$$\mu = \mu(0) - a\frac{T^2}{T_F}. \tag{7.111}$$

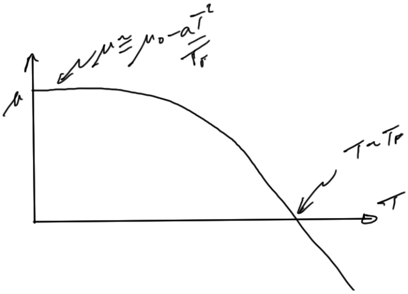


Figure 7.19: Fermi gas chemical potential.

Specific heat

$$E = \sum_{\mathbf{k}} n_{\mathrm{F}}(\epsilon_{\mathbf{k}}, T)\epsilon_{\mathbf{k}} \tag{7.112}$$

$$\begin{aligned} \frac{E}{V} &= \frac{1}{(2\pi)^3} \int d^3\mathbf{k} n_{\mathrm{F}}(\epsilon_{\mathbf{k}}, T)\epsilon_{\mathbf{k}} \\ &= \int d\epsilon N(\epsilon) n_{\mathrm{F}}(\epsilon, T)\epsilon, \end{aligned} \tag{7.113}$$

where

$$N(\epsilon) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon}. \tag{7.114}$$

Low temperature C_{V}

$$\frac{\Delta E(T)}{V} = \int_0^\infty d\epsilon N(\epsilon)\left(n_{\mathrm{F}}(\epsilon, T) - n_{\mathrm{F}}(\epsilon, 0)\right) \tag{7.115}$$

The only change in the distribution fig. 7.20, that is of interest is over the step portion of the distribution, and over this range of interest $N(\epsilon)$ is approximately constant as in fig. 7.21.

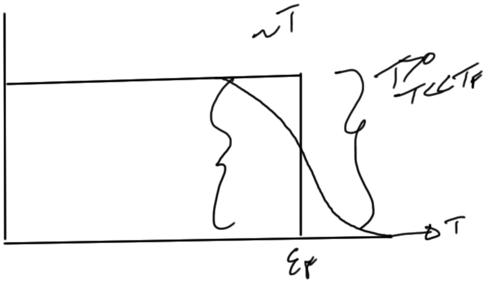


Figure 7.20: Fermi distribution.

$$N(\epsilon) \approx N(\mu) \tag{7.116a}$$

$$\mu \approx \epsilon_{\mathrm{F}}, \tag{7.116b}$$

so that

$$\begin{aligned} \Delta e &\equiv \frac{\Delta E(T)}{V} \\ &\approx N(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \left(n_{\mathrm{F}}(\epsilon, T) - n_{\mathrm{F}}(\epsilon, 0)\right) \\ &= N(\epsilon_{\mathrm{F}}) \int_{-\epsilon_{\mathrm{F}}}^\infty dx(\epsilon_{\mathrm{F}} + x)\left(n_{\mathrm{F}}(\epsilon + x, T) - n_{\mathrm{F}}(\epsilon_{\mathrm{F}} + x, 0)\right). \end{aligned} \tag{7.117}$$

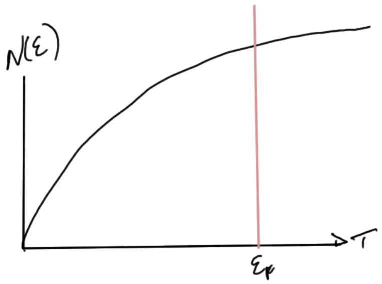


Figure 7.21: Fermi gas density of states.

Here we've made a change of variables $\epsilon = \epsilon_{\mathrm{F}} + x$, so that we have near cancellation of the ϵ_{F} factor

$$\begin{aligned}\Delta e &= N(\epsilon_{\mathrm{F}})\epsilon_{\mathrm{F}} \int_{-\epsilon_{\mathrm{F}}}^{\infty} dx \overset{\text{almost equal everywhere}}{\boxed{\left(n_{\mathrm{F}}(\epsilon + x, T) - n_{\mathrm{F}}(\epsilon_{\mathrm{F}} + x, 0)\right)}} \\ &\quad + N(\epsilon_{\mathrm{F}}) \int_{-\epsilon_{\mathrm{F}}}^{\infty} dx x \left(n_{\mathrm{F}}(\epsilon + x, T) - n_{\mathrm{F}}(\epsilon_{\mathrm{F}} + x, 0)\right) \\ &\approx N(\epsilon_{\mathrm{F}}) \int_{-\infty}^{\infty} dx x \left(\frac{1}{e^{\beta x} + 1} - \left.\frac{1}{e^{\beta x} + 1}\right|_{T \rightarrow 0} \right).\end{aligned} \tag{7.118}$$

Here we've extended the integration range to $-\infty$ since this doesn't change much. FIXME: justify this to myself? Taking derivatives with respect to temperature we have

$$\begin{aligned}\frac{\delta e}{T} &= -N(\epsilon_{\mathrm{F}}) \int_{-\infty}^{\infty} dx x \frac{1}{(e^{\beta x} + 1)^2} \frac{d}{dT} e^{\beta x} \\ &= N(\epsilon_{\mathrm{F}}) \int_{-\infty}^{\infty} dx x \frac{1}{(e^{\beta x} + 1)^2} e^{\beta x} \frac{x}{k_{\mathrm{B}} T^2}.\end{aligned} \tag{7.119}$$

With $\beta x = y$, we have for $T \ll T_{\mathrm{F}}$

$$\begin{aligned}\frac{C}{V} &= N(\epsilon_{\mathrm{F}}) \int_{-\infty}^{\infty} \frac{dy y^2 e^y}{(e^y + 1)^2 k_{\mathrm{B}} T^2} (k_{\mathrm{B}} T)^3 \\ &= N(\epsilon_{\mathrm{F}}) k_{\mathrm{B}}^2 T \overset{\pi^2/3}{\boxed{\int_{-\infty}^{\infty} \frac{dy y^2 e^y}{(e^y + 1)^2}}} \\ &= \frac{\pi^2}{3} N(\epsilon_{\mathrm{F}}) k_{\mathrm{B}} (k_{\mathrm{B}} T).\end{aligned} \tag{7.120}$$

Using eq. (7.114) at the Fermi energy and

$$\frac{N}{V} = \rho \tag{7.121a}$$

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m} \tag{7.121b}$$

$$k_{\mathrm{F}} = \left(6\pi^2\rho\right)^{1/3}, \tag{7.121c}$$

we have

$$\begin{aligned}
N(\epsilon_{\mathrm{F}}) &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon_{\mathrm{F}}} \\
&= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\hbar k_{\mathrm{F}}}{\sqrt{2m}} \\
&= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\hbar}{\sqrt{2m}}\left(6\pi^2\rho\right)^{1/3} \\
&= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)\left(6\pi^2\frac{N}{V}\right)^{1/3}.
\end{aligned} \tag{7.122}$$

Giving

$$\begin{aligned}
\frac{C}{N} &= \frac{\pi^2}{3}\frac{V}{N}\frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)\left(6\pi^2\frac{N}{V}\right)^{1/3} k_{\mathrm{B}}(k_{\mathrm{B}}T) \\
&= \left(\frac{m}{6\hbar^2}\right)\left(\frac{V}{N}\right)^{2/3}\left(6\pi^2\right)^{1/3} k_{\mathrm{B}}(k_{\mathrm{B}}T) \\
&= \left(\frac{\pi^2 m}{3\hbar^2}\right)\left(\frac{V}{\pi^2 N}\right)^{2/3} k_{\mathrm{B}}(k_{\mathrm{B}}T) \\
&= \left(\frac{\pi^2 m}{\hbar^2}\right)\frac{\hbar^2}{2m\epsilon_{\mathrm{F}}} k_{\mathrm{B}}(k_{\mathrm{B}}T),
\end{aligned} \tag{7.123}$$

or

$$\boxed{\frac{C}{N} = \frac{\pi^2}{2} k_{\mathrm{B}} \frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}.} \tag{7.124}$$

This is illustrated in fig. 7.22. Note that [13] outlines this derivation in the tail end of §8.1, and you can look there to see the high level view without any of the details above obscuring things.

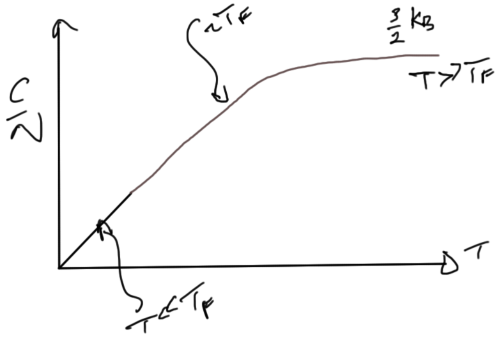


Figure 7.22: Specific heat per Fermion.

7.4 BOSONS.

Linear energy momentum relationships Suppose that we have a linear energy momentum relationship like

$$\epsilon_{\mathbf{k}} = v|\mathbf{k}|. \tag{7.125}$$

An example of such a relationship is the high velocity relation between the energy and momentum of a particle

$$\begin{aligned}\epsilon_{\mathbf{k}} &= \sqrt{m_0^2 c^4 + p^2 c^2} \\ &\sim |\mathbf{p}|c.\end{aligned} \tag{7.126}$$

Another example is graphene, a carbon structure of the form fig. 7.23. The energy and momentum for such a structure is related in roughly as shown in fig. 7.24, where

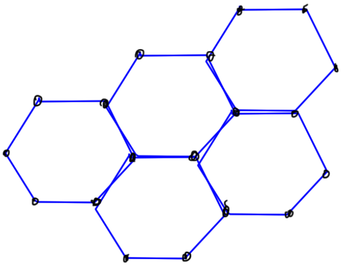


Figure 7.23: Graphene bond structure.

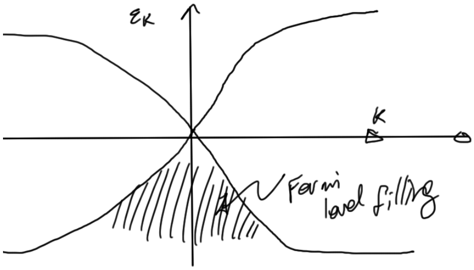


Figure 7.24: Graphene energy momentum dependence.

$$\epsilon_{\mathbf{k}} = \pm v_{\mathrm{F}} |\mathbf{k}|. \tag{7.127}$$

Some examples of linear energy momentum materials are

- Relativistic gas

$$\epsilon_{\mathbf{k}} = \pm \hbar v |\mathbf{k}|. \tag{7.128}$$

$$\epsilon = \sqrt{(m_0 c^2)^2 + c^2 (\hbar \mathbf{k})^2}. \tag{7.129}$$

- graphene
- massless Dirac Fermion

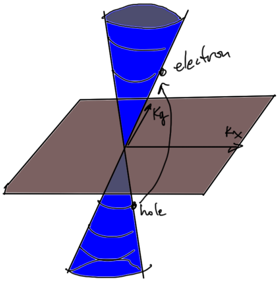


Figure 7.25: Relativistic gas energy distribution.

We can think of this state distribution in a condensed matter view, where we can have a hole to electron state transition by supplying energy to the system (i.e. shining light on the substrate). This can also be thought of in a relativistic particle view where the same state transition can be thought of as a positron electron pair transition. A round trip transition will have to supply energy like $2 m_0 c^2$ as illustrated in fig. 7.26.

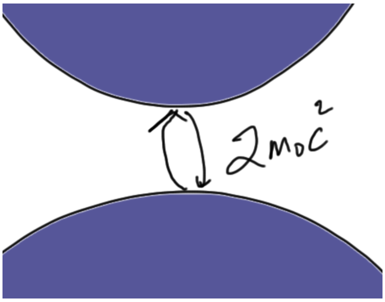


Figure 7.26: Hole to electron round trip transition energy requirement.

Graphene Consider graphene, a 2D system. We want to determine the density of states $N(\epsilon)$,

$$\int \frac{d^2\mathbf{k}}{(2\pi)^2} \rightarrow \int_{-\infty}^{\infty} d\epsilon N(\epsilon), \tag{7.130}$$

We'll find a density of states distribution like fig. 7.27.

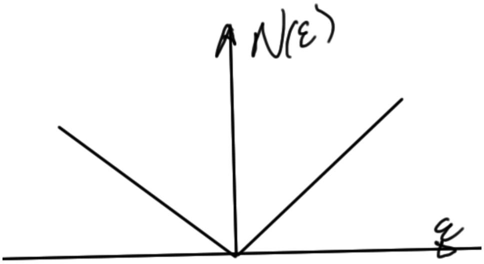


Figure 7.27: Density of states for 2D linear energy momentum distribution.

$$N(\epsilon) = \text{constant factor} \frac{|\epsilon|}{v}, \tag{7.131}$$

$$C \sim \frac{d}{dT} \int N(\epsilon) n_{\mathrm{F}}(\epsilon) \epsilon d\epsilon, \tag{7.132}$$

$$\begin{aligned}\Delta E &\sim \overset{\text{window}}{\boxed{T}} \times \underset{\text{energy}}{\boxed{T}} \times \overset{\text{number of states}}{\boxed{T}} \\ &\sim T^3,\end{aligned} \tag{7.133}$$

so that

$$C_{\text{Dimensionless}} \sim T^2. \tag{7.134}$$

Summary of our Fermion approach We've considered a momentum sphere as in fig. 7.28, and performed various appromations of the occupation sums fig. 7.29.

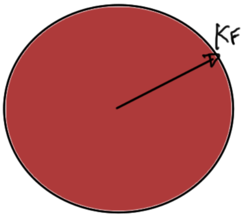


Figure 7.28: Summation over momentum sphere.

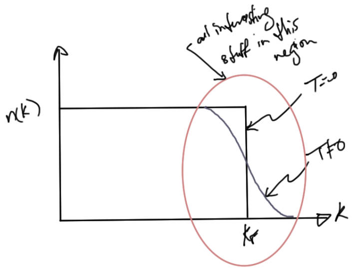


Figure 7.29: Fermion occupation.

$$\epsilon \sim T^2 \tag{7.135a}$$

$$C \sim T \tag{7.135b}$$

$$P \sim \text{constant}. \tag{7.135c}$$

The physics of Fermi gases has an extremely wide range of applicability. Illustrating some of this range, here are some examples of Fermi temperatures (from $E_{\mathrm{F}} = k_{\mathrm{B}} T_{\mathrm{F}}$)

- Electrons in copper: $T_{\mathrm{F}} \sim 10^4 \mathrm{K}$
- Neutrons in neutron star: $T_{\mathrm{F}} \sim 10^7 - 10^8 \mathrm{K}$
- Ultracold atomic gases: $T_{\mathrm{F}} \sim (10 - 100) \mathrm{n}\ \mathrm{K}$

Moving on to Bosons We'd like to work with a fixed number of particles, but the calculations are hard, so we move to the grand canonical ensemble

$$n_{\mathrm{B}}(\mathbf{k}) = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1}. \tag{7.136}$$

Again, we'll consider free particles with energy as in fig. 7.30, or

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}. \tag{7.137}$$

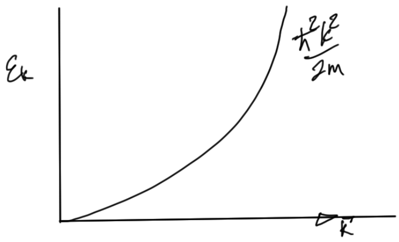


Figure 7.30: Free particle energy momentum distribution.

Again introducing fugacity $z = e^{\beta\mu}$, we have

$$n_{\mathrm{B}}(\mathbf{k}) = \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1}. \tag{7.138}$$

We'll consider systems for which

$$
\begin{aligned}
N &= \sum_{\mathbf{k}} n_{\mathrm{B}}(\mathbf{k}) \\
&= \text{fixed}.
\end{aligned}
\tag{7.139}
$$

Observe that at large energies we have

$$
n_{\mathrm{B}}(\text{large}\,\mathbf{k}) \sim z e^{-\beta \epsilon_{\mathbf{k}}}. \tag{7.140}
$$

For small energies

$$
\begin{aligned}
n_{\mathrm{B}}(\mathbf{k} \rightarrow 0) \sim \frac{1}{z^{-1} - 1} \\
= \frac{z}{1 - z}.
\end{aligned}
\tag{7.141}
$$

Observe that we require $z < 1$ (or $\mu < 0$) so that the number distribution is strictly positive for all energies. This tells us that the fugacity is a function of temperature, but there will be a point at which it must saturate. This is illustrated in fig. 7.31.

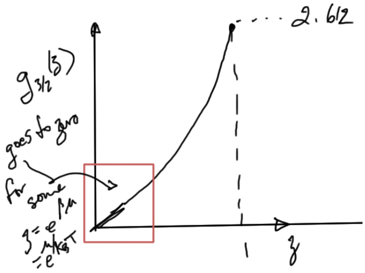


Figure 7.31: Density times cubed thermal de Broglie wavelength.

Let's calculate this density (assumed fixed for all temperatures)

$$
\begin{aligned}
\rho &= \frac{N}{V} \\
&= \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1} \\
&= \frac{2}{(2\pi)^2} \int_0^\infty k^2 dk \frac{1}{z^{-1} e^{\beta \hbar^2 k^2/2m} - 1} \\
&= \frac{2}{(2\pi)^2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^\infty \left(\frac{\beta \hbar^2}{2m} \right)^{3/2} k^2 dk \frac{1}{z^{-1} e^{\beta \hbar^2 k^2/2m} - 1}.
\end{aligned}
\tag{7.142}
$$

With the substitution

$$x^2 = \beta\frac{\hbar^2 k^2}{2m}, \tag{7.143}$$

we find

$$\begin{aligned}\rho\lambda^3 &= \frac{2}{(2\pi)^2}\left(\frac{2\cancel{m}}{\cancel{\beta\hbar^2}}\right)^{3/2}\left(\frac{2\pi\cancel{\hbar^2\beta}}{\cancel{m}}\right)^{3/2}\int_0^\infty x^2 dx\frac{1}{z^{-1}e^{x^2}-1} \\ &= \frac{4}{\sqrt{\pi}}\int_0^\infty dx\frac{x^2}{z^{-1}e^{x^2}-1} \\ &\equiv g_{3/2}(z).\end{aligned} \tag{7.144}$$

An exact plot of this is shown in fig. 7.32.

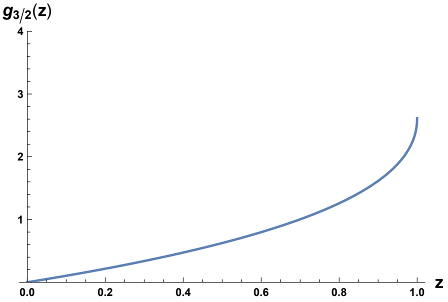


Figure 7.32: $g_{3/2}(z)$.

This implicitly defines a relationship for the fugacity as a function of temperature $z = z(T)$. It can be shown that

$$g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots \tag{7.145}$$

As $z \rightarrow 1$ we end up with a zeta function, for which we can look up the value

$$g_{3/2}(z \rightarrow 1) = \sum_{n=1}^{\infty}\frac{1}{n^{3/2}} = \zeta(3/2) \approx 2.612, \tag{7.146}$$

where the Riemann zeta function is defined as

$$\zeta(s) = \sum_{n=1}\frac{1}{n^s}. \tag{7.147}$$

$$g_{3/2}(z) = \rho\lambda^3. \tag{7.148}$$

At high temperatures we have

$$\rho\lambda^3 \rightarrow 0, \tag{7.149}$$

(as T does down, $\rho\lambda^3$ goes up) Looking at $g_{3/2}(z = 1) = \rho\lambda^3(T_c)$ leads to

$$\boxed{k_B T_c = \left(\frac{\rho}{\zeta(3/2)}\right)^{2/3} \frac{2\pi\hbar^2}{m}.} \tag{7.150}$$

How do I satisfy number conservation? We have a problem here since as $T \rightarrow 0$ the $1/\lambda^3 \sim T^{3/2}$ term in ρ above drops to zero, yet $g_{3/2}(z)$ cannot keep increasing without bounds to compensate and keep the density fixed. The way to deal with this was worked out by

- Bose (1924) for photons (examining statistics for symmetric wave functions).
- Einstein (1925) for conserved particles.

To deal with this issue, we (somewhat arbitrarily, because we need to) introduce a non-zero density for $\mathbf{k} = 0$. This is an adjustment of the approximation so that we have

$$\sum_{\mathbf{k}} \rightarrow \int \frac{d^3\mathbf{k}}{(2\pi)^3} \qquad \text{Except around } \mathbf{k} = 0, \tag{7.151}$$

as in fig. 7.33, so that

$$\sum_{\mathbf{k}} = (\text{Contribution at } \mathbf{k} = 0) + V \int \frac{d^3\mathbf{k}}{(2\pi)^3}. \tag{7.152}$$

Given this, we have

$$N = N_{\mathbf{k}=0} + V \int \frac{d^3\mathbf{k}}{(2\pi)^3} n_B(\mathbf{k}). \tag{7.153}$$

We can illustrate this as in fig. 7.34.

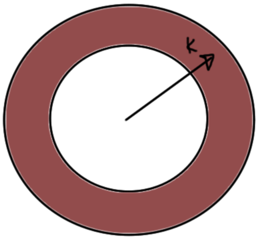


Figure 7.33: Momentum sphere with origin omitted.

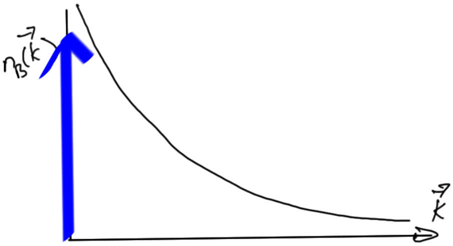


Figure 7.34: Boson occupation vs momentum.

$$\begin{aligned}\rho &= \rho_{\mathbf{k}=0} + \frac{1}{\lambda^3} g_{3/2}(z) \\ &= \rho_{\mathbf{k}=0} + \frac{\lambda(T_c)}{\lambda(T)} \frac{1}{\lambda^3(T_c)} g_{3/2}(z).\end{aligned} \tag{7.154}$$

At $T > T_c$ we have $\rho_{\mathbf{k}=0}$, whereas at $T < T_c$ we must introduce a non-zero density if we want to be able to keep a constant density constraint.

Bose condensate In order to maintain a conservation of particles in a Bose condensate as we decrease temperature, we are forced to change the chemical potential to compensate. This is illustrated in fig. 7.35.

Bose condensation occurs for $T < T_{\text{BEC}}$. At this point our number density becomes (except at $\mathbf{k} = 0$)

$$n(\mathbf{k}) = \frac{1}{e^{\beta \epsilon_{\mathbf{k}}} - 1}. \tag{7.155}$$

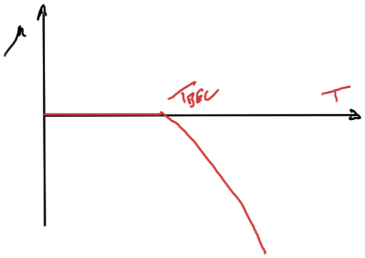


Figure 7.35: Chemical potential in Bose condensation region.

Except for $\mathbf{k} = 0$, $n(\mathbf{k})$ is well defined, and not described by this distribution. We are forced to say that

$$\begin{aligned} N &= N_0 + \sum_{\mathbf{k} \neq 0} n(\mathbf{k}) \\ &= N_0 + V \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{1}{e^{\beta\epsilon_\mathbf{k}} - 1}. \end{aligned} \tag{7.156}$$

Introducing the density of states, our density is

$$\rho = \rho_0 + \int_0^\infty d\epsilon \frac{N(\epsilon)}{e^{\beta\epsilon} - 1}, \tag{7.157}$$

where

$$N(\epsilon) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar} \right)^{3/2} \epsilon^{1/2}. \tag{7.158}$$

We worked out last time that

$$\rho = \rho_0 + \rho \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2}, \tag{7.159}$$

or

$$\rho_0 = \rho \left(1 - \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} \right). \tag{7.160}$$

This is plotted in fig. 7.36.

$$\rho_0 = \frac{N_{\mathbf{k}=0}}{V}. \tag{7.161}$$

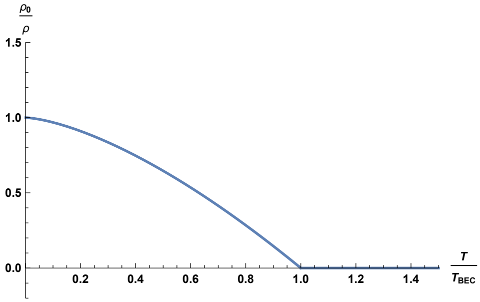


Figure 7.36: Boson density variation with temperature.

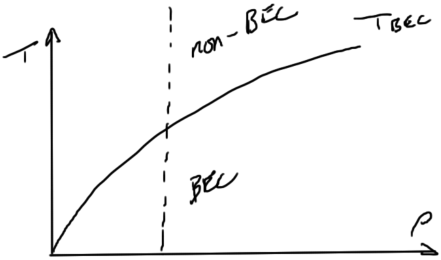


Figure 7.37: Temperature vs pressure demarcation by T_{BEC} curve.

For $T \geq T_{\text{BEC}}$, we have $\rho_0 = 0$. This condensation temperature is

$$T_{\text{BEC}} \propto \rho^{2/3}. \tag{7.162}$$

This is plotted in fig. 7.37.

There is a line for each density that marks the boundary temperature for which we have or do not have this condensation phenomena where $\mathbf{k} = 0$ states start filling up.

Specific heat: $T < T_{\text{BEC}}$

$$\begin{aligned}
\frac{E}{V} &= \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{1}{e^{\beta \hbar^2 k^2/2m} - 1} \frac{\hbar^2 k^2}{2m} \\
&= \int_0^\infty d\epsilon N(\epsilon) \frac{1}{e^{\beta\epsilon} - 1} \epsilon \\
&\propto \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta\epsilon} - 1} \\
&\propto (k_B T)^{5/2},
\end{aligned} \tag{7.163}$$

so that

$$\frac{C}{V} \propto (k_{\mathrm{B}} T)^{3/2} . \tag{7.164}$$

Compare this to the classical and Fermionic specific heat as plotted in fig. 7.38.

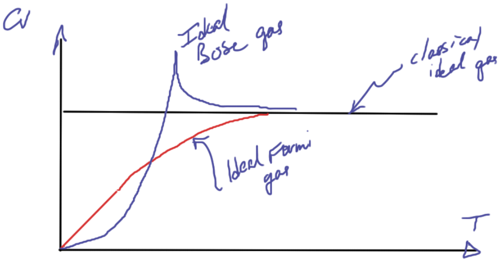


Figure 7.38: Specific heat for Bosons, Fermions, and classical ideal gases.

One can measure the specific heat in this Bose condensation phenomena for materials such as Helium-4 (spin 0). However, it turns out that Helium-4 is actually quite far from an ideal Bose gas.

Photon gas A system that is much closer to an ideal Bose gas is that of a gas of photons. To a large extent, photons do not interact with each other. This allows us to calculate black body phenomena and the low temperature (cosmic) background radiation in the universe.

An important distinction between a photon sea and some of these other systems is that the photon number is actually not fixed.

Photon numbers are not "conserved".

If a photon interacts with an atom, it can impart energy and disappear. An excited atom can emit a photon and change its energy level. In a thermodynamic system we can generally expect that introducing heat will generate more photons, whereas a cold sink will tend to generate fewer photons.

We have a few special details that distinguish photons that we'll have to consider.

- spin 1.

- massless, moving at the speed of light.
- have two polarization states.

Because we do not have a constraint on the number of particles, we essentially have no chemical potential, even in the grand canonical scheme.

Writing

$$\lambda = \begin{cases} +1 & \text{Right circular polarization} \\ -1 & \text{Left circular polarization} \end{cases} \tag{7.165}$$

Our number density, since we have no chemical potential, is of the form

$$n_{\mathbf{k},\lambda} = \frac{1}{e^{\beta\epsilon_{\mathbf{k},\lambda}} - 1}, \tag{7.166}$$

Observe that the average number of photons in this system is temperature dependent. Because this chemical potential is not there, it can be quite easy to work out a number of the thermodynamic results.

Photon average energy density We'll now calculate the average energy density of the photons. The energy of a single photon is

$$\epsilon_{\mathbf{k},\lambda} = \hbar c k = \hbar\omega, \tag{7.167}$$

so that the average energy density is

$$\frac{E}{V} = \sum_{\mathbf{k},\lambda} \frac{1}{e^{\beta\epsilon_{\mathbf{k}}} - 1}\epsilon_{\mathbf{k}}$$

number of polarizations

$$\to \boxed{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{\hbar c k}{e^{\beta\epsilon_{\mathbf{k}}} - 1} \tag{7.168}$$

Photon density of states eq. (H.11)

$$\begin{aligned} &= 2 \int_0^\infty d\epsilon \boxed{\frac{1}{(2\pi)^3} 4\pi \frac{\epsilon^2}{(\hbar c)^3}} \frac{\epsilon}{e^{\beta\epsilon} - 1} \\ &= \frac{1}{\pi^2} \frac{1}{(\hbar c)^3} \int_0^\infty d\epsilon \frac{\epsilon^3}{e^{\beta\epsilon} - 1}. \end{aligned}$$

This integral is calculated in lecture20PlotAndIntegral.nb , with the result

$$\int_0^\infty d\epsilon \frac{\epsilon^3}{e^{\beta\epsilon} - 1} = \frac{\pi^4}{15\beta^4}, \tag{7.169}$$

for an end result of

$$\frac{E}{V} = \frac{\pi^2}{15} \frac{1}{(\hbar c)^3} \left(k_\mathrm{B} T\right)^4, \tag{7.170}$$

from which we see that the specific heat of a 3D Bose system is of the form

$$C_\mathrm{V} \propto T^3. \tag{7.171}$$

7.5 PHONON MODES.

We have phenomena in matter that are very similar to Boson particle statistics. We can discuss lattice vibrations in a solid. These are called phonon modes, and will have the same distribution function where the only difference is that the speed of light is replaced by the speed of the sound wave in the solid. Once we understand the photon system, we are able to look at other Bose distributions such as these phonon systems.

If we model a solid as a set of interconnected springs, as in fig. 7.39, then the potentials are of the form

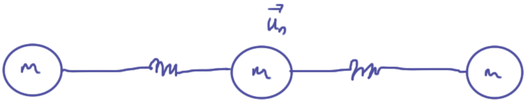


Figure 7.39: Solid oscillator model.

$$V = \frac{1}{2} C \sum_n \left(u_n - u_{n+1} \right)^2, \tag{7.172}$$

with kinetic energies

$$K = \sum_n \frac{p_n^2}{2m}. \tag{7.173}$$

It's possible to introduce generalized forces

$$F = -\frac{\partial V}{\partial u_n}, \tag{7.174}$$

and can differentiate

$$m \frac{d^2 u_n}{dt^2} = -C \left(u_n - u_{n+1} \right) - C \left(u_n - u_{n-1} \right). \tag{7.175}$$

Assuming a Fourier representation

$$u_n = \sum_k \tilde{u}(k) e^{ikna}, \tag{7.176}$$

we find

$$m \frac{d^2 \tilde{u}(k)}{dt^2} = -2C \left(1 - \cos ka \right) \tilde{u}(k). \tag{7.177}$$

This looks like a harmonic oscillator with

$$\omega(k) = \sqrt{\frac{2C}{m}(1 - \cos ka)}. \tag{7.178}$$

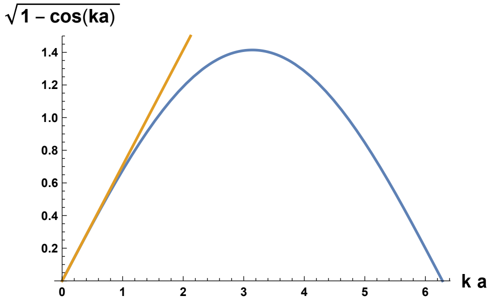


Figure 7.40: Angular frequency of solid oscillator model.

This is plotted in fig. 7.40. In particular note that for $ka \ll 1$ we can use a linear approximation

$$\omega(k) \approx \sqrt{\frac{C}{m} a^2} |k|. \tag{7.179}$$

Experimentally, looking at specific for a complex atomic structure like Gold, we find for example good fit for a model such as

Contribution due to electrons

$$C \sim \boxed{AT} + \boxed{BT^3.}, \tag{7.180}$$

Contribution due to phonon like modes

where the phonon like modes are associated with linear energy-momentum relationships.

7.6 PROBLEMS.

Exercise 7.1 Entropy as probability

[8] points out that entropy can be written as

$$S = -k_\mathrm{B} \sum_i P_i \ln P_i, \tag{7.181}$$

where

$$P_i = \frac{e^{-\beta E_i}}{Z} \tag{7.182a}$$

$$Z = \sum_i e^{-\beta E_i}. \tag{7.182b}$$

Show that this follows from the free energy $F = U - TS = -k_B \ln Z$.

Answer for Exercise 7.1

In terms of the free and average energies, we have

$$\begin{aligned}
\frac{S}{k_B} &= \frac{U - F}{k_B T} \\
&= \beta \left(-\frac{\partial \ln Z}{\partial \beta} \right) - \beta \left(-k_B T \ln Z \right) \\
&= \frac{\sum_i \beta E_i e^{-\beta E_i}}{Z} + \ln Z \\
&= -\sum_i P_i \ln e^{-\beta E_i} + \sum_i P_i \ln Z \\
&= -\sum_i P_i \ln \frac{e^{-\beta E_i}}{Z} P_i \\
&= -\sum_i P_i \ln P_i.
\end{aligned} \tag{7.183}$$

Exercise 7.2 Entropy, grand canonical scheme ([13] pr 4.1, [8] pr 3.15)

Generalize exercise 7.1 to the grand canonical scheme, where we have

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\Omega} \tag{7.184a}$$

$$\Omega = \sum_{r,s} e^{-\alpha N_r - \beta E_s} \tag{7.184b}$$

$$z = e^{-\alpha} = e^{\mu \beta} \tag{7.184c}$$

$$q = \ln \Omega, \tag{7.184d}$$

and show

$$S = -k_B \sum_{r,s} P_{r,s} \ln P_{r,s}. \tag{7.185}$$

Answer for Exercise 7.2

With

$$\beta P V = q, \tag{7.186}$$

the free energy takes the form

$$F = N\mu - PV = N\mu - q/\beta, \tag{7.187}$$

so that the entropy (scaled by k_{B}) leads us to the desired result

$$\begin{aligned}
\frac{S}{k_{\mathrm{B}}} &= \beta U - N\mu\beta + q/(\beta k_{\mathrm{B}} T) \\
&= -\beta \frac{\partial q}{\partial \beta} - z\mu\beta \frac{\partial q}{\partial z} + q \\
&= \frac{1}{\Omega} \sum_{r,s} \left(-\beta(-E_s) - \mu\beta N_r \right) e^{-\alpha N_r - \beta E_s} + \ln \Omega \\
&= \sum_{r,s} \ln e^{\alpha N_r + \beta E_s} P_{r,s} + \left(\sum_{r,s} P_{r,s} \right) \ln \Omega \\
&= -\sum_{r,s} \ln \frac{e^{-\alpha N_r - \beta E_s}}{\Omega} P_{r,s} \\
&= -\sum_{r,s} P_{r,s} \ln P_{r,s}
\end{aligned} \tag{7.188}$$

Exercise 7.3 N variance, open system (*[8] pr 3.14*, *[11] pr 5.10*)

Show that for an open system

$$\mathrm{var}(N) = \frac{1}{\beta} \left(\frac{\partial \overline{N}}{\partial \mu} \right)_{V,T}. \tag{7.189}$$

Answer for Exercise 7.3

In terms of the grand partition function, we find the (scaled) average number of particles

$$\begin{aligned}
\frac{\partial}{\partial \mu} \ln \Omega &= \frac{\partial}{\partial \mu} \ln \sum_{r,s} e^{\beta\mu N_r - \beta E_s} \\
&= \frac{1}{\Omega} \sum_{r,s} \beta N_r e^{\beta\mu N_r - \beta E_s} \\
&= \beta \overline{N}.
\end{aligned} \tag{7.190}$$

Our second derivative provides us a scaled variance

$$\begin{aligned}\frac{\partial^2}{\partial\mu^2}\ln\Omega &= \frac{\partial}{\partial\mu}\left(\frac{1}{\Omega}\sum_{r,s}\beta N_r e^{\beta\mu N_r-\beta E_s}\right)\\ &= \frac{1}{\Omega}\sum_{r,s}(\beta N_r)^2 e^{\beta\mu N_r-\beta E_s} - \frac{1}{\Omega^2}\left(\sum_{r,s}\beta N_r e^{\beta\mu N_r-\beta E_s}\right)^2\\ &= \beta^2\left(\overline{N^2}-\overline{N}^2\right).\end{aligned} \tag{7.191}$$

Together this gives us the desired result

$$\begin{aligned}\operatorname{var}(N) &= \frac{1}{\beta^2}\frac{\partial}{\partial\mu}\left(\beta\overline{N}\right)\\ &= \frac{1}{\beta}\frac{\partial\overline{N}}{\partial\mu}.\end{aligned} \tag{7.192}$$

Exercise 7.4 Gibbs sum for a two level system (*[11] pr. 6*)

a. Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ϵ. Find the Gibbs sum for this system. Our assumption excludes the possibility of one particle in each state at the same time.
b. Find the average thermal occupancy of the system.
c. Find the thermal average occupancy of the state at energy ϵ.
d. Find an expression for the thermal average energy of the system.

Answer for Exercise 7.4

Part a. Gibbs sum We can write the grand partition function immediately

$$\begin{aligned}\Omega &= \overset{N=0}{\boxed{1}}\, e^{-\beta(0)} + \underset{N=1}{\boxed{z^1}}\left(e^{-\beta(0)} + e^{-\beta\epsilon}\right)\\ &= 1 + z + z e^{-\beta\epsilon}.\end{aligned} \tag{7.193}$$

Part b. Thermal average occupancy This also follows almost immediately

$$\begin{aligned}\langle N\rangle &= \frac{0 \times 1 + 1 \times z\left(1 + e^{-\beta\epsilon}\right)}{\Omega} \\ &= \frac{z + z e^{-\beta\epsilon}}{\Omega}.\end{aligned} \tag{7.194}$$

Part c. Thermal average occupancy at energy ϵ The average occupancy at energy ϵ just has one contributing term in the sum

$$\langle N(\epsilon)\rangle = \frac{z e^{-\beta\epsilon}}{\Omega}. \tag{7.195}$$

Part d. Thermal average energy The average thermal energy is

$$\begin{aligned}\langle U\rangle &= \frac{0\,(1+z) + \epsilon z e^{-\beta\epsilon}}{\Omega} \\ &= \frac{\epsilon z e^{-\beta\epsilon}}{\Omega}.\end{aligned} \tag{7.196}$$

Exercise 7.5 Diatomic molecule (*[13] pr. 4.7*)

Consider a classical system of non-interacting, diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian of a single molecule is given by

$$H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \frac{1}{2m}\left(\mathbf{p}_1^2 + \mathbf{p}_2^2\right) + \frac{1}{2} K |\mathbf{r}_1 - \mathbf{r}_2|^2. \tag{7.197}$$

Study the thermodynamics of this system, including the dependence of the quantity $\left\langle r_{12}^2\right\rangle$ on T.

Answer for Exercise 7.5

Partition function First consider the partition function for a single diatomic pair

$$\begin{aligned}Z_1 &= \frac{1}{h^6}\int d^6\mathbf{p}\, d^6\mathbf{r}\, e^{-\beta\frac{\mathbf{p}_1^2+\mathbf{p}_2^2}{2m}} e^{-\beta K\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{2}} \\ &= \frac{1}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\, e^{-\beta K\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{2}}.\end{aligned} \tag{7.198}$$

Now we can make a change of variables to simplify the exponential. Let's write

$$\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2 \tag{7.199a}$$

$$\mathbf{v} = \mathbf{r}_2, \tag{7.199b}$$

or

$$\mathbf{r}_2 = \mathbf{v} \tag{7.200a}$$

$$\mathbf{r}_1 = \mathbf{u} + \mathbf{v}. \tag{7.200b}$$

Our volume element is

$$d^3\mathbf{r}_1 d^3\mathbf{r}_2 = d^3\mathbf{u} d^3\mathbf{v} \frac{\partial(\mathbf{r}_1, \mathbf{r}_2)}{\partial(\mathbf{u}, \mathbf{v})}. \tag{7.201}$$

It wasn't obvious to me that this change of variables preserves the volume element, but a quick calculation shows this to be the case

$$\begin{aligned}
&\frac{\partial(\mathbf{r}_1, \mathbf{r}_2)}{\partial(\mathbf{u}, \mathbf{v})} \\
&= \begin{vmatrix}
\partial r_{11}/\partial u_1 & \partial r_{11}/\partial u_2 & \partial r_{11}/\partial u_3 & \partial r_{11}/\partial v_1 & \partial r_{11}/\partial v_2 & \partial r_{11}/\partial v_3 \\
\partial r_{12}/\partial u_1 & \partial r_{12}/\partial u_2 & \partial r_{12}/\partial u_3 & \partial r_{12}/\partial v_1 & \partial r_{12}/\partial v_2 & \partial r_{12}/\partial v_3 \\
\partial r_{13}/\partial u_1 & \partial r_{13}/\partial u_2 & \partial r_{13}/\partial u_3 & \partial r_{13}/\partial v_1 & \partial r_{13}/\partial v_2 & \partial r_{13}/\partial v_3 \\
\partial r_{21}/\partial u_1 & \partial r_{21}/\partial u_2 & \partial r_{21}/\partial u_3 & \partial r_{21}/\partial v_1 & \partial r_{21}/\partial v_2 & \partial r_{21}/\partial v_3 \\
\partial r_{22}/\partial u_1 & \partial r_{22}/\partial u_2 & \partial r_{22}/\partial u_3 & \partial r_{22}/\partial v_1 & \partial r_{22}/\partial v_2 & \partial r_{22}/\partial v_3 \\
\partial r_{23}/\partial u_1 & \partial r_{23}/\partial u_2 & \partial r_{23}/\partial u_3 & \partial r_{23}/\partial v_1 & \partial r_{23}/\partial v_2 & \partial r_{23}/\partial v_3
\end{vmatrix} \\
&= \begin{vmatrix}
1 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{vmatrix} \\
&= 1.
\end{aligned} \tag{7.202}$$

Our remaining integral can now be evaluated

$$\begin{aligned}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta K \frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{2}} &= \int d^3\mathbf{u} d^3\mathbf{v} e^{-\beta K |\mathbf{u}|^2/2} \\ &= V \int d^3\mathbf{u} e^{-\beta K |\mathbf{u}|^2/2} \\ &= V \int d^3\mathbf{u} e^{-\beta K |\mathbf{u}|^2/2} \\ &= V \left(\frac{2\pi}{K\beta}\right)^{3/2}.\end{aligned} \tag{7.203}$$

Our partition function is now completely evaluated

$$Z_1 = V \frac{1}{h^6} \left(\frac{2\pi m}{\beta}\right)^3 \left(\frac{2\pi}{K\beta}\right)^{3/2}. \tag{7.204}$$

As a function of V and T as in the text, we write

$$Z_1 = V f(T) \tag{7.205a}$$

$$f(T) = \left(\frac{m}{h^2}\sqrt{\frac{(2\pi)^3}{K}}\right)^3 (k_B T)^{9/2}. \tag{7.205b}$$

Gibbs sum Our Gibbs sum, summing over the number of molecules (not atoms), is

$$\begin{aligned}\Omega &= \sum_{N_r=0}^{\infty} \frac{z^{N_r}}{N_r!} Z_1^{N_r} \\ &= e^{zVf(T)},\end{aligned} \tag{7.206}$$

or

$$q = \ln \Omega = zVf(T) = PV\beta. \tag{7.207}$$

The fact that we can sum this as an exponential series so nicely looks like it's one of the main advantages to this grand partition function (Gibbs sum). We can avoid any of the large $N!$ approximations that we have to use when the number of particles is explicitly fixed.

Pressure The pressure follows

$$\begin{aligned} P &= z f(T) k_\mathrm{B} T \\ &= e^{\mu/k_\mathrm{B} T} \left(\frac{m}{h^2} \sqrt{\frac{(2\pi)^3}{K}} \right)^3 (k_\mathrm{B} T)^{11/2} . \end{aligned} \tag{7.208}$$

Average energy

$$\begin{aligned} \langle H \rangle &= -\frac{\partial q}{\partial \beta} \\ &= -zV \frac{9}{2} \frac{f(T)}{T} \frac{\partial T}{\partial \beta} \\ &= zV \frac{9}{2} \frac{f(T)}{T^3} \frac{1}{k_\mathrm{B}}, \end{aligned} \tag{7.209}$$

or

$$\langle H \rangle = e^{\mu/k_\mathrm{B} T} V \frac{9}{2} k_\mathrm{B}^2 \left(\frac{m}{h^2} \sqrt{\frac{(2\pi)^3}{K}} \right)^3 (k_\mathrm{B} T)^{3/2} . \tag{7.210}$$

Average occupancy

$$\begin{aligned} \langle N \rangle &= z \frac{\partial}{\partial z} \ln \Omega \\ &= z \frac{\partial}{\partial z} \left(zV f(T) \right) \\ &= zV f(T), \end{aligned} \tag{7.211}$$

but this is just q, or

$$\langle N \rangle = e^{\mu/k_\mathrm{B} T} V \left(\frac{m}{h^2} \sqrt{\frac{(2\pi)^3}{K}} \right)^3 (k_\mathrm{B} T)^{9/2} . \tag{7.212}$$

Free energy

$$\begin{aligned} F &= -k_\mathrm{B} T \ln \frac{\Omega}{z^N} \\ &= -k_\mathrm{B} T \left(q - N \ln z \right) \\ &= N k_\mathrm{B} T \beta \mu - k_\mathrm{B} T q \\ &= zV f(T) \mu - k_\mathrm{B} T zV f(T) \\ &= zV f(T) \left(\mu - k_\mathrm{B} T \right) . \end{aligned} \tag{7.213}$$

$$F = e^{\mu/k_{\mathrm{B}}T} V \left(\mu - k_{\mathrm{B}}T\right) \left(\frac{m}{h^2}\sqrt{\frac{(2\pi)^3}{K}}\right)^3 \left(k_{\mathrm{B}}T\right)^{9/2}. \tag{7.214}$$

Entropy

$$\begin{aligned} S &= \frac{U - F}{T} \\ &= \frac{V}{T} e^{\mu/k_{\mathrm{B}}T} \left(k_{\mathrm{B}}T\right)^{3/2} \left(\frac{m}{h^2}\sqrt{\frac{(2\pi)^3}{K}}\right)^3 \left(\frac{9}{2}k_{\mathrm{B}}^2 - \left(\mu - k_{\mathrm{B}}T\right)\left(k_{\mathrm{B}}T\right)^3\right). \end{aligned} \tag{7.215}$$

Expectation of atomic separation The momentum portions of the average will just cancel out, leaving just

$$\begin{aligned} \left\langle r_{12}^2 \right\rangle &= \frac{\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \left(\mathbf{r}_1 - \mathbf{r}_2\right)^2 e^{-\beta K(\mathbf{r}_1 - \mathbf{r}_2)^2/2}}{\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta K(\mathbf{r}_1 - \mathbf{r}_2)^2/2}} \\ &= \frac{\int d^3\mathbf{u}\mathbf{u}^2 e^{-\beta K\mathbf{u}^2/2}}{\int d^3\mathbf{u} e^{-\beta K\mathbf{u}^2/2}} \\ &= \frac{\int dadbdc \left(a^2 + b^2 + c^2\right) e^{-\beta K\left(a^2+b^2+c^2\right)/2}}{\int e^{-\beta K\left(a^2+b^2+c^2\right)/2}} \\ &= 3\frac{\int daa^2 e^{-\beta K a^2/2} \int dbdce^{-\beta K\left(b^2+c^2\right)/2}}{\int e^{-\beta K\left(a^2+b^2+c^2\right)/2}} \\ &= 3\frac{\int daa^2 e^{-\beta K a^2/2}}{\int e^{-\beta K a^2/2}}. \end{aligned} \tag{7.216}$$

Expanding the numerator by parts we have

$$\int daa^2 e^{-\beta K a^2/2} = \int ad\left(\frac{e^{-\beta K a^2/2}}{-2\beta K/2}\right) = \frac{1}{\beta K}\int e^{-\beta K a^2/2}. \tag{7.217}$$

This gives us

$$\boxed{\left\langle r_{12}^2 \right\rangle = \frac{3}{\beta K} = \frac{3k_{\mathrm{B}}T}{K}.} \tag{7.218}$$

This result doesn't make sense as $T \rightarrow 0$. We need a QM treatment that will prevent the interatomic spacing in the molecule spacing from hitting zero at low temperatures. Is this valid for very high temperatures too? Does this linear temperature dependence model the bond breaking that would occur when enough energy is supplied to the molecule?

Exercise 7.6 Maximum entropy principle (*2013 ps6, p1*)

Consider the "Gibbs entropy"

$$S = -k_{\mathrm{B}} \sum_i p_i \ln p_i, \tag{7.219}$$

where p_i is the equilibrium probability of occurrence of a microstate i in the ensemble.

a. For a microcanonical ensemble with Ω configurations (each having the same energy), assigning an equal probability $p_i = 1/\Omega$ to each microstate leads to $S = k_{\mathrm{B}} \ln \Omega$. Show that this result follows from maximizing the Gibbs entropy with respect to the parameters p_i subject to the constraint of

$$\sum_i p_i = 1, \tag{7.220}$$

(for p_i to be meaningful as probabilities). In order to do the minimization with this constraint, use the method of Lagrange multipliers - first, do an unconstrained minimization of the function

$$S - \alpha \sum_i p_i, \tag{7.221}$$

then fix α by demanding that the constraint be satisfied.

b. For a canonical ensemble (no constraint on total energy, but all microstates having the same number of particles N), maximize the Gibbs entropy with respect to the parameters p_i subject to the constraint of

$$\sum_i p_i = 1, \tag{7.222}$$

(for p_i to be meaningful as probabilities) and with a given fixed average energy

$$\langle E \rangle = \sum_i E_i p_i, \tag{7.223}$$

where E_i is the energy of microstate i. Use the method of Lagrange multipliers, doing an unconstrained minimization of the function

$$S - \alpha \sum_i p_i - \beta \sum_i E_i p_i, \tag{7.224}$$

then fix α, β by demanding that the constraint be satisfied. What is the resulting p_i?

c. For a grand canonical ensemble (no constraint on total energy, or the number of particles), maximize the Gibbs entropy with respect to the parameters p_i subject to the constraint of

$$\sum_i p_i = 1, \tag{7.225}$$

(for p_i to be meaningful as probabilities) and with a given fixed average energy

$$\langle E \rangle = \sum_i E_i p_i, \tag{7.226}$$

and a given fixed average particle number

$$\langle N \rangle = \sum_i N_i p_i. \tag{7.227}$$

Here E_i, N_i represent the energy and number of particles in microstate i. Use the method of Lagrange multipliers, doing an unconstrained minimization of the function

$$S - \alpha \sum_i p_i - \beta \sum_i E_i p_i - \gamma \sum_i N_i p_i, \tag{7.228}$$

then fix α, β, γ by demanding that the constrains be satisfied. What is the resulting p_i?

Answer for Exercise 7.6

Part a. Writing

$$\begin{aligned} f &= S - \alpha \sum_{j=1}^{\Omega} p_j, \\ &= -\sum_{j=1}^{\Omega} p_j \left(k_{\mathrm{B}} \ln p_j + \alpha \right), \end{aligned} \tag{7.229}$$

our unconstrained minimization requires

$$\begin{aligned} 0 &= \frac{\partial f}{\partial p_i} \\ &= -\left(k_\mathrm{B}\left(\ln p_i + 1\right) + \alpha\right). \end{aligned} \tag{7.230}$$

Solving for p_i we have

$$p_i = e^{-\alpha/k_\mathrm{B} - 1}. \tag{7.231}$$

The probabilities for each state are constant. To fix that constant we employ our constraint

$$\begin{aligned} 1 &= \sum_{j=1}^{\Omega} p_j \\ &= \sum_{j=1}^{\Omega} e^{-\alpha/k_\mathrm{B}-1} \\ &= \Omega e^{-\alpha/k_\mathrm{B}-1}, \end{aligned} \tag{7.232}$$

or

$$\alpha/k_\mathrm{B} + 1 = \ln\Omega. \tag{7.233}$$

Inserting eq. (7.233) fixes the probability, giving us the first of the expected results

$$\boxed{p_i = e^{-\ln\Omega} = \frac{1}{\Omega}.} \tag{7.234}$$

Using this we our Gibbs entropy can be summed easily

$$\begin{aligned} S &= -k_\mathrm{B} \sum_{j=1}^{\Omega} p_j \ln p_j \\ &= -k_\mathrm{B} \sum_{j=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} \\ &= -k_\mathrm{B} \frac{\Omega}{\Omega} \left(-\ln\Omega\right), \end{aligned} \tag{7.235}$$

or

$$\boxed{S = k_\mathrm{B} \ln\Omega.} \tag{7.236}$$

Part b. For the "action" like quantity that we want to minimize, let's write

$$f = S - \alpha \sum_j p_j - \beta \sum_j E_j p_j, \tag{7.237}$$

for which we seek α, β such that

$$\begin{aligned} 0 &= \frac{\partial f}{\partial p_i} \\ &= -\frac{\partial}{\partial p_i} \sum_j p_j \left(k_\mathrm{B} \ln p_j + \alpha + \beta E_j \right) \\ &= -k_\mathrm{B}(\ln p_i + 1) - \alpha - \beta E_i, \end{aligned} \tag{7.238}$$

or

$$p_i = \exp\left(-\left(\alpha - \beta E_i\right)/k_\mathrm{B} - 1 \right). \tag{7.239}$$

Our probability constraint is

$$\begin{aligned} 1 &= \sum_j \exp\left(-\left(\alpha - \beta E_j\right)/k_\mathrm{B} - 1 \right) \\ &= \exp\left(-\alpha/k_\mathrm{B} - 1 \right) \sum_j \exp\left(-\beta E_j/k_\mathrm{B} \right), \end{aligned} \tag{7.240}$$

or

$$\exp\left(\alpha/k_\mathrm{B} + 1 \right) = \sum_j \exp\left(-\beta E_j/k_\mathrm{B} \right). \tag{7.241}$$

Taking logs we have

$$\alpha/k_\mathrm{B} + 1 = \ln \sum_j \exp\left(-\beta E_j/k_\mathrm{B} \right). \tag{7.242}$$

We could continue to solve for α explicitly but don't care any more than this. Plugging back into the probability eq. (7.239) obtained from the unconstrained minimization we have

$$p_i = \exp\left(-\ln \sum_j \exp\left(-\beta E_j/k_\mathrm{B} \right) \right) \exp\left(-\beta E_i/k_\mathrm{B} \right), \tag{7.243}$$

or

$$\boxed{p_i = \frac{\exp\left(-\beta E_i/k_\mathrm{B} \right)}{\sum_j \exp\left(-\beta E_j/k_\mathrm{B} \right)}.} \tag{7.244}$$

To determine β we must look implicitly to the energy constraint, which is

$$\begin{aligned}\langle E\rangle &= \sum_i E_i p_i \\ &= \sum_i E_i \left(\frac{\exp\left(-\beta E_i/k_{\mathrm{B}}\right)}{\sum_j \exp\left(-\beta E_j/k_{\mathrm{B}}\right)} \right),\end{aligned} \tag{7.245}$$

or

$$\boxed{\langle E\rangle = \frac{\sum_i E_i \exp\left(-\beta E_i/k_{\mathrm{B}}\right)}{\sum_j \exp\left(-\beta E_j/k_{\mathrm{B}}\right)}.} \tag{7.246}$$

The constraint β (= $1/T$) is given implicitly by this energy constraint.

Part c. Again write

$$f = S - \alpha \sum_j p_j - \beta \sum_j E_j p_j - \gamma \sum_j N_j p_j. \tag{7.247}$$

The unconstrained minimization requires

$$\begin{aligned}0 &= \frac{\partial f}{\partial p_i} \\ &= -\frac{\partial}{\partial p_i} \left(k_{\mathrm{B}}(\ln p_i + 1) + \alpha + \beta E_i + \gamma N_i \right),\end{aligned} \tag{7.248}$$

or

$$p_i = \exp\left(-\alpha/k_{\mathrm{B}} - 1\right) \exp\left(-(\beta E_i + \gamma N_i)/k_{\mathrm{B}}\right). \tag{7.249}$$

The unit probability constraint requires

$$\begin{aligned}1 &= \sum_j p_j \\ &= \exp\left(-\alpha/k_{\mathrm{B}} - 1\right) \sum_j \exp\left(-(\beta E_j + \gamma N_j)/k_{\mathrm{B}}\right),\end{aligned} \tag{7.250}$$

or

$$\exp\left(-\alpha/k_{\mathrm{B}} - 1\right) = \frac{1}{\sum_j \exp\left(-(\beta E_j + \gamma N_j)/k_{\mathrm{B}}\right)}. \tag{7.251}$$

Our probability is then

$$\boxed{p_i = \frac{\exp\left(-(\beta E_i + \gamma N_i)/k_{\mathrm{B}}\right)}{\sum_j \exp\left(-(\beta E_j + \gamma N_j)/k_{\mathrm{B}}\right)}.} \tag{7.252}$$

The average energy $\langle E \rangle = \sum_j p_j E_j$ and average number of particles $\langle N \rangle = \sum_j p_j N_j$ are given by

$$\langle E \rangle = \frac{E_i \exp\left(-(\beta E_i + \gamma N_i)/k_{\mathrm{B}}\right)}{\sum_j \exp\left(-(\beta E_j + \gamma N_j)/k_{\mathrm{B}}\right)} \tag{7.253a}$$

$$\langle N \rangle = \frac{N_i \exp\left(-(\beta E_i + \gamma N_i)/k_{\mathrm{B}}\right)}{\sum_j \exp\left(-(\beta E_j + \gamma N_j)/k_{\mathrm{B}}\right)}. \tag{7.253b}$$

The values β and γ are fixed implicitly by requiring simultaneous solutions of these equations.

Exercise 7.7 Fugacity expansion ([13] *Pathria, Appendix D, E*)

The theory of the ideal Fermi or Bose gases often involves integrals of the form

$$f_\nu^\pm(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x \pm 1}, \tag{7.254}$$

where

$$\Gamma(\nu) = \int_0^\infty dy y^{\nu-1} e^{-y}, \tag{7.255}$$

denotes the gamma function.

a. Obtain the behavior of $f_\nu^\pm(z)$ for $z \to 0$ keeping the two leading terms in the expansion.
b. For Fermions, obtain the behavior of $f_\nu^\pm(z)$ for $z \to \infty$ again keeping the two leading terms.
c. For Bosons, we must have $z \le 1$ (why?), obtain the leading term of $f_\nu^-(z)$ for $z \to 1$.

Answer for Exercise 7.7

Part a. For $z \rightarrow 0$ we can rewrite the integrand in a form that allows for series expansion

$$\begin{aligned}\frac{x^{\nu-1}}{z^{-1}e^x \pm 1} &= \frac{ze^{-x}x^{\nu-1}}{1 \pm ze^{-x}} \\ &= ze^{-x}x^{\nu-1}\left(1 \mp ze^{-x} + (ze^{-x})^2 \mp (ze^{-x})^3 + \cdots\right)\end{aligned} \tag{7.256}$$

For the kth power of ze^{-x} in this series our integral is

$$\begin{aligned}\int_0^\infty dxze^{-x}x^{\nu-1}(ze^{-x})^k &= z^{k+1}\int_0^\infty dxx^{\nu-1}e^{-(k+1)x} \\ &= \frac{z^{k+1}}{(k+1)^\nu}\int_0^\infty duu^{\nu-1}e^{-u} \\ &= \frac{z^{k+1}}{(k+1)^\nu}\Gamma(\nu).\end{aligned} \tag{7.257}$$

Putting everything back together we have for small z

$$\boxed{f_\nu^\pm(z) = z \mp \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} \mp \frac{z^4}{4^\nu} + \cdots} \tag{7.258}$$

Part b. We'll expand $\Gamma(\nu)f_\nu^+(e^y)$ about $z = e^y$, writing

$$\begin{aligned}F_\nu(e^y) &= \Gamma(\nu)f_\nu^+(e^y) \\ &= \int_0^\infty dx\frac{x^{\nu-1}}{e^{x-y}+1} \\ &= \int_0^y dx\frac{x^{\nu-1}}{e^{x-y}+1} + \int_y^\infty dx\frac{x^{\nu-1}}{e^{x-y}+1}.\end{aligned} \tag{7.259}$$

The integral has been split into two since the behavior of the exponential in the denominator is quite different in the $x < y$ and $x > y$ ranges. Observe that in the first integral we have

$$\frac{1}{2} \le \frac{1}{e^{x-y}+1} \le \frac{1}{1+e^{-y}}. \tag{7.260}$$

Since this term is of order 1, let's consider the difference of this from 1, writing

$$\frac{1}{e^{x-y}+1} = 1 + u, \tag{7.261}$$

or

$$\begin{aligned}
u &= \frac{1}{e^{x-y}+1} - 1 \\
&= \frac{1-(e^{x-y}+1)}{e^{x-y}+1} \\
&= \frac{-e^{x-y}}{e^{x-y}+1} \\
&= -\frac{1}{1+e^{y-x}}.
\end{aligned} \tag{7.262}$$

This gives us

$$\begin{aligned}
F_\nu(e^y) &= \int_0^y dx x^{\nu-1}\left(1-\frac{1}{1+e^{y-x}}\right) + \int_y^\infty dx \frac{x^{\nu-1}}{e^{x-y}+1} \\
&= \frac{y^\nu}{\nu} - \int_0^y dx \frac{x^{\nu-1}}{1+e^{y-x}} + \int_y^\infty dx \frac{x^{\nu-1}}{e^{x-y}+1}.
\end{aligned} \tag{7.263}$$

Now let's make a change of variables $a = y - x$ in the first integral and $b = x - y$ in the second. This gives

$$F_\nu(e^y) = \frac{y^\nu}{\nu} - \int_0^\infty da \frac{(y-a)^{\nu-1}}{1+e^a} + \int_0^\infty db \frac{(y+b)^{\nu-1}}{e^b+1}. \tag{7.264}$$

As a gets large in the first integral the integrand is approximately $e^{-a}(y-a)^{\nu-1}$. The exponential dominates this integrand. Since we are considering large y, we can approximate the upper bound of the integral by extending it to ∞. Also expanding in series we have

$$
\begin{aligned}
F_\nu(e^y) &\approx \frac{y^\nu}{\nu} + \int_0^\infty da \frac{(y+a)^{\nu-1} - (y-a)^{\nu-1}}{1+e^a} \\
&= \frac{y^\nu}{\nu} + \int_0^\infty da \frac{1}{e^a+1} \left(\left(\frac{1}{0!} y^{\nu-1} a^0 + \frac{1}{1!}(\nu-1) y^{\nu-2} a^1 \right.\right. \\
&\qquad \left. + \frac{1}{2!}(\nu-1)(\nu-2) y^{\nu-3} a^2 + \cdots \right) - \left(\frac{1}{0!} y^{\nu-1} (-a)^0 \right. \\
&\qquad \left.\left. + \frac{1}{1!}(\nu-1) y^{\nu-2} (-a)^1 + \frac{1}{2!}(\nu-1)(\nu-2) y^{\nu-3} (-a)^2 + \cdots \right) \right) \\
&= \frac{y^\nu}{\nu} + 2\int_0^\infty da \frac{1}{e^a+1} \left(\frac{1}{1!}(\nu-1) y^{\nu-2} a^1 \right. \\
&\qquad \left. + \frac{1}{3!}(\nu-1)(\nu-2)(\nu-3) y^{\nu-4} a^3 + \cdots \right) \\
&= \frac{y^\nu}{\nu} + 2 \sum_{j=1,3,5,\cdots} \frac{y^{\nu-1-j}}{j!} \left(\prod_{k=1}^{j} (\nu-k) \right) \int_0^\infty da \frac{a^j}{e^a+1} \\
&= \frac{y^\nu}{\nu} + 2 \sum_{j=1,3,5,\cdots} \frac{y^{\nu-1-j}}{j!} \frac{\Gamma(\nu)}{\Gamma(\nu-j)} \int_0^\infty da \frac{a^j}{e^a+1}.
\end{aligned}
\tag{7.265}
$$

For the remaining integral, we find in basicStatMechProblemSet6Problem2.nb

$$
\int_0^\infty da \frac{a^j}{e^a+1} = \left(1 - 2^{-j}\right) j!\, \zeta(j+1), \tag{7.266}
$$

where for $s > 1$

$$
\zeta(s) = \sum_{k=1}^{\infty} k^{-s}. \tag{7.267}
$$

This gives

$$
F_\nu(e^y) \approx \frac{y^\nu}{\nu} + 2 \sum_{j=1,3,5,\cdots} y^{\nu-1-j} \frac{\Gamma(\nu)}{\Gamma(\nu-j)} \left(1 - 2^{-j}\right) \zeta(j+1), \tag{7.268}
$$

or

$$
\begin{aligned}
f_\nu^+(e^y) &\approx y^\nu \left(\frac{1}{\nu\Gamma(\nu)} + 2 \sum_{j=1,3,5,\cdots} \frac{1}{\Gamma(\nu - j) y^{j+1}} \left(1 - 2^{-j}\right) \zeta(j+1) \right) \\
&= \frac{y^\nu}{\Gamma(\nu+1)} \left(1 + 2 \sum_{j=1,3,5,\cdots} \frac{\Gamma(\nu+1)}{\Gamma(\nu - j)} \left(1 - 2^{-j}\right) \frac{\zeta(j+1)}{y^{j+1}} \right),
\end{aligned}
\tag{7.269}
$$

or

$$
\boxed{
\begin{aligned}
f_\nu^+(e^y) \approx \frac{y^\nu}{\Gamma(\nu+1)} \times \\
\left(1 + 2\nu \sum_{j=1,3,5,\cdots} (\nu - 1)\cdots(\nu - j) \left(1 - 2^{-j}\right) \frac{\zeta(j+1)}{y^{j+1}} \right).
\end{aligned}
}
\tag{7.270}
$$

Evaluating the numerical portions explicitly, with

$$
c(j) = 2 \left(1 - 2^{-j}\right) \zeta(j+1),
\tag{7.271}
$$

$$
\begin{aligned}
c(1) &= \frac{\pi^2}{6} \\
c(3) &= \frac{7\pi^4}{360} \\
c(5) &= \frac{31\pi^6}{15120} \\
c(7) &= \frac{127\pi^8}{604800},
\end{aligned}
\tag{7.272}
$$

so to two terms ($j = 1, 3$), we have

$$
\boxed{
\begin{aligned}
f_\nu^+(e^y) \approx \frac{y^\nu}{\Gamma(\nu+1)} \times \\
\left(1 + \nu(\nu - 1)\frac{\pi^2}{6y^2} + \nu(\nu - 1)(\nu - 2)(\nu - 3)\frac{7\pi^4}{360y^4} \right).
\end{aligned}
}
$$

(7.273)

Part c. In order for the Boson occupation numbers to be non-singular we require μ less than all ϵ. If that lowest energy level is set to zero, this is equivalent to $z < 1$. Given this restriction, a $z = e^{-\alpha}$ substitution is convenient for investigation of the $z \rightarrow 1$ case. Following the text, we'll write

$$\begin{aligned} G_\nu(e^{-\alpha}) &= \Gamma(\nu) f_\nu^-(e^{-\alpha}) \\ &= \int_0^\infty dx \frac{x^{\nu-1}}{e^{x+\alpha} - 1}. \end{aligned} \tag{7.274}$$

For $\nu = 1$, this is integrable

$$\begin{aligned} \frac{d}{dx} \ln\left(1 - e^{-x-\alpha}\right) &= \frac{e^{-x-\alpha}}{1 - e^{-x-\alpha}} \\ &= \frac{1}{e^{x+\alpha} - 1}, \end{aligned} \tag{7.275}$$

so that

$$\begin{aligned} G_1(e^{-\alpha}) &= \int_0^\infty dx \frac{1}{e^{x+\alpha} - 1} \\ &= \ln\left(1 - e^{-x-\alpha}\right)\Big|_0^\infty \\ &= \ln 1 - \ln\left(1 - e^{-\alpha}\right) \\ &= -\ln\left(1 - e^{-\alpha}\right). \end{aligned} \tag{7.276}$$

Taylor expanding $1 - e^{-\alpha}$ we have

$$1 - e^{-\alpha} = 1 - \left(1 - \alpha + \alpha^2/2 - \cdots\right). \tag{7.277}$$

Noting that $\Gamma(1) = 1$, we have for the limit

$$\lim_{\alpha \rightarrow 0} G_1(e^{-\alpha}) \rightarrow -\ln \alpha, \tag{7.278}$$

or

$$\lim_{z \rightarrow 1} f_\nu^-(z) = -\ln(-\ln z). \tag{7.279}$$

For values of $\nu \neq 1$, the denominator is

$$e^{\alpha+x} - 1 = (\alpha + x) + (\alpha + x)^2/2 + \cdots \tag{7.280}$$

To first order this gives us

$$f_\nu^-(e^{-\alpha}) \approx \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{1}{x+\alpha}. \tag{7.281}$$

Of this integral Mathematica says it can be evaluated for $0 < \nu < 1$, and has the value

$$\frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{1}{x+\alpha} = \frac{\pi}{\sin(\pi\nu)} \frac{1}{\alpha^{1-\nu}\Gamma(\nu)}. \tag{7.282}$$

From [1] 6.1.17 we find

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin(\pi z)}, \tag{7.283}$$

with which we can write

$$\boxed{f_\nu^-(e^{-\alpha}) \approx \frac{\Gamma(1-\nu)}{\alpha^{1-\nu}}.} \tag{7.284}$$

Exercise 7.8 Nuclear matter (*[7], prob 9.2*)

Consider a heavy nucleus of mass number A. i.e., having A total nucleons including neutrons and protons. Assume that the number of neutrons and protons is equal, and recall that each of them has spin-1/2 (so possessing two spin states). Treating these nucleons as a free ideal Fermi gas of uniform density contained in a radius $R = r_0 A^{1/3}$, where $r_0 = 1.4 \times 10^{-13}$cm, calculate the Fermi energy and the average energy per nucleon in MeV.

Answer for Exercise 7.8

Our nucleon particle density is

$$\begin{aligned}\rho &= \frac{N}{V} \\ &= \frac{A}{\frac{4\pi}{3} R^3} \\ &= \frac{3A}{4\pi r_0^3 A} \\ &= \frac{3}{4\pi r_0^3} \\ &= \frac{3}{4\pi(1.4 \times 10^{-13}\text{cm})^3} \\ &= 8.7 \times 10^{37} (\text{cm})^{-3} \\ &= 8.7 \times 10^{43} (\text{m})^{-3}.\end{aligned} \tag{7.285}$$

With m for the mass of either the proton or the neutron, and $\rho_m = \rho_p = \rho/2$, the Fermi energy for these particles is

$$\epsilon_{\text{F}} = \frac{\hbar^2}{2m} \left(\frac{6\pi(\rho/2)}{2S+1} \right)^{2/3}, \tag{7.286}$$

With $S = 1/2$, and $2S + 1 = 2(1/2) + 1 = 2$ for either the proton or the neutron, this is

$$\epsilon_{\text{F}} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 \rho}{2} \right)^{2/3}. \tag{7.287}$$

$$\begin{aligned}\hbar &= 1.05 \times 10^{-34}\, m^2 \text{ kg } s^{-1} \\ m &= 1.67 \times 10^{-27}\, \text{kg}\end{aligned}. \tag{7.288}$$

This gives us

$$\begin{aligned}\epsilon_{\text{F}} &= \frac{(1.05 \times 10^{-34})^2}{2 \times 1.67 \times 10^{-27}} \left(\frac{3\pi^2}{2} \frac{8.7 \times 10^{43}}{2} \right)^{2/3} \text{m}^4 \frac{\text{kg}^2}{s^2} \frac{1}{\text{kg}} \frac{1}{\text{m}^2} \\ &= 3.9 \times 10^{-12}\, \text{J} \times \left(6.241509 \times 10^{12} \frac{\text{MeV}}{J} \right) \\ &\approx 24\text{MeV}.\end{aligned} \tag{7.289}$$

In lecture 16 we found that the total average energy for a Fermion gas of N particles was

$$E = \frac{3}{5} N \epsilon_{\mathrm{F}}, \tag{7.290}$$

so the average energy per nucleon is approximately

$$\frac{3}{5} \epsilon_{\mathrm{F}} \approx 15\,\mathrm{MeV}. \tag{7.291}$$

Exercise 7.9 Neutron star ([7], *prob 9.5*)

Model a neutron star as an ideal Fermi gas of neutrons at $T = 0$ moving in the gravitational field of a heavy point mass M at the center. Show that the pressure P obeys the equation

$$\frac{dP}{dr} = -\gamma M \frac{\rho(r)}{r^2}, \tag{7.292}$$

where γ is the gravitational constant, r is the distance from the center, and $\rho(r)$ is the density which only depends on distance from the center.

Answer for Exercise 7.9

In the grand canonical scheme the pressure for a Fermion system is given by

$$\begin{aligned} \beta P V &= \ln \Omega \\ &= \ln \prod_{\epsilon} \sum_{n=0}^{1} \left(z e^{-\beta \epsilon} \right)^n \\ &= \sum_{\epsilon} \ln \left(1 + z e^{-\beta \epsilon} \right). \end{aligned} \tag{7.293}$$

The kinetic energy of the particle is adjusted by the gravitational potential

$$\begin{aligned} \epsilon &= \epsilon_{\mathbf{k}} - \frac{\gamma m M}{r} \\ &= \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{\gamma m M}{r}. \end{aligned} \tag{7.294}$$

Differentiating eq. (7.293) with respect to the radius, we have

$$\begin{aligned}\beta V \frac{\partial P}{\partial r} &= -\beta \frac{\partial \epsilon}{\partial r} \sum_{\epsilon} \frac{z e^{-\beta\epsilon}}{1 + z e^{-\beta\epsilon}} \\ &= -\beta \left(\frac{\gamma m M}{r^2}\right) \sum_{\epsilon} \frac{1}{z^{-1} e^{\beta\epsilon} + 1} \\ &= -\beta \left(\frac{\gamma m M}{r^2}\right) \langle N \rangle .\end{aligned} \tag{7.295}$$

Noting that $\langle N \rangle m/V$ is the average density of the particles, presumed radial, we have

$$\boxed{\frac{\partial P}{\partial r} = -\frac{\gamma M}{r^2} \frac{m \langle N \rangle}{V} = -\frac{\gamma M}{r^2} \rho(r).} \tag{7.296}$$

Exercise 7.10 Relativisitic Fermi gas ([7], *pr. 9.3*)

Consider a relativistic gas of N particles of spin $1/2$ obeying Fermi statistics, enclosed in volume V, at absolute zero. The energy-momentum relation is

$$\epsilon = \sqrt{(pc)^2 + \epsilon_0^2}, \tag{7.297}$$

where $\epsilon_0 = mc^2$, and m is the rest mass.

a. Find the Fermi energy at density n.
b. With the pressure P defined as the average force per unit area exerted on a perfectly-reflecting wall of the container. Set up expressions for this in the form of an integral.
c. Define the internal energy U as the average $\epsilon - \epsilon_0$. Set up expressions for this in the form of an integral.
d. Show that $PV = 2U/3$ at low densities, and $PV = U/3$ at high densities. State the criteria for low and high densities.
e. There may exist a gas of neutrinos (and/or antineutrinos) in the cosmos. (Neutrinos are massless Fermions of spin $1/2$.) Calculate the Fermi energy (in eV) of such a gas, assuming a density of one particle per cm^3.
f. Attempt exact evaluation of the various integrals.

Answer for Exercise 7.10

Part a. We've found appendix H that the density of states associated with a 3D relativistic system is

$$\mathcal{D}(\epsilon) = \frac{4\pi V}{(ch)^3}\epsilon\sqrt{\epsilon^2 - \epsilon_0^2}, \tag{7.298}$$

For a given density n, we can find the Fermi energy in the same way as we did for the non-relativistic energies, with the exception that we have to integrate from a lowest energy of ϵ_0 instead of 0 (the energy at $\mathbf{p} = 0$). That is

$$\begin{aligned} n &= \frac{N}{V} \\ &= \left(2\frac{1}{2}+1\right)\frac{4\pi}{(ch)^3}\int_{\epsilon_0}^{\epsilon_{\mathrm{F}}} d\epsilon\epsilon\sqrt{\epsilon^2-\epsilon_0^2} \\ &= \frac{8\pi}{(ch)^3}\frac{1}{3}\left(x^2-\epsilon_0^2\right)^{3/2}\Big|_{\epsilon_0}^{\epsilon_{\mathrm{F}}} \\ &= \frac{8\pi}{3(ch)^3}\left(\epsilon_{\mathrm{F}}^2-\epsilon_0^2\right)^{3/2}. \end{aligned} \tag{7.299}$$

Solving for $\epsilon_{\mathrm{F}}/\epsilon_0$ we have

$$\frac{\epsilon_{\mathrm{F}}}{\epsilon_0} = \sqrt{\left(\frac{3(ch)^3 n}{8\pi\epsilon_0^3}\right)^{2/3}+1}. \tag{7.300}$$

We'll see the constant factor above a number of times below and designate it

$$n_0 = \frac{8\pi}{3}\left(\frac{\epsilon_0}{ch}\right)^3, \tag{7.301}$$

so that the Fermi energy is

$$\frac{\epsilon_{\mathrm{F}}}{\epsilon_0} = \sqrt{\left(\frac{n}{n_0}\right)^{2/3}+1}. \tag{7.302}$$

Part b. For the pressure calculation, let's suppose that we have a configuration with a plane in the x, y orientation as in fig. 7.41.

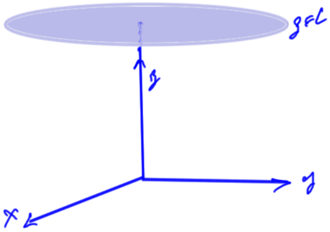


Figure 7.41: Pressure against x, y oriented plane.

It's argued in [13] §6.4 that the pressure for such a configuration is

$$P = n \int p_z u_z f(\mathbf{u}) d^3\mathbf{u}, \tag{7.303}$$

where n is the number density and $f(\mathbf{u})$ is a normalized distribution function for the velocities. The velocity and momentum components are related by the Hamiltonian equations. From the Hamiltonian eq. (7.297) we find [2] (for the x-component which is representative)

$$\begin{aligned} u_x &= \frac{\partial \epsilon}{\partial p_x} \\ &= \frac{\partial}{\partial p_x} \sqrt{(pc)^2 + \epsilon_0^2} \\ &= \frac{p_x c^2}{\sqrt{(pc)^2 + \epsilon_0^2}}. \end{aligned} \tag{7.304}$$

For $\alpha \in \{1, 2, 3\}$ we can summarize these velocity-momentum relationships as

$$\frac{u_\alpha}{c} = \frac{c p_\alpha}{\epsilon}. \tag{7.305}$$

Should we attempt to calculate the pressure with this parameterization of the velocity space we end up with convergence problems,

---

[2] Observe that by squaring and summing one can show that this is equivalent to the standard relativistic momentum $p_x = \frac{m v_x}{\sqrt{1 - \mathbf{u}^2/c^2}}$.

and can't express the results in terms of $f_\nu^+(z)$. Let's try instead with a distribution over momentum space

$$P = n \int \frac{(cp_z)^2}{\epsilon} f(c\mathbf{p}) d^3(c\mathbf{p}). \tag{7.306}$$

Here the momenta have been scaled to have units of energy since we want to express this integral in terms of energy in the end. Our normalized distribution function is

$$f(c\mathbf{p}) \propto \frac{\frac{1}{z^{-1}e^{\beta\epsilon}+1}}{\int \frac{1}{z^{-1}e^{\beta\epsilon}+1} d^3(c\mathbf{p})}, \tag{7.307}$$

but before evaluating anything, we first want to change our integration variable from momentum to energy. In spherical coordinates our volume element takes the form

$$\begin{aligned} d^3(c\mathbf{p}) &= 2\pi(cp)^2 d(cp) \sin\theta d\theta \\ &= 2\pi(cp)^2 \frac{d(cp)}{d\epsilon} d\epsilon \sin\theta d\theta. \end{aligned} \tag{7.308}$$

Implicit derivatives of

$$c^2p^2 = \epsilon^2 - \epsilon_0^2, \tag{7.309}$$

gives us

$$\frac{d(cp)}{d\epsilon} = \frac{\epsilon}{cp} = \frac{\epsilon}{\sqrt{\epsilon^2 - \epsilon_0^2}}. \tag{7.310}$$

Our momentum volume element becomes

$$\begin{aligned} d^3(c\mathbf{p}) &= 2\pi(cp)^2 \frac{\epsilon}{\sqrt{\epsilon^2 - \epsilon_0^2}} d\epsilon \sin\theta d\theta \\ &= 2\pi \left(\epsilon^2 - \epsilon_0^2\right) \frac{\epsilon}{\sqrt{\epsilon^2 - \epsilon_0^2}} d\epsilon \sin\theta d\theta \\ &= 2\pi\epsilon\sqrt{\epsilon^2 - \epsilon_0^2} d\epsilon \sin\theta d\theta. \end{aligned} \tag{7.311}$$

For our distribution function, we can now write

$$f(c\mathbf{p})d^3(c\mathbf{p}) = C \frac{\epsilon\sqrt{\epsilon^2 - \epsilon_0^2} d\epsilon}{z^{-1}e^{\beta\epsilon} + 1} \frac{2\pi \sin\theta d\theta}{4\pi\epsilon_0^3}, \tag{7.312}$$

where C is determined by the requirement $\int f(c\mathbf{p}) d^3(c\mathbf{p}) = 1$

$$C^{-1} = \int_0^\infty \frac{(y+1)\sqrt{(y+1)^2 - 1} dy}{z^{-1} e^{\beta\epsilon_0 (y+1)} + 1}. \tag{7.313}$$

The z component of our momentum can be written in spherical coordinates as

$$(c p_z)^2 = (cp)^2 \cos^2\theta = \left(\epsilon^2 - \epsilon_0^2\right) \cos^2\theta, \tag{7.314}$$

Noting that

$$\int_0^\pi \cos^2\theta \sin\theta d\theta = -\int_0^\pi \cos^2\theta d(\cos\theta) = \frac{2}{3}, \tag{7.315}$$

all the bits come together as

$$\begin{aligned} P &= \frac{Cn}{3\epsilon_0^3} \int_{\epsilon_0}^\infty \left(\epsilon^2 - \epsilon_0^2\right)^{3/2} \frac{1}{z^{-1} e^{\beta\epsilon} + 1} d\epsilon \\ &= \frac{n\epsilon_0}{3} \int_1^\infty \left(x^2 - 1\right)^{3/2} \frac{1}{z^{-1} e^{\beta\epsilon_0 x} + 1} dx. \end{aligned} \tag{7.316}$$

Letting $y = x - 1$, this is

$$P = \frac{Cn\epsilon_0}{3} \int_0^\infty \frac{\left((y+1)^2 - 1\right)^{3/2}}{z^{-1} e^{\beta\epsilon_0 (y+1)} + 1} dy. \tag{7.317}$$

We could conceivable expand the numerators of each of these integrals in power series, which could then be evaluated as a sum of $f_\nu^+(z e^{-\beta\epsilon_0})$ terms.

Note that above the Fermi energy n also has an integral representation

$$\begin{aligned} n &= \left(2\left(\frac{1}{2}\right) + 1\right) \int_{\epsilon_0}^\infty d\epsilon \mathcal{D}(\epsilon) \frac{1}{z^{-1} e^{\beta\epsilon} + 1} \\ &= \frac{8\pi}{(ch)^3} \int_{\epsilon_0}^\infty d\epsilon \frac{\epsilon\sqrt{\epsilon^2 - \epsilon_0^2}}{z^{-1} e^{\beta\epsilon} + 1} \\ &= \frac{8\pi\epsilon_0^3}{(ch)^3} \int_0^\infty dy \frac{(y+1)\sqrt{(y+1)^2 - 1}}{z^{-1} e^{\beta\epsilon_0 (y+1)} + 1}, \end{aligned} \tag{7.318}$$

or

$$\boxed{n = \frac{3 n_0}{C}.} \tag{7.319}$$

Observe that we can use this result to remove the dependence of pressure on this constant C

$$\boxed{\frac{P}{n_0 \epsilon_0} = \int_0^\infty dy \frac{\left((y+1)^2 - 1\right)^{3/2}}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1}.} \tag{7.320}$$

Part c. Now for the average energy difference from the rest energy ϵ_0

$$\begin{aligned} U &= \langle \epsilon - \epsilon_0 \rangle \\ &= \int_{\epsilon_0}^\infty d\epsilon \mathcal{D}(\epsilon) f(\epsilon) (\epsilon - \epsilon_0) \\ &= \frac{8\pi V}{(ch)^3} \int_{\epsilon_0}^\infty d\epsilon \frac{\epsilon(\epsilon - \epsilon_0)\sqrt{\epsilon^2 - \epsilon_0}}{z^{-1} e^{\beta\epsilon} + 1} \\ &= \frac{8\pi V \epsilon_0^4}{(ch)^3} \int_0^\infty dy \frac{y(y-1)\sqrt{(y+1)^2 - 1}}{z^{-1} e^{\beta\epsilon} + 1}. \end{aligned} \tag{7.321}$$

So the average energy density difference from the rest energy, relative to the rest energy, is

$$\boxed{\frac{\langle \epsilon - \epsilon_0 \rangle}{V \epsilon_0} = 3 n_0 \int_0^\infty dy \frac{y(y+1)\sqrt{(y+1)^2 - 1}}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1}.} \tag{7.322}$$

Part d. From eq. (7.320) and eq. (7.322) we have

$$\begin{aligned} \frac{1}{n_0} &= 3 \frac{V \epsilon_0}{\langle \epsilon - \epsilon_0 \rangle} \int_0^\infty \frac{y(y+1)\sqrt{(y+1)^2 - 1} dy}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1} \\ &= \frac{\epsilon_0}{P} \int_0^\infty \frac{\left((y+1)^2 - 1\right)^{3/2}}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1} dy, \end{aligned} \tag{7.323}$$

or

$$PV = \frac{U}{3} \frac{\int_0^\infty \frac{\left((y+1)^2 - 1\right)^{3/2}}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1} dy}{\int_0^\infty \frac{y(y+1)\sqrt{(y+1)^2 - 1} dy}{z^{-1} e^{\beta \epsilon_0 (y+1)} + 1}}. \tag{7.324}$$

This ratio of integrals is supposed to resolve to 1 and 2 in the low and high density limits. To consider this let's perform one final non-dimensionalization, writing

$$\begin{aligned} x &= \beta\epsilon_0 y \\ \theta &= \frac{1}{\beta\epsilon_0} = \frac{k_{\mathrm{B}}T}{\epsilon_0} \\ \bar{\mu} &= \mu - \epsilon_0 \\ \bar{z} &= e^{\beta\bar{\mu}}. \end{aligned} \tag{7.325}$$

The density, pressure, and energy take the form

$$\frac{n}{n_0} = 3\theta \int_0^\infty dx \frac{(\theta x + 1)\sqrt{(\theta x + 1)^2 - 1}}{\bar{z}^{-1}e^x + 1} \tag{7.326a}$$

$$\frac{P}{n_0\epsilon_0} = \theta \int_0^\infty dx \frac{\left((\theta x + 1)^2 - 1\right)^{3/2}}{\bar{z}^{-1}e^x + 1} \tag{7.326b}$$

$$\frac{\langle \epsilon - \epsilon_0 \rangle}{V\epsilon_0 n_0} = 3\theta^2 \int_0^\infty dx \frac{x(\theta x + 1)\sqrt{(\theta x + 1)^2 - 1}}{\bar{z}^{-1}e^x + 1}. \tag{7.326c}$$

We can rewrite the square roots in the number density and energy density expressions by expanding out the completion of the square

$$\begin{aligned} (1 + \theta x)\sqrt{(1 + \theta x)^2 - 1} &= (1 + \theta x)\sqrt{1 + \theta x + 1}\sqrt{1 + \theta x - 1} \\ &= \sqrt{2\theta} x^{1/2}(1 + \theta x)\sqrt{1 + \frac{\theta x}{2}}, \end{aligned} \tag{7.327}$$

Expanding the distribution about $\bar{z}e^{-x} = 0$, we have

$$\frac{1}{\bar{z}^{-1}e^x + 1} = \frac{\bar{z}e^{-x}}{1 + \bar{z}e^{-x}} = ze^{-x}\sum_{s=0}^\infty (-1)^s \left(\bar{z}e^{-x}\right)^s, \tag{7.328}$$

allowing us to write, in the low density limit with respect to $\bar{z}$

$$\frac{n}{n_0} = 3\sqrt{2}\theta^{3/2}\sum_{s=0}^\infty (-1)^s \bar{z}^{s+1} \int_0^\infty dx x^{1/2}(1 + \theta x)\sqrt{1 + \frac{\theta x}{2}} e^{-x(1+s)}$$

(7.329a)

$$\frac{P}{n_0 \epsilon_0} = \theta \sum_{s=0}^{\infty} (-1)^s \bar{z}^{s+1} \int_0^{\infty} dx \left((\theta x + 1)^2 - 1 \right)^{3/2} e^{-x(1+s)} \tag{7.329b}$$

$$\frac{\langle \epsilon - \epsilon_0 \rangle}{V \epsilon_0 n_0} = 3\sqrt{2} \theta^{5/2} \sum_{s=0}^{\infty} (-1)^s \bar{z}^{s+1} \int_0^{\infty} dx x^{3/2} (1 + \theta x) \sqrt{1 + \frac{\theta x}{2}} e^{-x(1+s)}. \tag{7.329c}$$

Low density result An exact integration of the various integrals above is possible in terms of special functions. However, that attempt (included below) introduced an erroneous extra factor of θ. Given that this end result was obtained by tossing all but the lowest order terms in θ and $\bar{z}$, let's try that right from the get go.

For the pressure we have an integrand containing a factor

$$\begin{aligned} \left((\theta x + 1)^2 - 1 \right)^{3/2} &= (\theta x + 1 - 1)^{3/2} (\theta x + 1 + 1)^{3/2} \\ &= \theta^{3/2} x^{3/2} 2^{3/2} \left(1 + \frac{\theta x}{2} \right)^{3/2} \\ &= 2\sqrt{2} \theta^{3/2} x^{3/2} \left(1 + \frac{\theta x}{2} \right)^{3/2} \\ &\approx 2\sqrt{2} \theta^{3/2} x^{3/2} \end{aligned} \tag{7.330}$$

Our pressure, to lowest order in θ and $\bar{z}$ is then

$$\begin{aligned} \frac{P}{\epsilon_0 n_0} &= 2\sqrt{2} \theta^{5/2} \bar{z} \int_0^{\infty} x^{3/2} e^{-x} dx \\ &= 2\sqrt{2} \theta^{5/2} \bar{z} \Gamma(5/2). \end{aligned} \tag{7.331}$$

Our energy density to lowest order in θ and $\bar{z}$ from eq. (7.329c) is

$$\begin{aligned} \frac{U}{V \epsilon_0 n_0} &= 3\sqrt{2} \theta^{5/2} \bar{z} \int_0^{\infty} dx x^{3/2} e^{-x} \\ &= 3\sqrt{2} \theta^{5/2} \bar{z} \Gamma(5/2). \end{aligned} \tag{7.332}$$

Comparing these, we have

$$\frac{1}{\epsilon_0 n_0 \sqrt{2}\theta^{5/2}\bar{z}\Gamma(5/2)} = 3\frac{V}{U} = \frac{2}{P}, \tag{7.333}$$

or in this low density limit

$$\boxed{PV = \frac{2}{3}U.} \tag{7.334}$$

High density limit For the high density limit write $\bar{z} = e^y$, so that the distribution takes the form

$$f(\bar{z}) = \frac{1}{\bar{z}^{-1}e^x + 1} = \frac{1}{e^{x-y} + 1}. \tag{7.335}$$

This can be approximated by a step function, so that

$$\frac{P}{n_0\epsilon_0} \approx \int_0^y \theta dx \left((\theta x + 1)^2 - 1\right)^{3/2} \tag{7.336a}$$

$$\frac{U}{V\epsilon_0 n_0} \approx 3\int_0^\infty \theta dx \theta x(\theta x + 1)\sqrt{(\theta x + 1)^2 - 1}. \tag{7.336b}$$

With a change of variables $u = \theta x + 1$, we have

$$\begin{aligned}\frac{P}{n_0\epsilon_0} &\approx \int_1^{\theta y + 1x} du \left(u^2 - 1\right)^{3/2} \\ &= \frac{1}{8}\Bigg((2\theta y(\theta y + 2) - 3)\sqrt{\theta y(\theta y + 2)}(\theta y + 1) \\ &\qquad + 3\ln\left(\theta y + \sqrt{\theta y(\theta y + 2)} + 1\right)\Bigg) \\ &\approx \frac{1}{4}\left(\theta \ln \bar{z}\right)^4\end{aligned} \tag{7.337a}$$

$$\begin{aligned}\frac{U}{V\epsilon_0 n_0} &\approx 3\int_1^{\theta y + 1x} (u^2 - u)\sqrt{u^2 - 1} \\ &= \frac{3}{24}\Bigg(\sqrt{\theta y(\theta y + 2)}(\theta y(2\theta y(3\theta y + 5) - 1) + 3) \\ &\qquad - 3\left(\ln\left(\theta y + \sqrt{\theta y(\theta y + 2)} + 1\right)\right)\Bigg) \\ &\approx \frac{3}{4}\left(\theta \ln \bar{z}\right)^4\end{aligned} . \tag{7.337b}$$

Comparing both we have

$$\frac{4}{\epsilon_0 n_0 \left(\theta \ln \bar{z}\right)} = \frac{1}{P} = \frac{3V}{U}, \tag{7.338}$$

or

$$\boxed{PV = \frac{1}{3}U.} \tag{7.339}$$

Part e.

$$\begin{aligned}\epsilon_\mathrm{F}\big|_{n=1/(0.01)^3} &= 6.12402 \times 10^{-35}\mathrm{J} \times 6.24150934 \times 10^{18}\frac{\mathrm{eV}}{\mathrm{J}} \\ &= 3.82231 \times 10^{-16}\mathrm{eV}.\end{aligned} \tag{7.340}$$

Wow. That's pretty low!

Part f.

Pressure integral Of these the pressure integral is yields directly to Mathematica

$$\begin{aligned}&\int_0^\infty dx \left((\theta x+1)^2 - 1\right)^{3/2} e^{-x(1+s)} \\ &= \frac{3\theta e^{(s+1)/\theta}}{(s+1)^2} K_2\left(\frac{s+1}{\theta}\right) \\ &= \frac{3\sqrt{\frac{\pi}{2}}\theta^{3/2}}{(s+1)^{5/2}} + \frac{45\sqrt{\frac{\pi}{2}}\theta^{5/2}}{8(s+1)^{7/2}} + \frac{315\sqrt{\frac{\pi}{2}}\theta^{7/2}}{128(s+1)^{9/2}} - \frac{945\sqrt{\frac{\pi}{2}}\theta^{9/2}}{1024(s+1)^{11/2}} + \cdots\end{aligned} \tag{7.341}$$

where $K_2(z)$ is a modified Bessel function [23] of the second kind as plotted in fig. 7.42.

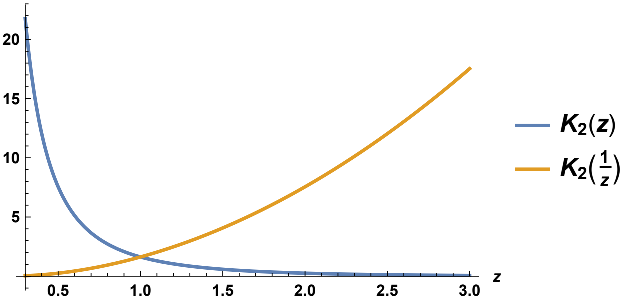


Figure 7.42: Modified Bessel function of the second kind.

Plugging this into the series for the pressure, we have

$$\frac{P}{n_0 \epsilon_0} = 3 \left(\frac{k_\mathrm{B} T}{\epsilon_0} \right)^2 \sum_{s=0}^{\infty} (-1)^s \frac{\left(\bar{z} e^{\epsilon_0 / k_\mathrm{B} T} \right)^{s+1}}{(s+1)^2} K_2\left((s+1) \epsilon_0 / k_\mathrm{B} T \right). \quad (7.342)$$

Plotting the summands $3(-1)^s \frac{\theta^2}{(s+1)^2} \left(\bar{z} e^{1/\theta} \right)^{s+1} K_2\left((s+1)/\theta \right)$ for $\bar{z} = 1$ in fig. 7.44 shows that this mix of exponential Bessel and quadratic terms decreases with s.

Plotting this sum in fig. 7.43 numerically to 10 terms, shows that we have a function that appears roughly polynomial in $\bar{z}$ and θ.

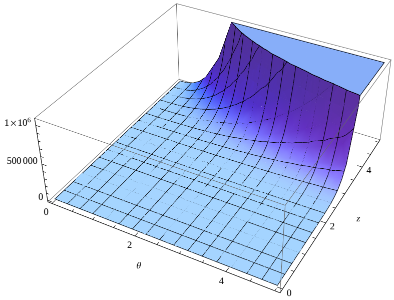


Figure 7.43: Pressure to ten terms in $\bar{z}$ and θ.

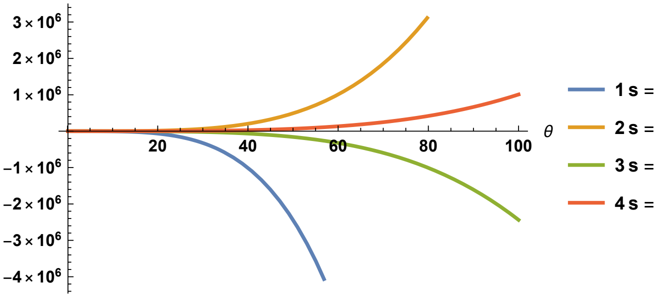


Figure 7.44: Pressure summands.

For small $\bar{z}$ it can be seen graphically that there is very little contribution from anything but the $s = 0$ term of this sum. An expansion in series for a few terms in $\bar{z}$ and θ gives us

$$\begin{aligned} \frac{P}{\epsilon_0 n_0} &= \sqrt{\pi} \theta^{5/2} \left(\frac{3\bar{z}}{\sqrt{2}} - \frac{3\bar{z}^2}{8} + \frac{\bar{z}^3}{3\sqrt{6}} - \frac{3\bar{z}^4}{32\sqrt{2}} + \frac{3\bar{z}^5}{25\sqrt{10}} \right) \\ &\quad + \sqrt{\pi} \theta^{7/2} \left(\frac{45\bar{z}}{8\sqrt{2}} \right) - \frac{45\bar{z}^2}{128} + \frac{5\bar{z}^3}{24\sqrt{6}} - \frac{45\bar{z}^4}{1024\sqrt{2}} + \frac{9\bar{z}^5}{200\sqrt{10}}. \end{aligned}$$

(7.343)

This allows a $k_\mathrm{B} T \ll mc^2$ and $\bar{z} \ll 1$ approximation of the pressure

$$\frac{P}{\epsilon_0 n_0} = \frac{3}{2}\sqrt{2\pi}\bar{z}\theta^{5/2}. \tag{7.344}$$

Number density integral For the number density, it appears that we can evaluate the integral using integration from parts applied to eq. (7.326)

$$\begin{aligned}
\frac{n}{n_0} &= \theta \int_0^\infty dx \frac{3(\theta x + 1)\sqrt{(\theta x + 1)^2 - 1}}{\bar{z}^{-1} e^x + 1} \\
&= \theta \int_0^\infty dx \left(\frac{d}{dx} \left((\theta x + 1)^2 - 1 \right)^{3/2} \right) \frac{1}{\bar{z}^{-1} e^x + 1} \\
&= \theta \left((\theta x + 1)^2 - 1 \right)^{3/2} \left. \frac{1}{\bar{z}^{-1} e^x + 1} \right|_0^\infty \\
&\quad - \theta \int_0^\infty dx \left((\theta x + 1)^2 - 1 \right)^{3/2} \frac{-\bar{z}^{-1} e^x}{\left(\bar{z}^{-1} e^x + 1 \right)^2} \\
&= \theta \int_0^\infty dx \left((\theta x + 1)^2 - 1 \right)^{3/2} \frac{\bar{z} e^{-x}}{(1 + \bar{z} e^{-x})^2}.
\end{aligned} \tag{7.345}$$

Expanding in series, gives us

$$\begin{aligned}
\frac{n}{n_0} &= \theta \sum_{s=0}^\infty \binom{-2}{s} \bar{z}^{s+1} \int_0^\infty dx \left((\theta x + 1)^2 - 1 \right)^{3/2} e^{-x(s+1)} \\
&= 3\theta^2 \sum_{s=0}^\infty \binom{-2}{s} \frac{\left(\bar{z} e^{1/\theta} \right)^{s+1}}{(s+1)^2} K_2 \left(\frac{s+1}{\theta} \right).
\end{aligned} \tag{7.346}$$

Here the binomial coefficient has the meaning given in the definitions of appendix K, where for negative integral values of b we have

$$\binom{b}{s} \equiv (-1)^s \frac{-b}{-b+s} \binom{-b+s}{-b}. \tag{7.347}$$

Expanding in series to a couple of orders in θ and $\bar{z}$ we have

$$\begin{aligned}
\frac{n}{n_0} &= \frac{\sqrt{2\pi}}{36} \theta^{1/2} \left(\left(2\sqrt{3}\bar{z} - 9/\sqrt{2} \right) \bar{z} + 18 \right) \bar{z} \\
&\quad + \frac{5\sqrt{2\pi}}{576} \theta^{3/2} \left(\left(4\sqrt{3}\bar{z} - 27/\sqrt{2} \right) \bar{z} + 108 \right) \bar{z} + \cdots
\end{aligned} \tag{7.348}$$

To first order in θ and $\bar{z}$ this is

$$\frac{n}{n_0} = \frac{1}{2}\sqrt{2\pi}\bar{z}\theta^{1/2}, \tag{7.349}$$

which allows a relation to pressure

$$PV = 3N(k_\mathrm{B}T)^2/\epsilon_0. \tag{7.350}$$

It's kind of odd seeming that this is quadratic in temperature. Is there an error?

Energy integral Starting from eq. (7.326c) and integrating by parts we have

$$\begin{aligned}
&\frac{\langle \epsilon - \epsilon_0 \rangle}{V\epsilon_0 n_0} \\
&= 3\theta^2 \int_0^\infty dx \frac{x(\theta x + 1)\sqrt{(\theta x + 1)^2 - 1}}{\bar{z}^{-1}e^x + 1} \\
&= -\theta^2 \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \frac{d}{dx}\left(\frac{x}{\bar{z}^{-1}e^x + 1}\right) \\
&= -\theta^2 \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \left(\frac{1}{\bar{z}^{-1}e^x + 1} - \frac{x\bar{z}^{-1}e^x}{\left(\bar{z}^{-1}e^x + 1\right)^2}\right) \\
&= \theta^2 \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \frac{(x-1)\bar{z}^{-1}e^x - 1}{\left(\bar{z}^{-1}e^x + 1\right)^2} \\
&= \theta^2 \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \frac{(x-1)\bar{z}e^{-x} - \bar{z}^2 e^{-2x}}{\left(1 + \bar{z}e^{-x}\right)^2} \\
&= \theta^2 \sum_{s=0}^\infty \binom{-2}{s} \times \\
&\quad \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \left((x-1)\bar{z}e^{-x} - \bar{z}^2 e^{-2x}\right) \left(\bar{z}e^{-x}\right)^s \\
&= \theta^2 \sum_{s=0}^\infty \binom{-2}{s} \bar{z}^{s+1} \times \\
&\quad \int_0^\infty dx \left((\theta x + 1)^2 - 1\right)^{3/2} \left((x-1)e^{-x(s+1)} - \bar{z}e^{-x(s+2)}\right).
\end{aligned} \tag{7.351}$$

The integral with the factor of x doesn't have a nice closed form as before (if you consider the K_2 a nice closed form), but instead evaluates to a confluent hypergeometric function [24]. That integral is

$$\int_0^\infty x\left((\theta x+1)^2-1\right)^{3/2} e^{-x(1+s)}dx = \frac{15\sqrt{\pi}\theta^3 U\left(-\frac{3}{2},-4,\frac{2(s+1)}{\theta}\right)}{8(s+1)^5}, \tag{7.352}$$

and looks like fig. 7.45. Series expansion shows that this hypergeometricU function has a $\theta^{3/2}$ singularity at the origin

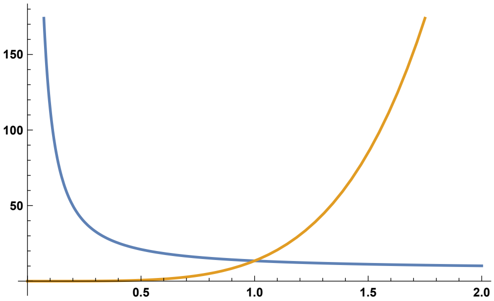


Figure 7.45: Plot of HypergeometricU, and with θ^5 scaling.

$$U\left(-\frac{3}{2},-4,\frac{2(s+1)}{\theta}\right) = \frac{2\sqrt{2}\sqrt{s+1}s+2\sqrt{2}\sqrt{s+1}}{\theta^{3/2}} + \frac{21\sqrt{s+1}}{2\sqrt{2}\sqrt{\theta}}+\cdots, \tag{7.353}$$

so our multiplication by θ^5 brings us to zero as seen in the plot. Evaluating the complete integral yields the unholy mess

$$\begin{aligned}\frac{\langle \epsilon - \epsilon_0 \rangle}{V \epsilon_0 n_0} = \sum_{s=0}^\infty \theta^2 (-1)^s (s+1) \bar{z}^{s+1} \times \\ \Bigg(& \frac{105 \sqrt{\pi} \theta^3 U\left(-\frac{1}{2}, -4, \frac{2(s+1)}{\theta}\right)}{16 (s+1)^5} - \frac{3 \sqrt{\pi} \theta^2 U\left(-\frac{1}{2}, -2, \frac{2(s+1)}{\theta}\right)}{2 (s+1)^3} \\ & - \frac{3 \sqrt{\pi} \theta^2 \bar{z} U\left(-\frac{1}{2}, -2, \frac{2(s+2)}{\theta}\right)}{2 (s+2)^3} \\ & + \frac{(\theta - 2)(-3\theta + 2s + 2) e^{\frac{s+1}{\theta}} K_2\left(\frac{s+1}{\theta}\right)}{\theta (s+1)^2} \\ & - \frac{2 (\theta - 2) e^{\frac{s+1}{\theta}} K_1\left(\frac{s+1}{\theta}\right)}{\theta (s+1)} + \frac{\bar{z} (-3\theta + 2s + 4) e^{\frac{s+2}{\theta}} K_2\left(\frac{s+2}{\theta}\right)}{(s+2)^2} \\ & - \frac{2 \bar{z} e^{\frac{s+2}{\theta}} K_1\left(\frac{s+2}{\theta}\right)}{s+2} \Bigg),\end{aligned} \tag{7.354}$$

to first order in $\bar{z}$ and θ this is

$$\frac{\langle \epsilon - \epsilon_0 \rangle}{V \epsilon_0 n_0} = \frac{9}{4} \sqrt{2\pi} \bar{z} \theta^{7/2}. \tag{7.355}$$

Comparing pressure and energy we have for low densities (where $\bar{z} \approx 0$)

$$\frac{1}{\epsilon_0 n_0 \sqrt{2\pi} \bar{z} \theta^{5/2}} = \frac{3}{2} \frac{1}{P} = \frac{9}{4} \theta \frac{V}{U}, \tag{7.356}$$

or

$$\theta P V = \frac{2}{3} U. \tag{7.357}$$

It appears that I've picked up an extra factor of θ somewhere, but at least I've got the $2/3$ low density expression. Given that I've Taylor expanded everything anyways around $\bar{z}$ and θ this could likely have been done right from the get go, instead of dragging along the messy geometric integrals. Reworking this part of this problem like that was done above.

Exercise 7.11 1D, 2D Bose-Einstein condensation (*2013 ps 7 p1*)

a. Obtain the density of states $N(\epsilon)$ in one and two dimensions for a particle with an energy-momentum relation

$$E_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}. \tag{7.358}$$

b. Using this, show that for particles whose number is conserved the BEC transition temperature vanishes in these cases - so we can always pick a chemical potential $\mu < 0$ which preserves a constant density at any temperature.

Answer for Exercise 7.11

Part a. We'd like to evaluate

$$\begin{aligned} N_d(\epsilon) &\equiv \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &\approx \frac{L^d}{(2\pi)^d} \int d^d\mathbf{k} \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right), \end{aligned} \tag{7.359}$$

We'll use

$$\delta(g(x)) = \sum_{x_0} \frac{\delta(x - x_0)}{|g'(x_0)|}, \tag{7.360}$$

where the roots of $g(x)$ are x_0. With

$$g(k) = \epsilon - \frac{\hbar^2 k^2}{2m}, \tag{7.361}$$

the roots k^* of $g(k) = 0$ are

$$k^* = \pm\sqrt{\frac{2m\epsilon}{\hbar^2}}. \tag{7.362}$$

The derivative of $g(k)$ evaluated at these roots are

$$\begin{aligned} g'(k^*) &= -\frac{\hbar^2 k^*}{m} \\ &= \mp \frac{\hbar^2}{m} \frac{\sqrt{2m\epsilon}}{\hbar} \\ &= \mp \frac{\hbar \sqrt{2m\epsilon}}{m}. \end{aligned} \tag{7.363}$$

In 2D, we can evaluate over a shell in k space

$$\begin{aligned} N_2(\epsilon) &= \frac{A}{(2\pi)^2} \int_0^\infty 2\pi k dk \left(\delta\left(k - k^*\right) + \delta\left(k + k^*\right)\right) \frac{m}{\hbar\sqrt{2m\epsilon}} \\ &= \frac{A}{2\pi} \cancel{k^*} \frac{m}{\hbar^2 \cancel{k^*}}, \end{aligned} \tag{7.364}$$

or

$$\boxed{N_2(\epsilon) = \frac{2\pi A m}{h^2}.} \tag{7.365}$$

In 1D we have

$$\begin{aligned} N_1(\epsilon) &= \frac{L}{2\pi} \int_{-\infty}^\infty dk \left(\delta\left(k - k^*\right) + \delta\left(k + k^*\right)\right) \frac{m}{\hbar\sqrt{2m\epsilon}} \\ &= \frac{2L}{2\pi} \frac{m}{\hbar\sqrt{2m\epsilon}}. \end{aligned} \tag{7.366}$$

Observe that this time for 1D, unlike in 2D when we used a radial shell in k space, we have contributions from both the delta function roots. Our end result is

$$\boxed{N_1(\epsilon) = \frac{2L}{h}\sqrt{\frac{m}{2\epsilon}}.} \tag{7.367}$$

Part b. To consider the question of the BEC temperature, we'll need to calculate the density. For the 2D case we have

$$\begin{aligned} \rho &= \frac{N}{A} \\ &= \frac{1}{A} A \int \frac{d^2\mathbf{k}}{(2\pi)^2} f(e_{\mathbf{k}}) \\ &= \frac{1}{A} \frac{2\pi A m}{h^2} \int_0^\infty d\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} - 1} \\ &= \frac{2\pi m}{h^2 \beta} \int_0^\infty dx \frac{1}{z^{-1} e^x - 1} \\ &= -\frac{2\pi m k_B T}{h^2} \ln(1 - z) \\ &= -\frac{1}{\lambda^2} \ln(1 - z). \end{aligned} \tag{7.368}$$

Recall for the 3D case that we had an upper bound as $z \rightarrow 1$. We don't have that for this 2D density, so for any value of $k_\mathrm{B}T > 0$, a corresponding value of z can be found. That is

$$z = 1 - e^{-\rho\lambda^2} = 1 - e^{-\rho h^4/(2\pi m k_\mathrm{B} T)^2}. \tag{7.369}$$

For the 1D case we have

$$\begin{aligned}
\rho &= \frac{N}{L} \\
&= \frac{1}{L} L \int \frac{dk}{2\pi} f(e_\mathbf{k}) \\
&= \frac{1}{L}\frac{2L}{h}\sqrt{\frac{m}{2}} \int_0^\infty d\epsilon \frac{1}{\sqrt{\epsilon}} \frac{1}{z^{-1}e^{\beta\epsilon} - 1} \\
&= \frac{1}{h}\sqrt{\frac{2m}{\beta}} \int_0^\infty \frac{x^{1/2-1}}{z^{-1}e^x - 1} \\
&= \frac{1}{h}\sqrt{\frac{2m}{\beta}} \Gamma(1/2) f^-_{1/2}(z),
\end{aligned} \tag{7.370}$$

or

$$\rho = \frac{1}{\lambda} f^-_{1/2}(z). \tag{7.371}$$

See fig. 7.46 for plots of $f^-_\nu(z)$ for $\nu \in \{1/2, 1, 3/2\}$, the respective results for the 1D, 2D and 3D densities respectively.

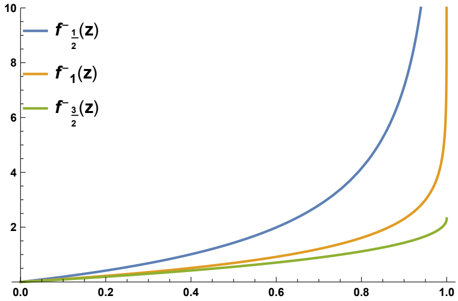


Figure 7.46: Density integrals for 1D, 2D and 3D cases.

We've found that $f^-_{1/2}(z)$ is also unbounded as $z \rightarrow 1$, so while we cannot invert this easily as in the 2D case, we can at least say that there will be some z for any value of $k_\mathrm{B}T > 0$ that allows the density (and thus the number of particles) to remain fixed.

Exercise 7.12 Estimating BEC transition temp. (*2013 ps7 p2*)

a. Find data for the atomic mass of liquid ^{4}He and its density at ambient atmospheric pressure and hence estimate its BEC temperature assuming interactions are unimportant (even though this assumption is a very bad one!).

b. For dilute atomic gases of the sort used in Professor Thywissen's lab , one typically has a cloud of 10^6 atoms confined to an approximate cubic region with linear dimension 1 μm. Find the density - it is pretty low, so interactions can be assumed to be extremely weak. Assuming these are ^{87} Rb atoms, estimate the BEC transition temperature.

Answer for Exercise 7.12

Part a. With an atomic weight of 4.0026, the mass in grams for one atom of Helium is

$$\begin{aligned} 4.0026\,\text{amu} \times \frac{\text{g}}{6.022 \times 10^{23}\text{amu}} &= 6.64 \times 10^{-24}\text{g} \\ &= 6.64 \times 10^{-27}\text{kg}. \end{aligned} \tag{7.372}$$

With the density of liquid ^{4}He, at 5.2K (boiling point): 125 grams per liter, the number density is

$$\begin{aligned} \rho &= \frac{\text{mass}}{\text{volume}} \times \frac{1}{\text{mass of one He atom}} \\ &= \frac{125\text{g}}{10^{-3}m^3} \times \frac{1}{6.64 \times 10^{-24}g} \\ &= \frac{125\text{g}}{10^{-3}m^3} \times \frac{1}{6.64 \times 10^{-24}g} \\ &= 1.88 \times 10^{28} m^{-3}. \end{aligned} \tag{7.373}$$

In class the T_{BEC} was found to be

$$\begin{aligned} T_{\text{BEC}} &= \frac{1}{k_{\text{B}}} \left(\frac{\rho}{\zeta(3/2)}\right)^{2/3} \frac{2\pi\hbar^2}{M} \\ &= \frac{1}{1.3806488 \times 10^{-23} m^2 kg/s^2/K} \left(\frac{\rho}{2.61238}\right)^{2/3} \times \\ &\quad \frac{2\pi(1.05457173 \times 10^{-34} m^2 kg/s)^2}{M} \\ &= 2.66824 \times 10^{-45} \frac{\rho^{2/3}}{M} K. \end{aligned} \tag{7.374}$$

So for liquid helium we have

$$\begin{aligned} T_{\text{BEC}} &= 2.66824 \times 10^{-45} \left(1.88 \times 10^{28}\right)^{2/3} \frac{1}{6.64 \times 10^{-27}} K \\ &= 2.84 K. \end{aligned} \tag{7.375}$$

Part b. The number density for the gas in Thywissen's lab is

$$\rho = \frac{10^6}{(10^{-6}\text{m})^3} = 10^{24} m^{-3}. \tag{7.376}$$

The mass of an atom of ^{87} Rb is

$$86.90\,\text{amu} \times \frac{10^{-3}\text{kg}}{6.022 \times 10^{23}\text{amu}} = 1.443 \times 10^{-25}\text{kg}, \tag{7.377}$$

which gives us

$$\begin{aligned} T_{\text{BEC}} &= 2.66824 \times 10^{-45} \left(10^{24}\right)^{2/3} \frac{1}{1.443 \times 10^{-25}} K \\ &= 1.85 \times 10^{-4} K. \end{aligned} \tag{7.378}$$

Exercise 7.13 Phonons in two dimensions (*2013 ps 7 p3*)

Consider phonons (quanta of lattice vibrations) which obey a dispersion relation

$$E_{\mathbf{k}} = \hbar v |\mathbf{k}|, \tag{7.379}$$

for small momenta $|\mathbf{k}|$, where v is the speed of sound. Assuming a two-dimensional crystal, phonons only propagate along the plane containing the atoms. Find the specific heat of this crystal due to phonons at low temperature. Recall that phonons are not conserved, so there is no chemical potential associated with maintaining a fixed phonon density.

Answer for Exercise 7.13

The energy density of the system is

$$\begin{aligned} \frac{E}{V} &= \int \frac{d^2\mathbf{k}}{(2\pi)^2} \frac{\epsilon}{e^{\beta\epsilon} - 1} \\ &= \int d\epsilon \frac{N(\epsilon)}{V} \frac{\epsilon}{e^{\beta\epsilon} - 1}. \end{aligned} \tag{7.380}$$

For the density of states we have

$$\begin{aligned}
\frac{N(\epsilon)}{V} &= \int \frac{d^2\mathbf{k}}{(2\pi)^2}\delta(\epsilon - \epsilon_{\mathbf{k}}) \\
&= \frac{1}{(2\pi)^2} 2\pi \int_0^\infty k dk \delta(\epsilon - \hbar v k) \\
&= \frac{1}{2\pi} \int_0^\infty k dk \delta\left(k - \frac{\epsilon}{\hbar v}\right) \frac{1}{\hbar v} \\
&= \frac{1}{2\pi} \frac{\epsilon}{(\hbar v)^2}.
\end{aligned} \tag{7.381}$$

Plugging back into the energy density we have

$$\begin{aligned}
\frac{E}{V} &= \frac{2\pi}{(\hbar v)^2} \int_0^\infty d\epsilon \frac{\epsilon^2}{e^{\beta\epsilon} - 1} \\
&= \frac{\pi \left(k_{\mathrm{B}} T\right)^3}{(\hbar v)^2} \zeta(3),
\end{aligned} \tag{7.382}$$

where $\zeta(3) \approx 2.40411$. Taking derivatives we have

$$\boxed{C_V = \frac{dE}{dT} = V \frac{3\pi k_{\mathrm{B}}^3 T^2}{(\hbar v)^2} \zeta(3).} \tag{7.383}$$

Exercise 7.14 Low temperature Fermi gas chemical potential

[13] §8.1 equation (33) provides an implicit function for $\mu \equiv k_{\mathrm{B}} T \ln z$

$$n = \frac{4\pi g}{3} \left(\frac{2m}{h^2}\right)^{3/2} \mu^{3/2} \left(1 + \frac{\pi^2}{8} \frac{(k_{\mathrm{B}} T)^2}{\mu^2} + \cdots\right), \tag{7.384}$$

or

$$\epsilon_{\mathrm{F}}^{3/2} = \mu^{3/2} \left(1 + \frac{\pi^2}{8} \frac{(k_{\mathrm{B}} T)^2}{\mu^2} + \cdots\right). \tag{7.385}$$

In class, we assumed that μ was quadratic in $k_{\mathrm{B}} T$ as a mechanism to invert this non-linear equation. Without making this quadratic assumption find the lowest order, non-constant approximation for $\mu(T)$.

Answer for Exercise 7.14

To determine an approximate inversion, let's start by multiplying eq. (7.385) by $\mu^{1/2}/\epsilon_{\mathrm{F}}^2$ to non-dimensionalize things

$$\left(\frac{\mu}{\epsilon_{\mathrm{F}}}\right)^{1/2} = \left(\frac{\mu}{\epsilon_{\mathrm{F}}}\right)^{2} + \frac{\pi^2}{8}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}, \tag{7.386}$$

or

$$\left(\frac{\mu}{\epsilon_{\mathrm{F}}}\right)^{1/2} = \frac{1}{1-\left(\frac{\mu}{\epsilon_{\mathrm{F}}}\right)^{3/2}}\frac{\pi^2}{8}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}. \tag{7.387}$$

If we are looking for an approximation in the neighborhood of $\mu = \epsilon_{\mathrm{F}}$, then the LHS factor is approximately one, whereas the fractional difference term is large (with a corresponding requirement for $k_{\mathrm{B}}T/\epsilon_{\mathrm{F}}$ to be small. We must then have

$$\left(\frac{\mu}{\epsilon_{\mathrm{F}}}\right)^{3/2} \approx 1 - \frac{\pi^2}{8}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}, \tag{7.388}$$

or

$$\begin{aligned}\mu &\approx \epsilon_{\mathrm{F}}\left(1 - \frac{\pi^2}{8}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}\right)^{2/3} \\ &\approx \epsilon_{\mathrm{F}}\left(1 - \frac{2}{3}\frac{\pi^2}{8}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}\right).\end{aligned} \tag{7.389}$$

This gives us the desired result

$$\boxed{\mu \approx \epsilon_{\mathrm{F}}\left(1 - \frac{\pi^2}{12}\left(\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}}\right)^{2}\right).} \tag{7.390}$$

Exercise 7.15 Relativistic spin zero BEC temp. (*2013 final, pr. 2*)

Consider a Bose gas with particles having no spin and obeying an ultra relativistic dispersion $E_{\mathbf{k}} = c|\mathbf{k}|$. Unlike photons or phonons, these particles are **conserved**, and hence we must determine the chemical potential μ which fixes their density. Working in three dimensions, show whether or not these particles will exhibit Bose condensation, and find T_c if it is nonzero.

Answer for Exercise 7.15

For the number of particles in the gas, as with photons, we still have

$$\begin{aligned}\langle N \rangle &= \sum_{\mathbf{k}} \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1} \\ &= \frac{1}{z^{-1} - 1} + \sum_{\mathbf{k} \neq 0} \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1}.\end{aligned} \tag{7.391}$$

As in the discussion of low velocity particles in [13] §7.1, the ground state term has been split out, before making any continuum approximation of the sum over the energetic states. Writing

$$\langle N \rangle = N_0 + N_e, \tag{7.392}$$

where the number of particles in the ground state is chemical potential and temperature dependent

$$N_0 = \frac{z}{1 - z}. \tag{7.393}$$

We proceed with the continuum approximation for the number of particles in the energetic states

$$\begin{aligned}N_e &= \sum_{\mathbf{k} \neq 0} \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1} \\ &\sim V \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{1}{z^{-1} e^{\beta \epsilon_{\mathbf{k}}} - 1} \\ &= \frac{4\pi V}{(2\pi)^3} \int_0^\infty k^2 dk \frac{1}{z^{-1} e^{\beta c k} - 1} \\ &= \frac{V}{2\pi^2} \left(\frac{1}{\beta c} \right)^3 \int_0^\infty x^2 dx \frac{1}{z^{-1} e^{x} - 1} \\ &= \frac{V}{2\pi^2} \left(\frac{1}{\beta c} \right)^3 \Gamma(3) g_3(z).\end{aligned} \tag{7.394}$$

So we have

$$N_e = \frac{V}{\pi^2} \left(\frac{k_{\mathrm{B}} T}{c} \right)^3 g_3(z) \le \frac{V}{\pi^2} \left(\frac{k_{\mathrm{B}} T}{c} \right)^3 \zeta(3). \tag{7.395}$$

Note that $\zeta(3) \approx 1.20206$, a fixed number. The key feature of Bose condensation remains. There is a finite limit to the number of particles that can be in the energetic state at a given temperature and volume. Any remaining particles are forced into the ground state.

In general the number of particles in the ground state is

$$N_0 = N - \frac{V}{\pi^2}\left(\frac{k_B T}{c}\right)^3 g_3(z), \tag{7.396}$$

and we will necessarily have particles in this state if

$$N - \frac{V}{\pi^2}\left(\frac{k_B T}{c}\right)^3 \zeta(3) > 0. \tag{7.397}$$

That temperature threshold $T \le T_c$ is the Bose condensation temperature

$$\boxed{k_B T_c = c\left(\frac{n\pi^2}{\zeta(3)}\right)^{1/3}.} \tag{7.398}$$

With $n = N/V$, $n_0 = N_0/V$, we have for the ground state average number density

$$n_0 = n\left(1 - \frac{g_3(z)}{\zeta(3)}\left(\frac{T}{T_c}\right)^3\right). \tag{7.399}$$

This is plotted in fig. 7.47.

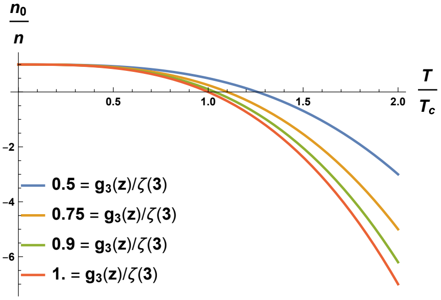


Figure 7.47: Ratio of ground state number density to total number density.

From the figure it appears that the notion of any sort of absolute condensation temperature is an approximation. We can start having particles go into the ground state at higher temperatures than

T_c, but once the chemical potential starts approaching zero, that temperature for which we start having particles in the ground state approaches T_c. The key takeout idea appears to be, once the temperature does drop below T_c, we necessarily start having a non-zero ground state population, and as the temperature drops more and more, the ratio of the number of particles in the ground state relative to the total approaches unity (all particles are forced into the ground state).

Exercise 7.16 Boson C_{V} above condensation temp. ([13] §7.1.37)

Equation 7.1.33 provides a relation for specific heat for a Bose gas

$$\frac{C_{\mathrm{V}}}{N k_{\mathrm{B}}} = \left(\frac{\partial}{\partial T} \left(\frac{3}{2} T \frac{g_{5/2}(z)}{g_{3/2}(z)} \right) \right)_v . \tag{7.400}$$

Fill in the details showing how this can be used to find

$$\frac{C_{\mathrm{V}}}{N k_{\mathrm{B}}} = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)}. \tag{7.401}$$

Answer for Exercise 7.16

With

$$g_{3/2}(z) = \frac{\lambda^3}{v} = \frac{h^3}{(2\pi m k_{\mathrm{B}} T)^{3/2}}, \tag{7.402}$$

we have for constant v

$$\left(\frac{\partial g_{3/2}}{\partial T} \right)_v = -\frac{3}{2} \frac{h^3}{(2\pi m k_{\mathrm{B}})^{3/2} T^{5/2}} = -\frac{3}{2T} g_{3/2}(z). \tag{7.403}$$

From the series expansion

$$g_\nu(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^\nu}, \tag{7.404}$$

we have

$$\begin{aligned} z \frac{\partial}{\partial z} g_\nu(z) &= z \sum_{k=1}^{\infty} k \frac{z^{k-1}}{k^\nu} \\ &= \sum_{k=1}^{\infty} \frac{z^k}{k^{\nu-1}} \\ &= g_{\nu-1}(z). \end{aligned} \tag{7.405}$$

Taken together we have

$$\begin{aligned}
-\frac{3}{2T}g_{3/2}(z) &= \left(\frac{\partial g_{3/2}}{\partial T}\right)_v \\
&= \left(\frac{\partial z}{\partial T}\right)_v \frac{\partial}{\partial z}g_{3/2}(z) \\
&= \frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_v z\frac{\partial}{\partial z}g_{3/2}(z) \\
&= \frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_v g_{1/2}(z),
\end{aligned} \tag{7.406}$$

or

$$\frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_v = -\frac{3}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}. \tag{7.407}$$

We are now ready to evaluate the derivative and find the specific heat

$$\begin{aligned}
\frac{C_{\mathrm{V}}}{Nk_{\mathrm{B}}} &= \left(\frac{\partial}{\partial T}\left(\frac{3}{2}T\frac{g_{5/2}(z)}{g_{3/2}(z)}\right)\right)_v \\
&= \frac{3}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} + \frac{3T}{2}\left(\frac{\partial z}{\partial T}\right)_v \frac{\partial}{\partial z}\left(\frac{g_{5/2}(z)}{g_{3/2}(z)}\right) \\
&= \frac{3}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9T}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}z\frac{\partial}{\partial z}\left(\frac{g_{5/2}(z)}{g_{3/2}(z)}\right) \\
&= \frac{3}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}\cancel{\frac{g_{3/2}(z)}{g_{3/2}(z)}} + \frac{9}{4}\frac{\cancel{g_{3/2}(z)}}{\cancel{g_{1/2}(z)}}\frac{g_{5/2}(z)\cancel{g_{1/2}(z)}}{\left(g_{3/2}(z)\right)^{\cancel{2}}} \\
&= \frac{3}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} + \frac{9}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} \\
&= \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}.
\end{aligned} \tag{7.408}$$

This is the desired result.

Exercise 7.17 Large volume Fermi gas density (*2013 final, pr. 1*)

a. Write down the expression for the grand canonical partition function Ω of an ideal three-dimensional Fermi gas with atoms having mass m at a temperature T and a chemical potential μ (or equivalently a fugacity $z = e^{\beta\mu}$). Consider the high temperature "classical limit" of this ideal gas, where $z \ll 1$ and one gets an effective Boltzmann distribution, and obtain the equation for the density of the particles

$$n = \frac{1}{V\beta}\frac{\partial \ln \Omega}{\partial \mu}, \tag{7.409}$$

by converting momentum sums into integrals. Invert this relationship to find the chemical potential μ as a function of the density n.
Hint: In the limit of a large volume V:

$$\sum_{\mathbf{k}} \rightarrow V \int \frac{d^3\mathbf{k}}{(2\pi)^3}. \tag{7.410}$$

Answer for Exercise 7.17

Part a. Since it was specified incorrectly in the original problem, let's start off by verifying the expression for the number of particles (and hence the number density)

$$\begin{aligned}
\frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \Omega &= \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \sum_N z^N e^{-\beta E_N} \\
&= \frac{1}{\beta}\frac{1}{\Omega}\frac{\partial}{\partial \mu}\sum_N z^N e^{-\beta E_N} \\
&= \frac{1}{\beta}\frac{1}{\Omega}\sum_N e^{-\beta E_N}\frac{\partial}{\partial \mu}e^{\mu\beta N} \\
&= \frac{1}{\Omega}\sum_N N z^N e^{-\beta E_N} \\
&= \langle N \rangle .
\end{aligned} \tag{7.411}$$

Moving on to the problem, we've seen that the Fermion grand canonical partition function can be written

$$\Omega = \prod_\epsilon \left(1 + z e^{-\beta\epsilon}\right), \tag{7.412}$$

so that our density is

$$\begin{aligned}
n &= \frac{N}{V} \\
&= \frac{1}{V\beta} \frac{\partial}{\partial \mu} \ln \prod_\epsilon \left(1 + z e^{-\beta\epsilon} \right) \\
&= \frac{1}{V\beta} \sum_\epsilon \frac{\partial}{\partial \mu} \ln \left(1 + z e^{-\beta\epsilon} \right) \\
&= \frac{1}{V\beta} \sum_\epsilon \frac{\partial z}{\partial \mu} \frac{e^{-\beta\epsilon}}{1 + z e^{-\beta\epsilon}} \\
&= \frac{1}{V} \sum_\epsilon z \frac{e^{-\beta\epsilon}}{1 + z e^{-\beta\epsilon}}.
\end{aligned} \tag{7.413}$$

In the high temperature classical limit, where $z \ll 1$ we have

$$\begin{aligned}
n &\approx \frac{1}{V} \sum_\epsilon z e^{-\beta\epsilon} \\
&\approx z \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-\beta\epsilon} \\
&= \frac{2z}{(2\pi)^2} \int_0^\infty k^2 dk e^{-\beta \frac{\hbar^2 k^2}{2m}} \\
&= \frac{z}{2\pi^2} \left(\frac{\beta \hbar^2}{2m} \right)^{-3/2} \int_0^\infty x^2 e^{-x^2} dx \\
&= \frac{z}{2\pi^2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{4} \\
&= \frac{z}{8\pi^{3/2}} \frac{\left(8\pi^2 m k_B T \right)^{3/2}}{h^3} \\
&= z \frac{(2\pi m k_B T)^{3/2}}{h^3}.
\end{aligned} \tag{7.414}$$

This is

$$\boxed{n = \frac{z}{\lambda^3},} \tag{7.415}$$

where

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \tag{7.416}$$

Inverting for μ we have

$$\mu = \frac{1}{\beta} \ln z, \tag{7.417}$$

or

$$\boxed{\mu = k_\mathrm{B} T \ln \left(n \lambda^3 \right) .} \tag{7.418}$$

A

CONDITIONAL PROBABILITY.

In [8] §1.5 while discussing statistical uncertainty is a mention of conditional probability. Once told that a die only rolls numbers up to four, we have a conditional probability for the die of

$$P(i|i \le 4) = \frac{P[iU(i \le 4)]}{P(i \le 4)} = \frac{\frac{1}{6}}{\frac{4}{6}} = \frac{1}{4}. \tag{A.1}$$

I was having trouble understanding the numerator in this expression. An initial confusion was, "what is this U". I came to the conclusion that this is just a typo, and was meant to be set intersection, as in

$$P(i|i \le 4) = \frac{P[i \cap (i \le 4)]}{P(i \le 4)} = \frac{\frac{1}{6}}{\frac{4}{6}} = \frac{1}{4}. \tag{A.2}$$

The denominator makes sense. I picture a sample space with 6 points as in fig. A.1

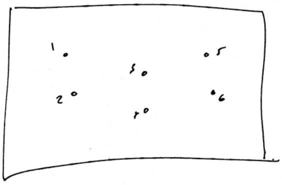


Figure A.1: Sample space for a die.

The points 1,2,3,4 represent the $i \le 4$ subspace, as in fig. A.2

So we have a 4/6 probability for that compound event.

I found it easy to get mixed up considering the numerator. I was envisioning, as in fig. A.3

a set of six intersecting with the set of points 1, 2, 3, 4, which is just that set of four. To clear up the confusion, imagine instead that we are asking about the probability of finding the $i = 2$ face in

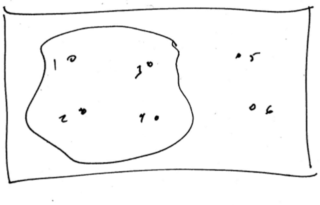


Figure A.2: $i \leq 4$ compound event.

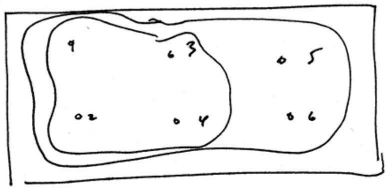


Figure A.3: Incorrect depiction of $i \cap (i \leq 4)$ compound event.

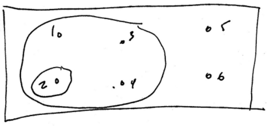


Figure A.4: Intersection of the $i = 2$ and $i \leq 4$ events.

the dice roll, given the fact that the die only rolls $i = 1, 2, 3, 4$. Our intersection sample space for that event is then shown in fig. A.4

The intersection is just the single point, so we have a $1/6$ probability for that compound event. The final result makes sense, since if we are looking for the probability for any of the $i = 1, 2, 3, 4$ events given that the die will only roll one of these values, we should have a value of $1/4$ as found through the compound probability formula.

OUTLINE OF MIDTERM I SOLUTIONS. B

1. Random walk

   This was a unit stepping problem as illustrated in fig. B.1.

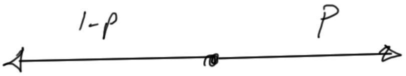


Figure B.1: Unit one dimensional random walk.

$$\langle X \rangle = \sum_i \langle x_i \rangle \tag{B.1}$$

$$\begin{aligned} \langle X^2 \rangle &= \left\langle \left(\sum_{i=1}^N x_i \right) \left(\sum_{j=1}^N x_i \right) \right\rangle \\ &= \left\langle \left(\sum_{i=1}^N x_i^2 \right) + \left(\sum_{i \neq j=1}^N x_i x_j \right) \right\rangle \end{aligned} \tag{B.2}$$

2. State and prove Liouville's theorem

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \frac{\partial \left(\dot{x}_i \rho \right)}{\partial x_i} + \frac{\partial \left(\dot{x}_i \rho \right)}{\partial x_i}. \tag{B.3}$$

3. Harmonic oscillator in 1D.

   This problem ends up essentially requiring the evaluation of the area in phase space of an ellipse in phase space as in fig. B.2.

   The result is of the form $\pi ab \times$ area (the exact expression should be that of eq. (4.142), with $N = 1$).

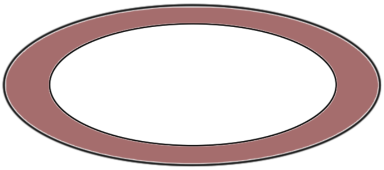


Figure B.2: 1D classical SHO phase space.

C

PHASE SPACE TRAJECTORIES FOR 1D SHO.

Let's review the 1D SHO to get a better feel for the ideas of phase space. Given a spring and mass system

$$F = -kx = -(\boldsymbol{\nabla}\phi)_x, \tag{C.1}$$

our potential is

$$\phi = \frac{1}{2}kx^2, \tag{C.2}$$

So, our Hamiltonian is

$$H = \frac{1}{2m}p^2 + \frac{1}{2}kx^2. \tag{C.3}$$

Hamilton's equations follow from $H = p\dot{x} - \mathcal{L}$

$$\frac{\partial H}{\partial p} = \dot{x} \tag{C.4a}$$

$$\frac{\partial H}{\partial x} = -\dot{p}. \tag{C.4b}$$

For the SHO this is

$$\frac{d}{dt}\begin{bmatrix} p \\ x \end{bmatrix} = \begin{bmatrix} -\frac{\partial H}{\partial x} \\ \frac{\partial H}{\partial p} \end{bmatrix} = \begin{bmatrix} -kx \\ p/m \end{bmatrix}. \tag{C.5}$$

It's convenient to non-dimensionalize this. Using $\omega = \sqrt{k/m}$, which has dimensions of $1/T$, we form

$$\begin{aligned}
\frac{d}{dt}\begin{bmatrix} p/m \\ \omega x \end{bmatrix} &= \begin{bmatrix} -(k/m)x \\ (\omega)p/m \end{bmatrix} \\
&= \omega \begin{bmatrix} -\omega x \\ p/m \end{bmatrix} \\
&= \omega \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} p/m \\ \omega x \end{bmatrix}
\end{aligned} \tag{C.6}$$

With definitions

$$i = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \tag{C.7a}$$

$$\mathbf{x} = \begin{bmatrix} p/m \\ \omega x \end{bmatrix}, \tag{C.7b}$$

the SHO Hamilton's equations are just

$$\boxed{\mathbf{x}' = i\omega\mathbf{x}.} \tag{C.8}$$

The solution follows immediately

$$\mathbf{x} = e^{i\omega t}\mathbf{x}_0. \tag{C.9}$$

We expect matrix exponential to have the structure of a rotation matrix, so let's write it out explicitly to see its structure

$$\begin{aligned} e^{i\omega t} &= I\cos(\omega t) + i\sin(\omega t) \\ &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \cos(\omega t) + \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \sin(\omega t) \\ &= \begin{bmatrix} \cos(\omega t) & -\sin(\omega t) \\ \sin(\omega t) & \cos(\omega t) \end{bmatrix}. \end{aligned} \tag{C.10}$$

In this non-dimensionalized phase space, with p/m on the horizontal axis and ωx on the vertical axis, this is a counterclockwise rotation. The (squared) radius of the rotation is

$$\begin{aligned} (p_0/m)^2 + (\omega x_0)^2 &= \frac{2}{m}\left(\frac{p_0^2}{m} + \frac{1}{2}\omega^2 m x_0^2\right) \\ &= \frac{2}{m}\left(\frac{p_0^2}{2m} + \frac{1}{2}k x_0^2\right) \\ &= \frac{2E}{m}. \end{aligned} \tag{C.11}$$

It makes sense to put the initial position in phase space in polar form too. We can write

$$\begin{bmatrix} p_0/m \\ \omega x_0 \end{bmatrix} = \sqrt{\frac{2E}{m}} e^{i\theta} \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \tag{C.12}$$

where

$$\theta = \text{atan}\left(\omega m \frac{x_0}{p_0}\right). \tag{C.13}$$

Now the non-dimensionalized phase space solution takes the particularly simple form

$$\boxed{\mathbf{x} = \sqrt{\frac{2E}{m}} e^{i(\omega t + \theta)} \begin{bmatrix} 1 \\ 0 \end{bmatrix}.} \tag{C.14}$$

Removing the non-dimensionalization Written explicitly, our momentum and position trace out, elliptical trajectories

$$p = p_0 \cos(\omega t) - \omega m x_0 \sin(\omega t) \tag{C.15a}$$

$$x = \frac{p_0}{m\omega} \sin(\omega t) + x_0 \cos(\omega t). \tag{C.15b}$$

With the initial phase space point specified as a rotation from the momentum axis as in eq. (C.13), this is just

$$p = \sqrt{\frac{2E}{m}} m \cos(\omega t + \theta) = \sqrt{2mE} \cos(\omega t + \theta) \tag{C.16a}$$

$$x = \sqrt{\frac{2E}{m}} \frac{1}{\omega} \sin(\omega t + \theta) = \sqrt{\frac{2E}{k}} \sin(\omega t + \theta). \tag{C.16b}$$

In fig. C.1 are trajectory plots for two different initial time pairs of phase space points (p_0, x_0), and (p_1, x_1). Roughly between these points a circular region of this phase space is plotted, with the same region plotted at a couple of other points in time. This shows the trajectory of a region of phase space. Observe that the area appears to visually be invariant, as we expect from Liouville's theorem. See shoPhaseSpacePlots.nb for an interactive way to play with this.

Observe that the rotation angle θ doesn't specify a geometric rotation of the ellipse. Instead, it is a function of the starting point of the elliptical trajectory through phase space.

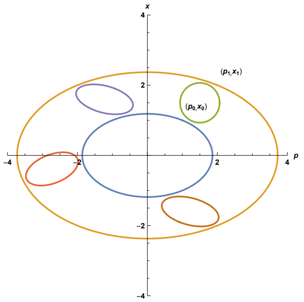


Figure C.1: A SHO phase space trajectory.

Aside. Complex representation of phase space points It's interesting to note that we can also work in a complex representation of phase space, instead of a matrix picture (for this 1D SHO problem).

$$\begin{aligned}\frac{d}{dt}\left(\frac{p}{m}+i\omega x\right) &= \omega\left(-\omega x+i\frac{p}{m}\right)\\ &= i\omega\left(\frac{p}{m}+i\omega x\right).\end{aligned} \tag{C.17}$$

Writing

$$z = \frac{p}{m} + i\omega x, \tag{C.18}$$

Hamilton's equations take the form

$$z' = i\omega z. \tag{C.19}$$

Again, we can read off the solution by inspection

$$z = e^{i\omega t} z_0. \tag{C.20}$$

The continuity equation Thinking back to the origin of the 3D continuity equation from fluid mechanics, we used the geometrical argument that any change to the mass in a volume had to leave through the boundary. This was

$$\frac{\partial}{\partial t}\int_V \rho dV = -\int_{\partial V} (\rho \mathbf{u}) \cdot \hat{\mathbf{n}} dA = -\int_V \boldsymbol{\nabla} \cdot (\rho \mathbf{u})\, dV. \tag{C.21}$$

We used Green's theorem above, allowing us to write, provided the volume is fixed

$$0 = \int_V \left(\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{u})\right) dV, \tag{C.22}$$

or

$$0 = \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{u}) \,. \tag{C.23}$$

Consider the following phase space picture fig. C.2. The time evolution of any individual particle (or set of particles that lie in the same element of phase space) is directed in the direction $(\dot{x}, \dot{p})$. So, the phase space density leaving through the surface is in proportion to the normal component of $\mathbf{j} = \rho(\dot{q}, \dot{p})$ (red in the figure).

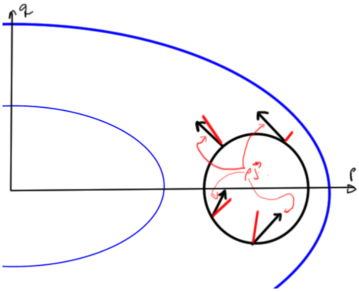


Figure C.2: Phase space current.

With this geometrical picture in mind, the $6N$ dimensional phase space equivalent of eq. (C.21), and a basis $\mathbf{e}_{i_\alpha}$ for the positions q_{i_α} and $\mathbf{f}_{i_\alpha}$ for the momentum components p_{i_α} is then

$$\begin{aligned} \frac{\partial}{\partial t} \int_{V_{6N}} \rho d^{3N} q d^{3N} p &= - \int_{\partial V_{6N}} \left(\rho \sum_{i_\alpha} \left(\mathbf{e}_{i_\alpha} \dot{q}_{i_\alpha} + \mathbf{f}_{i_\alpha} \dot{p}_{i_\alpha} \right) \right) \cdot \hat{\mathbf{n}} dA \\ &= - \int_{V_{6N}} d^{3N} q d^{3N} p \sum_{i_\alpha} \left(\frac{\partial (\rho \dot{q}_{i_\alpha})}{\partial q_{i_\alpha}} + \frac{\partial (\rho \dot{p}_{i_\alpha})}{\partial p_{i_\alpha}} \right) . \end{aligned} \tag{C.24}$$

Here dA is the surface area element for the phase space and $\hat{\mathbf{n}}$ is the unit normal to this surface. We have to assume the existence of a divergence theorem for the $6N$ dimensional space.

We can now regroup, and find for the integrand

$$0 = \frac{\partial \rho}{\partial t} + \sum_{i_\alpha} \left(\frac{\partial (\rho \dot{q}_{i_\alpha})}{\partial q_{i_\alpha}} + \frac{\partial (\rho \dot{p}_{i_\alpha})}{\partial p_{i_\alpha}} \right) , \tag{C.25}$$

which is the continuity equation. The assumptions that we have to make are that the flow of the density in phase space through the surface is proportional to the projection of the vector $\rho(\dot{q}_{i_\alpha}, \dot{p}_{i_\alpha})$, and then use the same old arguments (extended to a $6N$ dimensional space) as we did for the continuity equation for 3D masses.

THERMODYNAMIC IDENTITIES. D

Impressed with the clarity of Baez's entropic force discussion on differential forms [2], let's use that methodology to find all the possible identities that we can get from the thermodynamic identity (for now assuming N is fixed, ignoring the chemical potential.)

This isn't actually that much work to do, since a bit of editor regular expression magic can do most of the work.

Our starting point is the thermodynamic identity

$$dU = đQ + đW = TdS - PdV, \tag{D.1}$$

or

$$0 = dU - TdS + PdV. \tag{D.2}$$

It's quite likely that many of the identities that can be obtained will be useful, but this should at least provide a handy reference of possible conversions.

Differentials in P, V This first case illustrates the method.

$$\begin{aligned} 0 &= dU - TdS + PdV \\ &= \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \\ &- T\left(\left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV\right) + PdV \\ &= dP\left(\left(\frac{\partial U}{\partial P}\right)_V - T\left(\frac{\partial S}{\partial P}\right)_V\right) \\ &+ dV\left(\left(\frac{\partial U}{\partial V}\right)_P - T\left(\frac{\partial S}{\partial V}\right)_P + P\right). \end{aligned} \tag{D.3}$$

Taking wedge products with dV and dP respectively, we form two 2-forms

$$0 = dP \wedge dV\left(\left(\frac{\partial U}{\partial P}\right)_V - T\left(\frac{\partial S}{\partial P}\right)_V\right) \tag{D.4a}$$

$$0 = dV \wedge dP \left(\left(\frac{\partial U}{\partial V} \right)_P - T \left(\frac{\partial S}{\partial V} \right)_P + P \right). \tag{D.4b}$$

Since these must both be zero we find

$$\left(\frac{\partial U}{\partial P} \right)_V = T \left(\frac{\partial S}{\partial P} \right)_V \tag{D.5a}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_P - T \left(\frac{\partial S}{\partial V} \right)_P. \tag{D.5b}$$

Differentials in P, T

$$\begin{aligned} 0 &= dU - TdS + PdV \\ &= \left(\frac{\partial U}{\partial P} \right)_T dP + \left(\frac{\partial U}{\partial T} \right)_P dT \\ &\quad - T \left(\left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT \right) \\ &\quad + \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT, \end{aligned} \tag{D.6}$$

or

$$0 = \left(\frac{\partial U}{\partial P} \right)_T - T \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial V}{\partial P} \right)_T \tag{D.7a}$$

$$0 = \left(\frac{\partial U}{\partial T} \right)_P - T \left(\frac{\partial S}{\partial T} \right)_P + \left(\frac{\partial V}{\partial T} \right)_P. \tag{D.7b}$$

Differentials in P, S

$$\begin{aligned} 0 &= dU - TdS + PdV \\ &= \left(\frac{\partial U}{\partial P} \right)_S dP + \left(\frac{\partial U}{\partial S} \right)_P dS - TdS \\ &\quad + P \left(\left(\frac{\partial V}{\partial P} \right)_S dP + \left(\frac{\partial V}{\partial S} \right)_P dS \right), \end{aligned} \tag{D.8}$$

or

$$\left(\frac{\partial U}{\partial P} \right)_S = -P \left(\frac{\partial V}{\partial P} \right)_S \tag{D.9a}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_P + P \left(\frac{\partial V}{\partial S} \right)_P. \tag{D.9b}$$

Differentials in P, U

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= dU - T\left(\left(\frac{\partial S}{\partial P}\right)_U dP + \left(\frac{\partial S}{\partial U}\right)_P dU\right) \\ &+ P\left(\left(\frac{\partial V}{\partial P}\right)_U dP + \left(\frac{\partial V}{\partial U}\right)_P dU\right),\end{aligned} \tag{D.10}$$

or

$$0 = 1 - T\left(\frac{\partial S}{\partial U}\right)_P + P\left(\frac{\partial V}{\partial U}\right)_P \tag{D.11a}$$

$$T\left(\frac{\partial S}{\partial P}\right)_U = P\left(\frac{\partial V}{\partial P}\right)_U. \tag{D.11b}$$

Differentials in V, T

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \\ &- T\left(\left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT\right) + PdV,\end{aligned} \tag{D.12}$$

or

$$0 = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T + P \tag{D.13a}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V. \tag{D.13b}$$

Differentials in V, S

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS - TdS + PdV,\end{aligned} \tag{D.14}$$

or

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{D.15a}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V. \tag{D.15b}$$

Differentials in V, U

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= dU - T\left(\left(\frac{\partial S}{\partial V}\right)_U dV + \left(\frac{\partial S}{\partial U}\right)_V dU\right) \\ &+ P\left(\left(\frac{\partial V}{\partial V}\right)_U dV + \left(\frac{\partial V}{\partial U}\right)_V dU\right),\end{aligned} \tag{D.16}$$

or

$$0 = 1 - T\left(\frac{\partial S}{\partial U}\right)_V + P\left(\frac{\partial V}{\partial U}\right)_V \tag{D.17a}$$

$$T\left(\frac{\partial S}{\partial V}\right)_U = P\left(\frac{\partial V}{\partial V}\right)_U . \tag{D.17b}$$

Differentials in S, T

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= \left(\left(\frac{\partial U}{\partial S}\right)_T dS + \left(\frac{\partial U}{\partial T}\right)_S dT\right) - TdS \\ &+ P\left(\left(\frac{\partial V}{\partial S}\right)_T dS + \left(\frac{\partial V}{\partial T}\right)_S dT\right),\end{aligned} \tag{D.18}$$

or

$$0 = \left(\frac{\partial U}{\partial S}\right)_T - T + P\left(\frac{\partial V}{\partial S}\right)_T \tag{D.19a}$$

$$0 = \left(\frac{\partial U}{\partial T}\right)_S + P\left(\frac{\partial V}{\partial T}\right)_S . \tag{D.19b}$$

Differentials in S, U

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= dU - TdS + P\left(\left(\frac{\partial V}{\partial S}\right)_U dS + \left(\frac{\partial V}{\partial U}\right)_S dU\right),\end{aligned} \tag{D.20}$$

or

$$\frac{1}{P} = -\left(\frac{\partial V}{\partial U}\right)_S \tag{D.21a}$$

$$T = P\left(\frac{\partial V}{\partial S}\right)_U . \tag{D.21b}$$

Differentials in T, U

$$\begin{aligned}0 &= dU - TdS + PdV \\ &= dU - T\left(\left(\frac{\partial S}{\partial T}\right)_U dT + \left(\frac{\partial S}{\partial U}\right)_T dU\right) \\ &+ P\left(\left(\frac{\partial V}{\partial T}\right)_U dT + \left(\frac{\partial V}{\partial U}\right)_T dU\right),\end{aligned} \tag{D.22}$$

or

$$0 = 1 - T\left(\frac{\partial S}{\partial U}\right)_T + P\left(\frac{\partial V}{\partial U}\right)_T \tag{D.23a}$$

$$T\left(\frac{\partial S}{\partial T}\right)_U = P\left(\frac{\partial V}{\partial T}\right)_U. \tag{D.23b}$$

ADDITION OF TWO ONE HALF SPINS. E

In class an example of interacting spin was given where the Hamiltonian included a two spins dot product

$$H = \mathbf{S}_1 \cdot \mathbf{S}_2. \tag{E.1}$$

The energy eigenvalues for this Hamiltonian were derived by using the trick to rewrite this in terms of just squared spin operators

$$H = \frac{(\mathbf{S}_1 + \mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2}{2}. \tag{E.2}$$

For each of these terms we can calculate the total energy eigenvalues from

$$\mathbf{S}^2 \Psi = \hbar^2 S(S+1)\Psi, \tag{E.3}$$

where S takes on the values of the total spin for the (possibly composite) spin operator. Thinking about the spin operators in their matrix representation, it's not obvious to me that we can just add the total spins, so that if $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin operators for two respective particle, then the total system has a spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ (really $\mathbf{S} = \mathbf{S}_1 \otimes I_2 + I_1 \otimes \mathbf{S}_2$, since the respective spin operators only act on their respective particles).

Let's develop a bit of intuition on this, by calculating the energy eigenvalues of $\mathbf{S}_1 \cdot \mathbf{S}_2$ using Pauli matrices.

First lets look at how each of the Pauli matrices operate on the S_z eigenvectors

$$\sigma_x \left|+\right\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \left|-\right\rangle \tag{E.4a}$$

$$\sigma_x \left|-\right\rangle = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \left|+\right\rangle \tag{E.4b}$$

$$\sigma_y \left|+\right\rangle = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ i \end{bmatrix} = i \left|-\right\rangle \tag{E.4c}$$

$$\sigma_y \left|-\right\rangle = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} -i \\ 0 \end{bmatrix} = -i \left|+\right\rangle \tag{E.4d}$$

$$\sigma_z \left|+\right\rangle = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \left|+\right\rangle \tag{E.4e}$$

$$\sigma_z \left|-\right\rangle = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = - \begin{bmatrix} 0 \\ 1 \end{bmatrix} = - \left|-\right\rangle . \tag{E.4f}$$

Summarizing, these are

$$\sigma_x \left|\pm\right\rangle = \left|\mp\right\rangle \tag{E.5a}$$

$$\sigma_y \left|\pm\right\rangle = \pm i \left|\mp\right\rangle \tag{E.5b}$$

$$\sigma_z \left|\pm\right\rangle = \pm \left|\pm\right\rangle . \tag{E.5c}$$

For convenience let's avoid any sort of direct product notation, with the composite operations defined implicitly by

$$\begin{aligned} (S_{1k} \otimes S_{2k}) \left(\left|\alpha\right\rangle \otimes \left|\beta\right\rangle \right) &= S_{1k} S_{2k} \left|\alpha\beta\right\rangle \\ &= (S_{1k} \left|\alpha\right\rangle) \otimes \left(S_{2k} \left|\beta\right\rangle \right) . \end{aligned} \tag{E.6}$$

Now let's compute all the various operations

$$\begin{aligned} \sigma_{1x}\sigma_{2x} \left|++\right\rangle &= \left|--\right\rangle \\ \sigma_{1x}\sigma_{2x} \left|--\right\rangle &= \left|++\right\rangle \\ \sigma_{1x}\sigma_{2x} \left|+-\right\rangle &= \left|-+\right\rangle \\ \sigma_{1x}\sigma_{2x} \left|-+\right\rangle &= \left|+-\right\rangle \end{aligned} \tag{E.7a}$$

$$\begin{aligned}
\sigma_{1y}\sigma_{2y}\left|++\right\rangle &= i^2\left|--\right\rangle \\
\sigma_{1y}\sigma_{2y}\left|--\right\rangle &= (-i)^2\left|++\right\rangle \\
\sigma_{1y}\sigma_{2y}\left|+-\right\rangle &= i(-i)\left|-+\right\rangle \\
\sigma_{1y}\sigma_{2y}\left|-+\right\rangle &= (-i)i\left|+-\right\rangle
\end{aligned} \tag{E.7b}$$

$$\begin{aligned}
\sigma_{1z}\sigma_{2z}\left|++\right\rangle &= (-1)^2\left|--\right\rangle \\
\sigma_{1z}\sigma_{2z}\left|--\right\rangle &= \left|++\right\rangle \\
\sigma_{1z}\sigma_{2z}\left|+-\right\rangle &= -\left|-+\right\rangle \\
\sigma_{1z}\sigma_{2z}\left|-+\right\rangle &= -\left|+-\right\rangle .
\end{aligned} \tag{E.7c}$$

Tabulating first the action of the sum of the x and y operators we have

$$\begin{aligned}
\left(\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y}\right)\left|++\right\rangle &= 0 \\
\left(\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y}\right)\left|--\right\rangle &= 0 \\
\left(\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y}\right)\left|+-\right\rangle &= 2\left|-+\right\rangle \\
\left(\sigma_{1x}\sigma_{2x} + \sigma_{1y}\sigma_{2y}\right)\left|-+\right\rangle &= 2\left|+-\right\rangle
\end{aligned} \tag{E.8}$$

so that

$$\begin{aligned}
\mathbf{S}_1\cdot\mathbf{S}_2\left|++\right\rangle &= \left|++\right\rangle \\
\mathbf{S}_1\cdot\mathbf{S}_2\left|--\right\rangle &= \left|--\right\rangle \\
\mathbf{S}_1\cdot\mathbf{S}_2\left|+-\right\rangle &= 2\left|-+\right\rangle - \left|+-\right\rangle \\
\mathbf{S}_1\cdot\mathbf{S}_2\left|-+\right\rangle &= 2\left|+-\right\rangle - \left|-+\right\rangle .
\end{aligned} \tag{E.9}$$

Now we are set to write out the Hamiltonian matrix. Doing this with respect to the basis $\beta = \{\left|++\right\rangle, \left|--\right\rangle, \left|+-\right\rangle, \left|-+\right\rangle\}$, we have

$$\begin{aligned}
H &= \mathbf{S}_1\cdot\mathbf{S}_2 \qquad \text{(E.10)} \\
&= \frac{\hbar^2}{4}\begin{bmatrix}
\left\langle ++\right| H \left|++\right\rangle & \left\langle ++\right| H \left|--\right\rangle & \left\langle ++\right| H \left|+-\right\rangle & \left\langle ++\right| H \left|-+\right\rangle \\
\left\langle --\right| H \left|++\right\rangle & \left\langle --\right| H \left|--\right\rangle & \left\langle --\right| H \left|+-\right\rangle & \left\langle --\right| H \left|-+\right\rangle \\
\left\langle +-\right| H \left|++\right\rangle & \left\langle +-\right| H \left|--\right\rangle & \left\langle +-\right| H \left|+-\right\rangle & \left\langle +-\right| H \left|-+\right\rangle \\
\left\langle -+\right| H \left|++\right\rangle & \left\langle -+\right| H \left|--\right\rangle & \left\langle -+\right| H \left|+-\right\rangle & \left\langle -+\right| H \left|-+\right\rangle
\end{bmatrix} \\
&= \frac{\hbar^2}{4}\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 2 \\
0 & 0 & 2 & -1
\end{bmatrix} .
\end{aligned}$$

Two of the eigenvalues we can read off by inspection, and for the other two need to solve

$$\begin{aligned} 0 &= \begin{vmatrix} -\hbar^2/4 - \lambda & \hbar^2/2 \\ \hbar^2/2 & -\hbar^2/4 - \lambda \end{vmatrix} \\ &= (\hbar^2/4 + \lambda)^2 - (\hbar^2/2)^2, \end{aligned} \tag{E.11}$$

or

$$\begin{aligned} \lambda &= -\frac{\hbar^2}{4} \pm \frac{\hbar^2}{2} \\ &= \frac{\hbar^2}{4}, -\frac{3\hbar^2}{4}. \end{aligned} \tag{E.12}$$

These are the last of the triplet energy eigenvalues and the singlet value that we expected from the spin addition method. The eigenvectors for the $\hbar^2/4$ eigenvalue is given by the solution of

$$0 = \frac{\hbar^2}{2} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}, \tag{E.13}$$

so the eigenvector is

$$\frac{1}{\sqrt{2}} \left(\left|+-\right\rangle + \left|-+\right\rangle \right). \tag{E.14}$$

For our $-3\hbar^2/4$ eigenvalue we seek

$$0 = \frac{\hbar^2}{2} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}. \tag{E.15}$$

So the eigenvector is

$$\frac{1}{\sqrt{2}} \left(\left|+-\right\rangle - \left|-+\right\rangle \right). \tag{E.16}$$

An orthonormal basis with eigenvalues $\hbar^2/4(\times 3)$, and $-3\hbar^2/4$ is thus given by

$$\begin{aligned} \beta' = \Bigg\{ &\left|++\right\rangle, \left|--\right\rangle, \\ &\frac{1}{\sqrt{2}} \left(\left|+-\right\rangle + \left|-+\right\rangle \right), \frac{1}{\sqrt{2}} \left(\left|+-\right\rangle - \left|-+\right\rangle \right) \Bigg\}. \end{aligned} \tag{E.17}$$

Confirmation of spin additivity. Let's use this to confirm that for $H = (\mathbf{S}_1 + \mathbf{S}_2)^2$, the two spin 1/2 particles have a combined spin given by

$$S(S+1)\hbar^2. \tag{E.18}$$

With

$$(\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2, \tag{E.19}$$

we have for the $\hbar^2/4$ energy eigenstate of $\mathbf{S}_1 \cdot \mathbf{S}_2$

$$2\hbar^2 \frac{1}{2}\left(1 + \frac{1}{2}\right) + 2\frac{\hbar^2}{4} = 2\hbar^2, \tag{E.20}$$

and for the $-3\hbar^2/4$ energy eigenstate of $\mathbf{S}_1 \cdot \mathbf{S}_2$

$$2\hbar^2 \frac{1}{2}\left(1 + \frac{1}{2}\right) + 2\left(-\frac{3\hbar^2}{4}\right) = 0. \tag{E.21}$$

We get the $2\hbar^2$ and 0 eigenvalues respectively as expected.

LANGEVIN SMALL APPROXIMATION.

F

The Langevin function is given by

$$L(x) = \coth x - \frac{1}{x}. \tag{F.1}$$

According to [13], the small x approximation of this is

$$\frac{x}{3} - \frac{x^3}{45}. \tag{F.2}$$

Let's confirm this.

$$\begin{aligned}
L(x) &= \coth x - \frac{1}{x} \\
&= \frac{\cosh x}{\sinh x} - \frac{1}{x} \\
&= \left(\frac{\cosh x - (\sinh x)/x}{\sinh x} \right) \\
&= \frac{\left(1 + x^2/2! + x^4/4! + \cdots\right) - \left(1 + x^2/3! + x^4/5! + \cdots\right)}{\sinh x} \\
&= \frac{1}{\sinh x} \left(x^2 \left(\frac{1}{2!} - \frac{1}{3!} \right) + x^4 \left(\frac{1}{4!} - \frac{1}{5!} \right) + \cdots \right) \\
&= \frac{x^2 \left(\frac{1}{2!} - \frac{1}{3!}\right) + x^4 \left(\frac{1}{4!} - \frac{1}{5!}\right) + \cdots}{x + \frac{x^3}{3!} + \cdots} \\
&= \frac{x \left(\frac{1}{2!} - \frac{1}{3!}\right) + x^3 \left(\frac{1}{4!} - \frac{1}{5!}\right) + \cdots}{1 + \frac{x^2}{3!} + \cdots} \\
&\approx \left(x \left(\frac{1}{2!} - \frac{1}{3!} \right) + x^3 \left(\frac{1}{4!} - \frac{1}{5!} \right) + \cdots \right) \left(1 - \frac{x^2}{3!} - \frac{x^4}{5!} - \cdots \right) \\
&= x \left(\frac{1}{2!} - \frac{1}{3!} \right) + x^3 \left(\left(\frac{1}{4!} - \frac{1}{5!} \right) - \frac{1}{3!} \left(\frac{1}{2!} - \frac{1}{3!} \right) \right) + \cdots \\
&= x - \frac{x^3}{45} + \cdots
\end{aligned} \tag{F.3}$$

G

RELATIVISITIC STATISTICAL MECHANICS.

Motivation I was wondering how to generalize the arguments of [13] to relativistic systems. Here's a bit of blundering through the non-relativistic arguments of that text, tweaking them slightly.

I'm sure this has all been done before, but was a useful exercise to understand the non-relativistic arguments of Pathria better.

Generalizing from energy to four momentum Generalizing the arguments of §1.1.

Instead of considering that the total energy of the system is fixed, it makes sense that we'd have to instead consider the total four-momentum of the system fixed, so if we have N particles, we have a total four momentum

$$P = \sum_i n_i P_i = \sum n_i \left(\epsilon_i / c, \mathbf{p}_i \right), \tag{G.1}$$

where n_i is the total number of particles with four momentum P_i. We can probably expect that the n_i's in this relativistic system will be smaller than those in a non-relativistic system since we have many more states when considering that we can have both specific energies and specific momentum, and the combinatorics of those extra degrees of freedom. However, we'll still have

$$N = \sum_i n_i. \tag{G.2}$$

Only given a specific observer frame can these four-momentum components $(\epsilon_i/c, \mathbf{p}_i)$ be expressed explicitly, as in

$$\epsilon_i = \gamma_i m_i c^2 \tag{G.3a}$$

$$\mathbf{p}_i = \gamma_i m \mathbf{v}_i \tag{G.3b}$$

$$\gamma_i = \frac{1}{\sqrt{1 - \mathbf{v}_i^2/c^2}}, \tag{G.3c}$$

where $\mathbf{v}_i$ is the velocity of the particle in that observer frame.

Generalizing the number if microstates, and notion of thermodynamic equilibrium Generalizing the arguments of §1.2.

We can still count the number of all possible microstates, but that number, denoted $\Omega(N, V, E)$, for a given total energy needs to be parameterized differently. First off, any given volume is observer dependent, so we likely need to map

$$\begin{aligned} V &\rightarrow \int d^4x \\ &= \int dx^0 \wedge dx^1 \wedge dx^2 \wedge dx^3. \end{aligned} \tag{G.4}$$

Let's still call this V, but know that we mean this to be four volume element, bounded in both space and time, referred to a fixed observer's frame. So, lets write the total number of microstates as

$$\Omega(N, V, P) = \Omega\left(N, \int d^4x, E/c, P^1, P^2, P^3\right), \tag{G.5}$$

where $P = (E/c, \mathbf{P})$ is the total four momentum of the system. If we have a system subdivided into to two systems in contact as in fig. G.1, where the two systems have total four momentum P_1 and P_2 respectively.

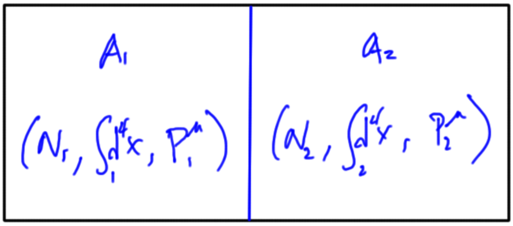


Figure G.1: Two physical systems in thermal contact.

In the text the total energy of both systems was written

$$E^{(0)} = E_1 + E_2, \tag{G.6}$$

so we'll write

$$P^{(0)\mu} = P_1^\mu + P_2^\mu = \text{constant}, \tag{G.7}$$

so that the total number of microstates of the combined system is now

$$\Omega^{(0)}(P_1, P_2) = \Omega_1(P_1)\Omega_2(P_2). \tag{G.8}$$

As before, if $\overline{P}_i^\mu$ denotes an equilibrium value of P_i^μ, then maximizing eq. (G.8) requires all the derivatives (no sum over μ here)

$$\begin{aligned} 0 &= \left(\frac{\partial \Omega_1(P_1)}{\partial P_1^\mu}\right)_{P_1=\overline{P_1}} \Omega_2(\overline{P}_2) \\ &+ \Omega_1(\overline{P}_1)\left(\frac{\partial \Omega_2(P_2)}{\partial P^\mu}\right)_{P_2=\overline{P_2}} \times \frac{\partial P_2^\mu}{\partial P_1^\mu}. \end{aligned} \tag{G.9}$$

With each of the components of the total four-momentum $P_1^\mu + P_2^\mu$ separately constant, we have $\partial P_2^\mu / \partial P_1^\mu = -1$, so that we have

$$\left(\frac{\partial \ln \Omega_1(P_1)}{\partial P_1^\mu}\right)_{P_1=\overline{P_1}} = \left(\frac{\partial \ln \Omega_2(P_2)}{\partial P^\mu}\right)_{P_2=\overline{P_2}}, \tag{G.10}$$

as before. However, we now have one such identity for each component of the total four momentum P which has been held constant. Let's now define

$$\beta_\mu \equiv \left(\frac{\partial \ln \Omega(N,V,P)}{\partial P^\mu}\right)_{N,V,P=\overline{P}}. \tag{G.11}$$

Our old scalar temperature is then

$$\begin{aligned} \beta_0 &= c\left(\frac{\partial \ln \Omega(N,V,P)}{\partial E}\right)_{N,V,P=\overline{P}} \\ &= c\beta \\ &= \frac{c}{k_\mathrm{B} T}, \end{aligned} \tag{G.12}$$

but now we have three additional such constants to figure out what to do with. A first start would be figuring out how the Boltzmann probabilities should be generalized.

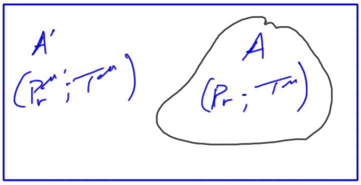


Figure G.2: A system A immersed in heat reservoir A'.

Equilibrium between a system and a heat reservoir Generalizing the arguments of §3.1.

As in the text, let's consider a very large heat reservoir A' and a subsystem A as in fig. G.2 that has come to a state of mutual equilibrium. This likely needs to be defined as a state in which the four vector β_μ is common, as opposed to just β_0 the temperature field being common.

If the four momentum of the heat reservoir is P'_r with P_r for the subsystem, and

$$P_r + P'_r = P^{(0)} = \text{constant}. \tag{G.13}$$

Writing

$$\Omega'(P_r^{\mu'}) = \Omega'(P^{(0)} - P_r^{\mu}) \propto P_r, \tag{G.14}$$

for the number of microstates in the reservoir, so that a Taylor expansion of the logarithm around $P'_r = P^{(0)}$ (with sums implied) is

$$\begin{aligned} \ln \Omega'(P_r^{\mu'}) &= \ln \Omega'(P^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial P^{\mu'}} \right)_{P' = P^{(0)}} \left(P^{(0)} - P^{\mu} \right) \\ &\approx \text{constant} - \beta'_\mu P^\mu. \end{aligned} \tag{G.15}$$

Here we've inserted the definition of β^μ from eq. (G.11), so that at equilibrium, with $\beta'_\mu = \beta_\mu$, we obtain

$$\begin{aligned} \Omega'(P_r^{\mu'}) &= \exp\left(-\beta_\mu P^\mu\right) \\ &= \exp\left(-\beta E\right) \exp\left(-\beta_1 P^1\right) \exp\left(-\beta_2 P^3\right) \exp\left(-\beta_3 P^3\right). \end{aligned} \tag{G.16}$$

Next steps This looks consistent with the outline provided in https://physics.stackexchange.com/a/4950/3621 by Lubos to the stackexchange "is there a relativistic quantum thermodynamics" question. Looking for references on these topics I found [16], which shows that I got the Boltzmann factor correct. However, it looks like study of relativistic fluid mechanics would be a good first step before attempting to further study this text. It is also formulated using the old Minkowski (imaginary time) style relativistic notation, which requires a bit of "translation" when reading. A more modern treatment can be found in [6], but this is a very inimidating text, with currents and the energy momentum tensor written in delta function current notation.

It would be interesting to explore these to look for an explaination of why non-relativistic stat mech can be used for photon problems, and also to find examples of what sort of problems this relativistic approach is required for. The domain of application for this relativistic theory appears to be cosmological (and perhaps also nuclear and high energy systems).

H

RELATIVISITIC DENSITY OF STATES.

Setup For photons and high velocity particles our non-relativistic density of states is insufficient. Let's redo these calculations for particles for which the energy is given by

$$\epsilon = \sqrt{\left(mc^2\right)^2 + (pc)^2}. \tag{H.1}$$

We want to convert a sum over momentum values to an energy integral

$$\begin{aligned} \mathcal{D}_3(\epsilon) &= \sum_{\mathbf{p}} \delta(\epsilon - \epsilon_{\mathbf{p}}) \\ &\rightarrow L^d \int \frac{d^d \mathbf{k}}{(2\pi)^d} \delta(\epsilon - \epsilon_{\mathbf{p}}) \\ &= L^d \int \frac{d^3 \mathbf{p}}{(2\pi \hbar)^d} \delta(\epsilon - \epsilon_{\mathbf{p}}) \\ &= L^d \int \frac{d^d (c\mathbf{p})}{(ch)^d} \delta(\epsilon - \epsilon_{\mathbf{p}}). \end{aligned} \tag{H.2}$$

Now we want to use

$$\delta(g(x)) = \sum_{x_0} \frac{\delta(x - x_0)}{\left|g'(x)\right|_{x=x_0}}, \tag{H.3}$$

where x_0 are the roots of $g(x)$. With

$$g(cp) = \epsilon - \sqrt{\left(mc^2\right)^2 + (cp)^2}. \tag{H.4}$$

Writing p^* for the roots we have

$$cp^* = \sqrt{\epsilon^2 - \left(mc^2\right)^2}. \tag{H.5}$$

Note that

$$\sqrt{\left(mc^2\right)^2 + (cp^*)^2} = \sqrt{\epsilon^2} = \epsilon. \tag{H.6}$$

we have

$$\begin{aligned}\left|g'(cp)\right|_{p=p^*} &= \frac{1}{2}\frac{2(cp^*)}{\sqrt{\left(mc^2\right)^2 + (cp^*)^2}} \\ &= \frac{\sqrt{\epsilon^2 - \left(mc^2\right)^2}}{\epsilon}.\end{aligned} \tag{H.7}$$

3D case We can now evaluate the density of states, and do the 3D case first. We have

$$\begin{aligned}\mathcal{D}_3(\epsilon) = \frac{V}{(ch)^3}\int_0^\infty & 4\pi(cp)^2 d(cp) \times \\ &\left(\delta\left(cp - \sqrt{\epsilon^2 - \left(mc^2\right)^2}\right)\right. \\ &\left.+\,\delta\left(cp + \sqrt{\epsilon^2 - \left(mc^2\right)^2}\right)\right)\frac{\sqrt{\epsilon^2 - \left(mc^2\right)^2}}{\epsilon}.\end{aligned} \tag{H.8}$$

Observe that in the switch to spherical coordinates in momentum space, our integration is now over a "radius" of momentum space, requiring just integration over the positive values. This will kill off one of our delta functions, leaving just

$$\mathcal{D}_3(\epsilon) = \frac{4\pi V}{(ch)^3}\left(\epsilon^2 - \left(mc^2\right)^2\right)\frac{\sqrt{\epsilon^2 - \left(mc^2\right)^2}}{\epsilon}, \tag{H.9}$$

or

$$\boxed{\mathcal{D}_3(\epsilon) = \frac{4\pi V}{(ch)^3}\frac{\left(\epsilon^2 - \left(mc^2\right)^2\right)^{3/2}}{\epsilon}.} \tag{H.10}$$

In particular, for very high energy particles where $\epsilon \gg \left(mc^2\right)$, our 3D density of states is

$$\boxed{\mathcal{D}_3(\epsilon) \approx \frac{4\pi V}{(ch)^3}\epsilon^2} \tag{H.11}$$

This is also the desired result for photons or other massless particles.

2D case For 2D we have

$$\begin{aligned}\mathcal{D}_2(\epsilon) = \frac{A}{(ch)^2}\int_0^\infty 2\pi|cp|d(cp)\frac{\sqrt{\epsilon^2-\left(mc^2\right)^2}}{\epsilon}\times \\ \left(\delta\left(cp-\sqrt{\epsilon^2-\left(mc^2\right)^2}\right)\right. \\ \left.+\,\delta\left(cp+\sqrt{\epsilon^2-\left(mc^2\right)^2}\right)\right).\end{aligned} \tag{H.12}$$

Note again that we are dealing with a "radius" over this shell of momentum space volume. This is a strictly positive value. That and the corresponding integration range is important in this case since including the negative range of cp would kill the entire density function because of the pair of delta functions. That wasn't the case in 3D, where it would have resulted in an off by two error instead. Continuing the evaluation we have

$$\mathcal{D}_2(\epsilon) = \frac{2\pi A}{(ch)^2}\sqrt{\epsilon^2-\left(mc^2\right)^2}\frac{\sqrt{\epsilon^2-\left(mc^2\right)^2}}{\epsilon}, \tag{H.13}$$

or

$$\boxed{\mathcal{D}_2(\epsilon) = \frac{2\pi A}{(ch)^2}\frac{\epsilon^2-\left(mc^2\right)^2}{\epsilon}.} \tag{H.14}$$

For an extreme relativistic gas where $\epsilon \gg mc^2$ (or photons where $m = 0$), we have

$$\boxed{\mathcal{D}_2(\epsilon) \approx \frac{2\pi A}{(ch)^2}\epsilon.} \tag{H.15}$$

1D case

$$\begin{aligned}\mathcal{D}_1(\epsilon) = \frac{L}{ch}\int d(cp)\frac{\sqrt{\epsilon^2-\left(mc^2\right)^2}}{\epsilon}\times \\ \left(\delta\left(cp-\sqrt{\epsilon^2-\left(mc^2\right)^2}\right)+\delta\left(cp+\sqrt{\epsilon^2-\left(mc^2\right)^2}\right)\right)\end{aligned} \tag{H.16}$$

We have to be a bit careful here. In this 1D case, we don't have to make a switch to spherical or cylindrical coordinates, and must include the effects of the second delta function, maintaining the full integration range over positive and negative values of cp. This gives us

$$\boxed{\mathcal{D}_1(\epsilon) = \frac{2L}{ch} \frac{\sqrt{\epsilon^2 - \left(mc^2\right)^2}}{\epsilon}.} \tag{H.17}$$

For $\epsilon \gg mc^2$ or $m = 0$ this reduces to

$$\boxed{\mathcal{D}_1(\epsilon) = \frac{2L}{ch}.} \tag{H.18}$$

Integration range Note that the integration range given a non-zero mass in the density of states has to be adjusted slightly, since the zero momentum ($\mathbf{p} = 0$) energy is $\epsilon = mc^2$. This gives

$$\begin{aligned} \sum_{\mathbf{k}} f(\mathbf{k}) &\rightarrow \int \frac{d^d\mathbf{k}}{(2\pi)^d} f(\mathbf{k}) \\ &\rightarrow \frac{1}{L^d} \int_{mc^2}^{\infty} d\epsilon D_d(\epsilon) f(\epsilon). \end{aligned} \tag{H.19}$$

I

VELOCITY AND MOMENTUM VOLUME ELEMENTS.

One of the problems I attempted had integrals over velocity space with volume element $d^3\mathbf{u}$. Initially I thought that I'd need a change of variables to momentum space, and calculated the corresponding momentum space volume element. Here's that calculation.

We are working with a Hamiltonian

$$\epsilon = \sqrt{(pc)^2 + \epsilon_0^2}, \tag{I.1}$$

where the rest energy is

$$\epsilon_0 = mc^2. \tag{I.2}$$

Hamilton's equations give us

$$u_\alpha = \frac{p_\alpha/c^2}{\epsilon}, \tag{I.3}$$

or

$$p_\alpha = \frac{mu_\alpha}{\sqrt{1 - \mathbf{u}^2/c^2}}. \tag{I.4}$$

This is enough to calculate the Jacobian for our volume element change of variables

$$\begin{aligned} du_x \wedge du_y \wedge du_z &= \frac{\partial(u_x, u_y, u_z)}{\partial(p_x, p_y, p_z)} dp_x \wedge dp_y \wedge dp_z \\ &= \frac{dp_x \wedge dp_y \wedge dp_z}{c^6 \left(m^2 + (\mathbf{p}/c)^2\right)^{9/2}} \times \\ &\begin{vmatrix} m^2c^2 + p_y^2 + p_z^2 & -p_y p_x & -p_z p_x \\ -p_x p_y & m^2c^2 + p_x^2 + p_z^2 & -p_z p_y \\ -p_x p_z & -p_y p_z & m^2c^2 + p_x^2 + p_y^2 \end{vmatrix} \\ &= m^2 \left(m^2 + \mathbf{p}^2/c^2\right)^{-5/2} dp_x \wedge dp_y \wedge dp_z. \end{aligned} \tag{I.5}$$

That final simplification of the determinant was a little hairy, but yielded nicely to Mathematica huang93relativisiticGas.nb .

Our final result for the velocity volume element in momentum space, in terms of the particle energy is

$$d^3\mathbf{u} = \frac{c^6 \epsilon_0^2}{\epsilon^5} d^3\mathbf{p}. \tag{I.6}$$

DISTRIBUTION AROUND MEAN ENERGY. J

In [13] is an expansion of

$$P(E) \propto e^{-\beta E} g(E), \tag{J.1}$$

around the mean energy $E^* = U$. The first derivative part of the expansion is simple enough

$$\begin{aligned} \frac{\partial}{\partial E}\left(e^{-\beta E} g(E)\right) &= \left(-\beta g(E) + g'(E)\right) e^{-\beta E} \\ &= g(E) e^{-\beta E} \left(-\beta + (\ln g(E))'\right). \end{aligned} \tag{J.2}$$

The peak energy E^* will be where this derivative equals zero. That is

$$0 = g(E^*) e^{-\beta E^*} \left(-\beta + (\ln g(E))'\big|_{E=E^*}\right), \tag{J.3}$$

or

$$\left.\frac{\partial}{\partial E} (\ln g(E))\right|_{E=E^*} = \beta. \tag{J.4}$$

With

$$S = k_\mathrm{B} \ln g \tag{J.5a}$$

$$\frac{1}{k_\mathrm{B}} \left(\frac{\partial S}{\partial E}\right)_{E=U} = \frac{1}{k_\mathrm{B} T} = \beta. \tag{J.5b}$$

We have

$$\left(\frac{\partial \ln g(E)}{\partial E}\right)_{E=U} = \beta, \tag{J.6}$$

so that

$$E^* = U. \tag{J.7}$$

So far so good. Reading the text, the expansion of the logarithm of $P(E)$ around $E = E^* = U$ wasn't clear. Let's write that out in full. To two terms that is

$$
\begin{aligned}
\ln e^{-\beta E} g(E) = \overset{-\beta U + \frac{1}{k_B} S}{\boxed{\ln e^{-\beta U} g(U)}} + \frac{\partial}{\partial E} \left(\ln e^{-\beta E} g(E) \right)\Bigg|_{E=U} \\
+ \frac{1}{2} \frac{\partial^2}{\partial E^2} \left(\ln e^{-\beta E} g(E) \right)\Bigg|_{E=U} (E - U)^2.
\end{aligned}
\tag{J.8}
$$

The first order term has the derivative of the logarithm of $e^{-\beta E} g(E)$. Since the logarithm is monotonic and the derivative of $e^{-\beta E} g(E)$ has been shown to be zero at $E = U$, this must be zero. We can also see this explicitly by computation

$$
\begin{aligned}
\frac{\partial}{\partial E} \ln e^{-\beta E} g(E)\Bigg|_{E=U} &= \frac{-\beta e^{-\beta E} g(E) + e^{-\beta E} g'(E)}{e^{-\beta E} g(E)}\Bigg|_{E=U} \\
&= \frac{-\beta g + g'}{g}\Bigg|_{E=U} \\
&= -\beta + (\ln g)'\big|_{E=U} \\
&= -\beta + \frac{1}{k_B} \frac{\partial S}{\partial E}\Bigg|_{E=U} \\
&= -\beta + \frac{1}{k_B T} \\
&= -\beta + \beta \\
&= 0.
\end{aligned}
\tag{J.9}
$$

For the second derivative we have

$$
\begin{aligned}
\frac{\partial}{\partial E} \ln e^{-\beta E} g(E)\Bigg|_{E=U} &= \frac{\partial}{\partial E} \left(-\beta + (\ln g)' \right)\Bigg|_{E=U} \\
&= \frac{\partial}{\partial E} \frac{g'}{g}\Bigg|_{E=U} \\
&= \frac{g''}{g} - \frac{(g')^2}{g^2}\Bigg|_{E=U} \\
&= \frac{g''}{g}\Bigg|_{E=U} - ((\ln g)')^2 \\
&= \frac{g''}{g}\Bigg|_{E=U} - \beta^2.
\end{aligned}
\tag{J.10}
$$

Somehow this is supposed to come out to $k_\mathrm{B} T^2 C_\mathrm{V}$? Backing up, we have

$$\begin{aligned}\left.\frac{\partial}{\partial E} \ln e^{-\beta E} g(E)\right|_{E=U} &= \left.\frac{\partial^2}{\partial E^2} \ln g\right|_{E=U} \\ &= \left.\frac{1}{k_\mathrm{B}} \frac{\partial^2 S}{\partial E^2}\right|_{E=U}.\end{aligned} \tag{J.11}$$

I still don't see how to get $C_\mathrm{V} = \partial U/\partial T$ out of this? C_V is a derivative with respect to temperature, but here we have derivatives with respect to energy (keeping $\beta = 1/k_\mathrm{B} T$ fixed)?

GENERAL BINOMIAL COEFFICIENTS. K

In [13] appendix §F was the use of binomial coefficients in a non-integral binomial expansion. This surprised me, since I'd never seen that before. However, on reflection, this is a very sensible notation, provided the binomial coefficients are defined in terms of the gamma function. Let's explore this little detail explicitly.

Taylor series We start with a Taylor expansion of

$$f(x) = (a + x)^b. \tag{K.1}$$

Our derivatives are

$$\begin{aligned} f'(x) &= b(a+x)^{b-1} \\ f''(x) &= b(b-1)(a+x)^{b-2} \\ f^3(x) &= b(b-1)(b-(3-1))(a+x)^{b-3} \\ &\vdots \\ f^k(x) &= b(b-1)\cdots(b-(k-1))(a+x)^{b-k}. \end{aligned} \tag{K.2}$$

Our Taylor series is then

$$(a+x)^b = \sum_{k=0}^{\infty} \frac{1}{k!} b(b-1)\cdots(b-(k-1))a^{b-k}x^k. \tag{K.3}$$

Note that if b is a positive integer, then all the elements of this series become zero at $b = k - 1$, or

$$(a+x)^b = \sum_{k=0}^{k} \frac{1}{k!} b(b-1)\cdots(b-(k-1))a^{b-k}x^k. \tag{K.4}$$

Gamma function Let's now relate this to the gamma function. From [1] §6.1.1 we have

$$\Gamma(z) = \int_0^{\infty} t^{z-1}e^{-t}dt. \tag{K.5}$$

Iteratively integrating by parts, we find the usual relation between gamma functions of integral separation

$$\begin{aligned}\Gamma(z+1) &= \int_0^\infty t^z e^{-t} dt \\ &= \int_0^\infty t^z d\left(\frac{e^{-t}}{-1}\right) \\ &= t^z \frac{e^{-t}}{-1}\bigg|_0^\infty - \int_0^\infty z t^{z-1} \frac{e^{-t}}{-1} dt \\ &= z \int_0^\infty t^{z-1} e^{-t} dt \\ &= z(z-1) \int_0^\infty t^{z-2} e^{-t} dt \\ &= z(z-1)(z-(3-1)) \int_0^\infty t^{z-3} e^{-t} dt \\ &= z(z-1)\cdots(z-(k-1)) \int_0^\infty t^{z-k} e^{-t} dt \\ &= z(z-1)\cdots(z-(k-1)) \int_0^\infty t^{(z+1-k)-1} e^{-t} dt,\end{aligned} \tag{K.6}$$

or

$$\Gamma(z+1) = z(z-1)\cdots(z-(k-1))\Gamma(z-(k-1)). \tag{K.7}$$

Flipping this gives us a nice closed form expression for the products of a number of positive unit separated values

$$z(z-1)\cdots(z-k) = \frac{\Gamma(z+1)}{\Gamma(z-(k-1))}. \tag{K.8}$$

Binomial coefficient for positive exponents and non-integer negative exponents Considering first positive exponents b, we can now use this in our Taylor expansion eq. (K.3)

$$\begin{aligned}(a+x)^b &= \sum_{k=0}^\infty \frac{1}{k!} \frac{\Gamma(b+1)}{\Gamma(b-k+1)} a^{b-k} x^k \\ &= \sum_{k=0}^\infty \frac{\Gamma(b+1)}{\Gamma(k+1)\Gamma(b-k+1)} a^{b-k} x^k.\end{aligned} \tag{K.9}$$

Observe that when b is a positive integer we have

$$\frac{\Gamma(b+1)}{\Gamma(k+1)\Gamma(b-k+1)} = \frac{b!}{k!\,(b-k)!} = \binom{b}{k}. \tag{K.10}$$

So for positive values of b, integer or otherwise, and negative non-integer values, we see that is then very reasonable to define the binomial coefficient explicitly in terms of the gamma function

$$\binom{b}{k} \equiv \frac{\Gamma(b+1)}{\Gamma(k+1)\Gamma(b-k+1)}. \tag{K.11}$$

If we do that, then the binomial expansion for non-integral values of b is simply

$$(a+x)^b = \sum_{k=0}^{\infty} \binom{b}{k} a^{b-k} x^k. \tag{K.12}$$

Binomial coefficient for negative integer exponents Using the relation eq. (K.11) blindly leads to some trouble, since $\Gamma(-|m|)$ goes to infinity for integer values of $m > 0$. We have to modify the definition of the binomial coefficient for negative integer values. Let's rewrite eq. (K.3) for negative integer values of $b = -m$ as

$$\begin{aligned}(a+x)^{-m} &= \sum_{k=0}^{\infty} \frac{1}{k!}(-m)(-m-1)\cdots(-m-(k-1))a^{-m-k}x^k \\ &= \sum_{k=0}^{\infty} \frac{1}{k!}(-1)^k m(m+1)\cdots(m+(k-1))a^{-m-k}x^k.\end{aligned} \tag{K.13}$$

Let's also put the ratio of gamma functions relation of eq. (K.8), in a slightly more general form. For $u, v > 0$, where $u - v$ is an integer, we can write

$$u(u-1)\cdots(v) = \frac{\Gamma(u+1)}{\Gamma(v)}. \tag{K.14}$$

Our Taylor series takes the form

$$\begin{aligned}(a+x)^{-m} &= \sum_{k=0}^{\infty} \frac{1}{k!}(-1)^k(m+k-1)(m+k-2)\cdots(m)a^{-m-k}x^k \\ &= \sum_{k=0}^{\infty}(-1)^k \frac{\Gamma(m+k)}{\Gamma(m)\Gamma(k+1)}a^{-m-k}x^k.\end{aligned} \tag{K.15}$$

We can now define, for negative integers $-m$

$$\binom{-m}{k} \equiv (-1)^k \frac{\Gamma(m+k)}{\Gamma(m)\Gamma(k+1)}. \tag{K.16}$$

With such a definition, our Taylor series takes the tidy form

$$(a+x)^{-m} = \sum_{k=0}^{\infty} \binom{-m}{k} a^{-m-k} x^k. \tag{K.17}$$

For negative integer values of $b = -m$, this is now consistent with eq. (K.12).

Observe that we can put eq. (K.16) into the standard binomial form with a bit of manipulation

$$\begin{aligned}\binom{-m}{k} &= (-1)^k \frac{\Gamma(m+k)}{\Gamma(m)\Gamma(k+1)} \\ &= (-1)^k \frac{(m+k-1)!}{(m-1)!\,k!} \\ &= (-1)^k \frac{m(m+k)!}{(m+k)m!\,k!},\end{aligned} \tag{K.18}$$

or

$$\binom{-m}{k} = (-1)^k \frac{m}{m+k} \binom{m+k}{m}. \tag{K.19}$$

L

FERMI-DIRAC EXPANSIONS.

In §8.1 of [13] are some Fermi-Dirac expansions for P, N, and U. Let's work through these in detail.

Our starting point is the relations

$$PV\beta = \ln \Omega = \sum \ln \left(1 + ze^{-\beta\epsilon}\right) \tag{L.1a}$$

$$N = \sum \frac{1}{z^{-1}e^{\beta\epsilon} + 1}. \tag{L.1b}$$

Recap. Density of states We'll employ the 3D non-relativistic density of states

$$\begin{aligned}
\mathcal{D}(\epsilon) &= \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\
&\sim V \int \frac{d^3\mathbf{k}}{(2\pi)^3} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\
&= \frac{4\pi V}{(2\pi)^3} \int dk k^2 \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right) \\
&= \frac{4\pi V}{(2\pi)^3} \int dk k^2 \frac{\delta\left(k - \sqrt{2m\epsilon}/\hbar\right)}{\frac{\hbar^2}{m}\frac{\sqrt{2m\epsilon}}{\hbar}} \\
&= \frac{2V}{(2\pi)^2} \frac{m}{\hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}},
\end{aligned} \tag{L.2}$$

or

$$\boxed{\mathcal{D}(\epsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}.} \tag{L.3}$$

Density Now let's make our integral approximation of the sum for N. That is

$$\begin{aligned}
N &= g \int d\epsilon \mathcal{D}(\epsilon) \frac{1}{z^{-1} e^{\beta\epsilon} + 1} \\
&= g \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{z^{-1} e^{\beta\epsilon} + 1} \\
&= g \frac{V}{(2\pi)^2 \beta^{3/2}} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty du \frac{u^{1/2}}{z^{-1} e^{u} + 1} \\
&= g \frac{V}{(2\pi)^2 \beta^{3/2}} \left(\frac{2m}{\hbar^2} \right)^{3/2} \Gamma(3/2) f_{3/2}(z) \\
&= g \frac{V}{(2\pi)^2 \beta^{3/2}} \frac{(2mk_\mathrm{B}T)^{3/2}}{\hbar^3} \frac{1}{2} \sqrt{\pi} f_{3/2}(z) \\
&= gV \cancel{2}\pi \frac{(2mk_\mathrm{B}T)^{3/2}}{h^3} \frac{1}{\cancel{2}} \sqrt{\pi} f_{3/2}(z),
\end{aligned} \tag{L.4}$$

or

$$\frac{N}{V} = g \frac{(2\pi m k_\mathrm{B} T)^{3/2}}{h^3} f_{3/2}(z). \tag{L.5}$$

With

$$\lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}}, \tag{L.6}$$

this gives us the desired density result from the text

$$\boxed{\frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z).} \tag{L.7}$$

Pressure For the pressure, we can do the same, but have to integrate by parts

$$\begin{aligned}
PV\beta &= g\sum \ln\left(1 + ze^{-\beta\epsilon}\right) \\
&\sim g\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\epsilon \epsilon^{1/2}\ln\left(1 + ze^{-\beta\epsilon}\right) \\
&= -g\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\epsilon\frac{2}{3}\epsilon^{3/2}\frac{-\beta ze^{-\beta\epsilon}}{1 + ze^{-\beta\epsilon}} \\
&= g\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{3}\frac{1}{\beta^{3/2}}\int_0^\infty dx\frac{x^{3/2}}{z^{-1}e^x + 1} \\
&= g\frac{2}{3}2\pi V\frac{(2mk_{\mathrm{B}}T)^{3/2}}{h^3}\Gamma(5/2)f_{5/2}(z) \\
&= g\frac{2}{3}2\pi V\frac{(2mk_{\mathrm{B}}T)^{3/2}}{h^3}\frac{3}{2}\frac{1}{2}\sqrt{\pi}f_{5/2}(z) \\
&= gV\frac{(2\pi mk_{\mathrm{B}}T)^{3/2}}{h^3}f_{5/2}(z),
\end{aligned} \tag{L.8}$$

or

$$\boxed{P\beta = \frac{g}{\lambda^3}f_{5/2}(z).} \tag{L.9}$$

Energy The average energy is the last thermodynamic quantity to come very easily. We have

$$\begin{aligned}
U &= -\frac{\partial}{\partial\beta}\ln\Omega \\
&= -\frac{\partial T}{\partial\beta}\frac{\partial}{\partial T}\ln\Omega \\
&= -\frac{\partial(1/k_{\mathrm{B}}T)}{\partial\beta}\frac{\partial}{\partial T}PV\beta \\
&= \frac{1}{k_{\mathrm{B}}\beta^2}\frac{\partial}{\partial T}\frac{gV}{\lambda^3}f_{5/2}(z) \\
&= gVk_{\mathrm{B}}T^2 f_{5/2}(z)\frac{\partial}{\partial T}\frac{(2\pi mk_{\mathrm{B}}T)^{3/2}}{h^3} \\
&= \frac{3}{2}\frac{gVk_{\mathrm{B}}T}{\lambda^3}f_{5/2}(z).
\end{aligned} \tag{L.10}$$

From eq. (L.7), we have

$$\frac{gV}{\lambda^3} = \frac{N}{f_{3/2}(z)}, \tag{L.11}$$

so the energy takes the form

$$\boxed{U = \frac{3}{2} N k_{\mathrm{B}} T \frac{f_{5/2}(z)}{f_{3/2}(z)}.} \tag{L.12}$$

We can compare this to the ratio of pressure to density

$$\frac{P\beta}{n} = \frac{f_{5/2}(z)}{f_{3/2}(z)}, \tag{L.13}$$

to find

$$\begin{aligned} U &= \frac{3}{2} N k_{\mathrm{B}} T \frac{P V \beta}{N} \\ &= \frac{3}{2} P V, \end{aligned} \tag{L.14}$$

or

$$\boxed{PV = \frac{2}{3} U.} \tag{L.15}$$

M

EULER-MACLAUREN SUMMATION.

Motivation In [13] I saw the Euler-summation formula casually used in a few places (§6.5.19, §8.3.44, §B.29), allowing an approximation of a sum with evaluations of the function and its derivatives at the origin. This rather powerful relationship was used in passing, and seemed like it was worth some exploration.

Bernoulli polynomials and numbers Before tackling Euler summation, we first need to understand some properties of Bernoulli polynomials [19] , and Bernoulli numbers [18]. The properties of interest required for the derivation of the Euler summation formula appear to follow fairly easily with the following choice for the definition of the Bernoulli polynomials $B_k(x)$ and Bernoulli numbers B_k

$$B_m(z) = \sum_{k=0}^{m} \binom{m}{k} B_k z^{m-k} \tag{M.1a}$$

$$0 = \sum_{k=0}^{m-1} \binom{m}{k} B_k \frac{1}{m!}, \qquad \text{m > 1.} \tag{M.1b}$$

It is conventional to fix $B_0 = 1$. Equation (M.1b) provides an iterative method to calculate all the higher Bernoulli numbers. Without calculating the Bernoulli numbers explicitly, we can relate these to the values of the polynomials at the origin

$$\boxed{B_m(0) = B_m.} \tag{M.2}$$

Now, let's calculate the first few of these, to verify that we've got the conventions right. Starting with $m = 2$ we have

$$\begin{aligned} 0 &= \sum_{k=0}^{1} \binom{2}{k} B_k \frac{1}{2!} \\ &= \frac{1}{2!} \left(B_0 + 2B_1 \right), \end{aligned} \tag{M.3}$$

or $B_1 = -1/2$. Next with $m = 3$

$$\begin{aligned} 0 &= \sum_{k=0}^{2} \binom{3}{k} B_k \frac{1}{3!} \\ &= \frac{B_0}{6} + \frac{B_1}{2} + \frac{B_2}{2} \\ &= \frac{1}{2}\left(\frac{1}{3} - \frac{1}{2} + B_2\right), \end{aligned} \tag{M.4}$$

or $B_2 = 1/6$. Thus the first few Bernoulli polynomials are

$$\begin{aligned} B_0(z) &= 1 \\ B_1(z) &= z - \frac{1}{2} \\ B_2(z) &= z^2 - z + \frac{1}{6}. \end{aligned} \tag{M.5a}$$

The Bernoulli polynomials have a simple relation to their derivative. Proceeding directly, taking derivatives we have

$$\begin{aligned} B'_m(z) &= \sum_{k=0}^{m-1} (m-k) \binom{m}{k} B_k z^{m-k-1} \\ &= \sum_{k=0}^{m-1} \frac{m!}{(m-k-1)!\,k!} B_k z^{m-k-1} \\ &= m \sum_{k=0}^{m-1} \frac{(m-1)!}{(m-1-k)!\,k!} B_k z^{m-1-k}, \end{aligned} \tag{M.6}$$

or

$$\boxed{B'_m(z) = m B_{m-1}(z)} \tag{M.7}$$

There's a number of difference relations that the polynomials satisfy. The one that we need is

$$\boxed{B_m(z+1) - B_m(z) = m z^{m-1}.} \tag{M.8}$$

To prepare for demonstrating this difference in general, let's perform this calculation for the specific cases of $m = 1$ and $m = 3$

to remove some of the index abstraction from the mix. For $m = 1$ we have

$$\begin{aligned} B_1(z+1) - B_1(z) &= \sum_{k=0}^{1} \binom{1}{k} B_k \left((z+1)^{1-k} - z^{1-k} \right) \\ &= B_0 \left((z+1)^1 - z^1 \right) + 1 B_1 \left((z+1)^0 - z^0 \right) \\ &= B_0 \\ &= 1. \end{aligned} \tag{M.9}$$

For $m = 3$ (a value of $m > 1$ that is representative) we have

$$\begin{aligned} B_3(z+1) - B_3(z) &= \sum_{k=0}^{3} \binom{3}{k} B_k \left((z+1)^{3-k} - z^{3-k} \right) \\ &= B_0 \left((z+1)^3 - z^3 \right) + 3B_1 \left((z+1)^2 - z^2 \right) \\ &\quad + 3B_2 \left((z+1)^1 - z^1 \right) + B_3 \left(\cancel{(z+1)^0 - z^0} \right) \\ &= B_0 \left(3z^2 + 3z + 1 \right) + 3B_1 (2z + 1) + 3B_2 \\ &= 3z^2 + z^1 (3 - 3) + z^0 \left(1 - \frac{3}{2} + \frac{3}{6} \right) \\ &= 3z^2. \end{aligned} \tag{M.10}$$

Evaluating this in general, we see that the term with the highest order Bernoulli number is immediately killed, and we'll have just one highest order monomial out of the mix. We expect all the remaining monomial terms to be killed term by term. That general difference is, for $m \ge 2$ is

$$\begin{aligned}
B_m(z+1) - B_m(z) &= \sum_{k=0}^{m-1} \binom{m}{k} B_k \left((z+1)^{m-k} - z^{m-k} \right) \\
&= \sum_{k=0}^{m-1} \binom{m}{k} B_k \sum_{s=0}^{m-k-1} \binom{m-k}{s} z^s \\
&= m! \sum_{s=0}^{m-1} \frac{z^s}{s!} \sum_{k=0}^{m-s-1} \frac{1}{\cancel{(m-k)!}k!} \frac{\cancel{(m-k)!}}{(m-k-s)!} B_k \\
&= \frac{m!}{(m-1)!} z^{m-1} \sum_{k=0}^{m-m+1-1} \frac{1}{k!\,(m-k-m+1)!} B_k \\
&\quad + m! \sum_{s=0}^{m-2} \frac{z^s}{s!} \sum_{k=0}^{m-s-1} \frac{1}{k!\,(m-k-s)!} B_k \\
&= m z^{m-1} \\
&\quad + m! \sum_{s=0}^{m-2} \frac{z^s}{s!} \left(\sum_{k=0}^{(m-s)-1} \binom{m-s}{s} B_k \frac{1}{(m-s)!} \right).
\end{aligned} \tag{M.11}$$

This last sum up to $m - s - 1$ has the form of eq. (M.1b), so is killed off. This proves eq. (M.8) as desired.

From this difference result we find for $m > 1$

$$\begin{aligned}
B_m(1) &= \sum_{k=0}^{m} \binom{m}{k} B_k \\
&= m! \sum_{k=0}^{m-1} \binom{m}{k} B_k \frac{1}{m!} + B_m \\
&= B_m,
\end{aligned} \tag{M.12}$$

and for $m = 1$

$$\begin{aligned}
B_1(1) &= 1 + B_1(0) \\
&= 1 - 1/2 \\
&= -B_1.
\end{aligned} \tag{M.13}$$

We find that either of the end points in the $[0, 1]$ interval provide us (up to a sign) with the Bernoulli numbers

$$\boxed{B_m(1) = \begin{cases} B_m & \text{if } m > 1 \\ -B_1 & \text{if } m = 1 \end{cases}} \tag{M.14}$$

Integrating eq. (M.7) after an $m \rightarrow m+1$ substitution, and comparing to the difference equation, we have

$$(m+1)z^m = B_{m+1}(z+1) - B_{m+1}(z) = (m+1)\int_z^{z+1} B_m(z)dz, \tag{M.15}$$

or

$$\boxed{\int_z^{z+1} B_m(z)dz = z^m.} \tag{M.16}$$

Evaluating this at $z = 0$ shows that our polynomials are odd functions around the center of the $[0,1]$ interval, or

$$\boxed{\int_0^1 B_m(z)dz = 0.} \tag{M.17}$$

We also obtain Bernoulli's sum of powers result

$$\begin{aligned}\int_0^n B_m(z)dz &= \int_0^1 B_m(z)dz + \int_1^2 B_m(z)dz + \cdots + \int_n^{n-1} B_m(z)dz \\ &= 0 + 1^m + 2^m + \cdots (n-1)^m,\end{aligned} \tag{M.18}$$

or

$$\boxed{\sum_{k=1}^{n-1} k^m = \int_1^n B_m(z)dz.} \tag{M.19}$$

We don't need this result for the Euler summation formula, but it's cool!

To arrive at some of these results I've followed, in part, portions of the approach outlined in [3]. That treatment however, starts by deriving some difference calculus results and uses associated generating functions for a more abstract difference equation related to the Bernoulli polynomials. In this summary of relationships above, I've attempted to avoid any requirement to first study the difference equation formalism (although that is also cool too, and not actually that difficult).

Euler-MacLauren summation Following wikipedia [20], we utilize the simple boundary conditions for the Bernoulli polynomials in the $[0, 1]$ interval. We can exploit these using integration by parts if we do a periodic extension of these polynomials in that interval.

Writing $\lfloor x \rfloor$ for the largest integer less than or equal to x, our periodical extension of the $[0, 1]$ interval Bernoulli polynomial is

$$P_m(x) = B_m\left(x = \lfloor x \rfloor\right). \tag{M.20}$$

From eq. (M.2) and eq. (M.14), our end points are

$$P_m(1) = \begin{cases} B_m(0) = B_m & \text{if } m > 1 \\ -B_1(0) = -B_1 & \text{if } m = 1 \end{cases} \tag{M.21}$$

Utilizing eq. (M.7) we can integrate by parts in a specific unit interval

$$\begin{aligned} \int_k^{k+1} f(x)dx &= \int_k^{k+1} f(x)P_0(x)dx \\ &= \int_k^{k+1} f(x)d\left(\frac{P_1(x)}{1}\right) \\ &= \left(f(x)P_1(x)\right)\Big|_k^{k+1} - \int_k^{k+1} f'(x)P_1(x)dx \\ &= -B_1 f(k+1) - B_1 f(k) - \int_k^{k+1} f'(x)P_1(x) \\ &= \frac{1}{2}\left(f(k+1) + f(k)\right) - \int_k^{k+1} f'(x)P_1(x). \end{aligned} \tag{M.22}$$

Summing gives us

$$\begin{aligned} \int_0^n f(x)dx &= \sum_{k=0}^{n-1} \int_k^{k+1} f(x)dx \\ &= \frac{1}{2}f(0) + \sum_{k=1}^{n-1} f(k) + f(n) - \int_0^n f'(x)P_1(x)dx, \end{aligned} \tag{M.23}$$

or

$$\sum_{k=0}^{n} f(k) = \int_0^n f(x)dx + \frac{1}{2}\left(f(0) + f(n)\right) - \int_0^n f'(x)P_1(x)dx. \tag{M.24}$$

Continuing the integration by parts we have

$$\begin{aligned}
\int_0^n f'(x)P_1(x)dx &= \sum_{k=0}^{n-1} \int_k^{k+1} f'(x)P_1(x)dx \\
&= \sum_{k=0}^{n-1} \int_k^{k+1} f'(x)d\left(\frac{P_2(x)}{2}\right) \\
&= \sum_{k=0}^{n-1} \frac{B_2}{2}\left(f'(k+1)-f'(k)\right) - \sum_{k=0}^{n-1} \int_k^{k+1} f''(x)\frac{P_2(x)}{2}dx \\
&= \frac{B_2}{2}\left(f'(n)-f'(0)\right) - \int_0^n f''(x)\frac{P_2(x)}{2}dx \\
&= \frac{B_2}{2}\left(f'(n)-f'(0)\right) - \frac{B_3}{3!}\left(f''(n)-f''(0)\right) \\
&\quad + \int_0^n f'''(x)\frac{P_3(x)}{3!}dx \\
&= \sum_{s=1}^{m}(-1)^{s-1}\frac{B_{s+1}}{(s+1)!}\left(f^s(n)-f^s(0)\right) \\
&\quad + (-1)^{m-1}\int_0^n f^m(x)\frac{P_m(x)}{m!}dx,
\end{aligned} \tag{M.25}$$

or

$$\boxed{\begin{aligned}
\sum_{k=0}^{n} f(k) &= \int_0^n f(x)dx + \frac{1}{2}\left(f(0)+f(n)\right) \\
&\quad + \sum_{s=1}^{m}(-1)^s\frac{B_{s+1}}{(s+1)!}\left(f^s(n)-f^s(0)\right) + (-1)^m\int_0^n f^m(x)\frac{P_m(x)}{m!}dx.
\end{aligned}} \tag{M.26}$$

N

HELPFUL FORMULAS.

Central limit theorem If $\langle x\rangle = \mu$ and $\sigma^2 = \left\langle x^2\right\rangle - \langle x\rangle^2$, and $X = \sum x$, then in the limit

$$\lim_{N\to\infty} P(X) = \frac{1}{\sigma\sqrt{2\pi N}} \exp\left(-\frac{(x-N\mu)^2}{2N\sigma^2}\right) \tag{N.1a}$$

$$\langle X\rangle = N\mu \tag{N.1b}$$

$$\left\langle X^2\right\rangle - \langle X\rangle^2 = N\sigma^2. \tag{N.1c}$$

Binomial distribution

$$P_N(X) = \begin{cases} \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N-X}{2}\right)!\left(\frac{N+X}{2}\right)!} & \text{if } X \text{ and } N \text{ have same parity} \\ 0 & \text{otherwise} \end{cases}, \tag{N.2}$$

where X was something like number of Heads minus number of Tails.

Generating function Given the Fourier transform of a probability distribution $\tilde{P}(k)$ we have

$$\left.\frac{\partial^n}{\partial k^n}\tilde{P}(k)\right|_{k=0} = (-i)^n \left\langle x^n\right\rangle \tag{N.3}$$

Handy mathematics

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \tag{N.4}$$

$$N! \approx \sqrt{2\pi N} N^N e^{-N} \tag{N.5}$$

$$\ln N! \approx \frac{1}{2}\ln 2\pi - N + \left(N + \frac{1}{2}\right)\ln N \approx N\ln N - N \tag{N.6}$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}dt \tag{N.7}$$

$$\Gamma(\alpha) = \int_0^\infty dy e^{-y}y^{\alpha-1} \tag{N.8}$$

$$\Gamma(\alpha+1) = \alpha\Gamma(\alpha) \tag{N.9}$$

$$\Gamma\left(1/2\right) = \sqrt{\pi} \tag{N.10}$$

$$\zeta(s) = \sum_{k=1}^\infty k^{-s} \tag{N.11}$$

$$\begin{aligned} \zeta(3/2) &\approx 2.61238 \\ \zeta(2) &\approx 1.64493 \\ \zeta(5/2) &\approx 1.34149 \\ \zeta(3) &\approx 1.20206 \end{aligned} \tag{N.12}$$

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin(\pi z)} \tag{N.13}$$

$$P(x,t) = \int_{-\infty}^\infty \frac{dk}{2\pi}\tilde{P}(k,t)\exp\left(ikx\right) \tag{N.14a}$$

$$\tilde{P}(k,t) = \int_{-\infty}^\infty dx P(x,t)\exp\left(-ikx\right) \tag{N.14b}$$

Heavyside theta

$$\Theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \tag{N.15a}$$

$$\frac{d\Theta}{dx} = \delta(x) \tag{N.15b}$$

$$\sum_{m=-l}^{l} a^m = \frac{a^{l+1/2} - a^{-(l+1/2)}}{a^{1/2} - a^{-1/2}} \tag{N.16a}$$

$$\sum_{m=-l}^{l} e^{bm} = \frac{\sinh(b(l+1/2))}{\sinh(b/2)} \tag{N.16b}$$

$$\int_{-\infty}^{\infty} q^{2N} e^{-aq^2} dq = \frac{(2N-1)!!}{(2a)^N} \sqrt{\frac{\pi}{a}} \tag{N.17a}$$

$$\int_{-\infty}^{\infty} e^{-aq^2} dq = \sqrt{\frac{\pi}{a}} \tag{N.17b}$$

$$\binom{-|m|}{k} = (-1)^k \frac{|m|}{|m|+k} \binom{|m|+k}{|m|} \tag{N.18}$$

$$\int_{0}^{\infty} d\epsilon \frac{\epsilon^3}{e^{\beta\epsilon} - 1} = \frac{\pi^4}{15\beta^4}, \tag{N.19}$$

volume in mD

$$V_m = \frac{\pi^{m/2} R^m}{\Gamma\left(m/2 + 1\right)} \tag{N.20}$$

area of ellipse

$$A = \pi a b \tag{N.21}$$

Radius of gyration of a 3D polymer With radius a, we have

$$r_N \approx a\sqrt{N} \tag{N.22}$$

Velocity random walk Find

$$\mathcal{P}_{N_c}(\mathbf{v}) \propto e^{-\frac{(\mathbf{v}-\mathbf{v}_0)^2}{2N_c}} \tag{N.23}$$

Random walk 1D Random walk

$$\mathcal{P}(x, t) = \frac{1}{2}\mathcal{P}(x + \delta x, t - \delta t) + \frac{1}{2}\mathcal{P}(x - \delta x, t - \delta t) \tag{N.24}$$

leads to

$$\frac{\partial \mathcal{P}}{\partial t}(x, t) = \frac{1}{2}\frac{(\delta x)^2}{\delta t}\frac{\partial^2 \mathcal{P}}{\partial x^2}(x, t) = D\frac{\partial^2 \mathcal{P}}{\partial x^2}(x, t) = -\frac{\partial J}{\partial x}, \tag{N.25}$$

The diffusion constant relation to the probability current is referred to as Fick's law

$$D = -\frac{\partial J}{\partial x} \tag{N.26}$$

with which we can cast the probability diffusion identity into a continuity equation form

$$\frac{\partial \mathcal{P}}{\partial t} + \frac{\partial J}{\partial x} = 0 \tag{N.27}$$

In 3D (with the Maxwell distribution frictional term), this takes the form

$$\mathbf{j} = -D\boldsymbol{\nabla}_{\mathbf{v}} c(\mathbf{v}, t) - \eta \mathbf{v} c(\mathbf{v}, t) \tag{N.28a}$$

$$\frac{\partial}{\partial t} c(\mathbf{v}, t) + \boldsymbol{\nabla}_{\mathbf{v}} \cdot \mathbf{j}(\mathbf{v}, t) = 0 \tag{N.28b}$$

Maxwell distribution Add a frictional term to the velocity space diffusion current

$$j_v = -D\frac{\partial c}{\partial v}(v, t) - \eta v c(v). \tag{N.29}$$

For steady state the continuity equation $0 = \frac{dc}{dt} = -\frac{\partial j_v}{\partial v}$ leads to

$$c(v) \propto \exp\left(-\frac{\eta v^2}{2D}\right). \tag{N.30}$$

We also find

$$\left\langle v^2 \right\rangle = \frac{D}{\eta}, \tag{N.31}$$

and identify

$$\frac{1}{2}m\left\langle \mathbf{v}^2 \right\rangle = \frac{1}{2}m\left(\frac{D}{\eta}\right) = \frac{1}{2}k_\mathrm{B} T \tag{N.32}$$

Hamilton's equations

$$\frac{\partial H}{\partial p} = \dot{x} \tag{N.33a}$$

$$\frac{\partial H}{\partial x} = -\dot{p} \tag{N.33b}$$

SHO

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 \tag{N.34a}$$

$$\omega^2 = \frac{k}{m} \tag{N.34b}$$

Quantum energy eigenvalues

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \tag{N.35}$$

Liouville's theorem

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \dot{x}\frac{\partial \rho}{\partial x} + \dot{p}\frac{\partial \rho}{\partial p} \\
&= \cdots \\
&= \frac{\partial \rho}{\partial t} + \frac{\partial\left(\dot{x}\rho\right)}{\partial x} + \frac{\partial\left(\dot{x}\rho\right)}{\partial p} \\
&= \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}_{x,p} \cdot (\rho\dot{x}, \rho\dot{p}) \\
&= \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{J} \\
&= 0,
\end{aligned} \tag{N.36}$$

Regardless of whether we have a steady state system, if we sit on a region of phase space volume, the probability density in that neighborhood will be constant.

Ergodic A system for which all accessible phase space is swept out by the trajectories. This and Liouville's theorem allows us to assume that we can treat any given small phase space volume as if it is equally probable to the same time evolved phase space region, and switch to ensemble averaging instead of time averaging.

Thermodynamics

$$dE = TdS - PdV + \mu dN \tag{N.37a}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{N.37b}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \tag{N.37c}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{V,E} \tag{N.37d}$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \tag{N.37e}$$

$$\begin{aligned}\mu &= \left(\frac{\partial E}{\partial N}\right)_{V,S} \\ &= \left(\frac{\partial F}{\partial N}\right)_{V,T}\end{aligned} \tag{N.37f}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} \tag{N.37g}$$

$$F = E - TS \tag{N.37h}$$

$$G = F + PV = E - TS + PV = \mu N \tag{N.37i}$$

$$H = E + PV = G + TS \tag{N.37j}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{N,V} \tag{N.37k}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P} \tag{N.37l}$$

$$dE = đW + đQ \tag{N.38}$$

Example (work on gas): $đW = -PdV$. Adiabatic: $đQ = 0$. Cyclic: $dE = 0$.

Microstates

$$\beta = \frac{1}{k_B T} \tag{N.39}$$

$$S = k_B \ln \Omega \tag{N.40}$$

$$\begin{aligned}\Omega(N, V, E) &= \frac{1}{h^{3N} N!} \int_V d\mathbf{x}_1 \cdots d\mathbf{x}_N \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \delta \left(E - \frac{\mathbf{p}_1^2}{2m} \cdots \right. \\ &\qquad \left. - \frac{\mathbf{p}_N^2}{2m} \right) \\ &= \frac{V^N}{h^{3N} N!} \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \delta \left(E - \frac{\mathbf{p}_1^2}{2m} \cdots - \frac{\mathbf{p}_N^2}{2m} \right)\end{aligned} \tag{N.41}$$

$$\Omega = \frac{d\gamma}{dE} \tag{N.42}$$

$$\gamma = \frac{V^N}{h^{3N} N!} \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \Theta \left(E - \frac{\mathbf{p}_1^2}{2m} \cdots - \frac{\mathbf{p}_N^2}{2m} \right) \tag{N.43}$$

quantum

$$\gamma = \sum_i \Theta(E - \epsilon_i) \tag{N.44}$$

Ideal gas

$$\Omega = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{E} \frac{1}{\Gamma(3N/2)} \tag{N.45}$$

$$S_{\text{ideal}} = k_B \left(N \ln \frac{V}{N} + \frac{3N}{2} \ln \left(\frac{4\pi m E}{3N h^2} \right) + \frac{5N}{2} \right) \tag{N.46}$$

Quantum free particle in a box

$$\Psi_{n_1,n_2,n_3}(x, y, z) = \left(\frac{2}{L} \right)^{3/2} \sin \left(\frac{n_1 \pi x}{L} \right) \sin \left(\frac{n_2 \pi x}{L} \right) \sin \left(\frac{n_3 \pi x}{L} \right) \tag{N.47a}$$

$$\epsilon_{n_1,n_2,n_3} = \frac{h^2}{8mL^2} \left(n_1^2 + n_2^2 + n_3^2 \right) \tag{N.47b}$$

$$\epsilon_k = \frac{\hbar^2 k^2}{2m}, \tag{N.47c}$$

Spin magnetization

$$\mu = \frac{\partial F}{\partial B} \tag{N.48}$$

moment per particle

$$m = \mu/N \tag{N.49}$$

spin matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{N.50a}$$

$$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{N.50b}$$

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{N.50c}$$

$l \geq 0, -l \leq m \leq l$

$$\mathbf{L}^2 \left| lm \right\rangle = l(l+1)\hbar^2 \left| lm \right\rangle \tag{N.51a}$$

$$L_z \left| lm \right\rangle = \hbar m \left| lm \right\rangle \tag{N.51b}$$

spin addition

$$S(S+1)\hbar^2 \tag{N.52}$$

Canonical ensemble classical

$$\Omega(N, E) = \frac{V}{h^3 N} \int d\mathbf{p}_1 e^{\frac{S}{k_\mathrm{B}}(N,E)} e^{-\frac{1}{k_\mathrm{B}}\left(\frac{\partial S}{\partial N}\right)_{E,V}} e^{-\frac{\mathbf{p}_1^2}{2mk_\mathrm{B}}\left(\frac{\partial S}{\partial E}\right)_{N,V}} \tag{N.53}$$

quantum

$$\Omega(E) \approx \sum_{m \in \mathrm{subsystem}} e^{\frac{1}{k_\mathrm{B}} S(E)} e^{-\beta \mathcal{E}_m} \tag{N.54a}$$

$$Z = \sum_m e^{-\beta \mathcal{E}_m} = \text{tr}\left(e^{-\beta \hat{H}_{\text{subsystem}}}\right) \tag{N.54b}$$

$$\langle E \rangle = \frac{\int H e^{-\beta H}}{\int e^{-\beta H}} \tag{N.55a}$$

$$\left\langle E^2 \right\rangle = \frac{\int H^2 e^{-\beta H}}{\int e^{-\beta H}} \tag{N.55b}$$

$$Z \equiv \frac{1}{h^{3N} N!} \int e^{-\beta H} \tag{N.55c}$$

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial (\beta F)}{\partial \beta} \tag{N.55d}$$

$$\sigma_{\text{E}}^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = k_{\text{B}} T^2 \frac{\partial \langle E \rangle}{\partial T} = k_{\text{B}} T^2 C_{\text{V}} \propto N \tag{N.55e}$$

$$Z = e^{-\beta(\langle E \rangle - TS)} = e^{-\beta F} \tag{N.55f}$$

$$F = \langle E \rangle - TS = -k_{\text{B}} T \ln Z \tag{N.55g}$$

Grand Canonical ensemble

$$S = -k_{\text{B}} \sum_{r,s} P_{r,s} \ln P_{r,s} \tag{N.56}$$

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\Omega} \tag{N.57a}$$

$$\Omega = \sum_{r,s} e^{-\alpha N_r - \beta E_s} = \sum_{r,s} z^{N_r} e^{-\beta E_s} = \sum_{N_r} z^{N_r} Z_{N_r} \tag{N.57b}$$

$$z = e^{-\alpha} = e^{\mu\beta} \tag{N.57c}$$

$$q = \ln \Omega = PV\beta \tag{N.57d}$$

$$\langle H \rangle = -\left(\frac{\partial q}{\partial \beta}\right)_{z,V} = k_\mathrm{B} T^2 \left(\frac{\partial q}{\partial \mu}\right)_{z,V} = \sum_\epsilon \frac{\epsilon}{z^{-1} e^{\beta\epsilon} \pm 1} \tag{N.57e}$$

$$\langle N \rangle = z \left(\frac{\partial q}{\partial z}\right)_{V,T} = \sum_\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} \pm 1} \tag{N.57f}$$

$$F = -k_\mathrm{B} T \ln \frac{\Omega}{z^N} \tag{N.57g}$$

$$\langle n_\epsilon \rangle = -\frac{1}{\beta} \left(\frac{\partial q}{\partial \epsilon}\right)_{z,T,\text{other}\,\epsilon} = \frac{1}{z^{-1} e^{\beta\epsilon} \pm 1} \tag{N.57h}$$

$$\begin{aligned} \operatorname{var}(N) &= \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} \\ &= -\frac{1}{\beta} \left(\frac{\partial \langle n_\epsilon \rangle}{\partial \epsilon}\right)_{z,T} \\ &= z^{-1} e^{\beta\epsilon} \end{aligned} \tag{N.58}$$

$$\mathcal{P} \propto e^{\frac{\mu}{k_\mathrm{B} T} N_S} e^{-\frac{E_S}{k_\mathrm{B} T}} \tag{N.59a}$$

$$\Omega = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{n_k, \sum n_m = N} e^{-\beta \sum_m n_m \epsilon_m} = \prod_k \left(\sum_{n_k} e^{-\beta(\epsilon_k - \mu) n_k} \right) \tag{N.59b}$$

$$\Omega^{\mathrm{QM}} = \mathrm{tr}_{\{\text{energy},N\}} \left(e^{-\beta(\hat{H} - \mu \hat{N})} \right) \tag{N.59c}$$

$$PV = \frac{2}{3} U \tag{N.60a}$$

$$f^{\pm}_{\nu}(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^{x} \pm 1} \tag{N.60b}$$

$$f^{\pm}_{\nu}(z \approx 0) = z \mp \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} \mp \frac{z^4}{4^\nu} + \cdots \tag{N.60c}$$

$$z \frac{d f^{\pm}_{\nu}(z)}{dz} = f^{\pm}_{\nu-1}(z) \tag{N.61}$$

$$\frac{d f^{\pm}_{3/2}(z)}{dT} = -\frac{3}{2T} f^{\pm}_{3/2}(z) f^{\pm}_{\nu-1}(z) \tag{N.62}$$

Fermions

$$\sum_{n_k=0}^{1} e^{-\beta(\epsilon_k - \mu)n_k} = 1 + e^{-\beta(\epsilon_k - \mu)} \tag{N.63}$$

$$N = (2S+1)V \int_0^{k_{\mathrm{F}}} \frac{4\pi k^2 dk}{(2\pi)^3} \tag{N.64}$$

$$k_{\mathrm{F}} = \left(\frac{6\pi^2 \rho}{2S+1} \right)^{1/3} \tag{N.65a}$$

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2}{2m} \left(\frac{6\pi\rho}{2S+1} \right)^{2/3} \tag{N.65b}$$

$$\mu = \epsilon_{\mathrm{F}} - \frac{\pi^2}{12} \frac{(k_{\mathrm{B}}T)^2}{\epsilon_{\mathrm{F}}} + \cdots \tag{N.66}$$

$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}} \tag{N.67}$$

$$\frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z) = \frac{g}{\lambda^3} \left(e^{\beta\mu} - \frac{e^{2\beta\mu}}{2^{3/2}} + \cdots \right) \tag{N.68}$$

(so $n = \frac{g}{\lambda^3} e^{\beta\mu}$ for large temperatures)

$$P\beta = \frac{g}{\lambda^3} f_{5/2}(z) \tag{N.69a}$$

$$U = \frac{3}{2} N k_{\mathrm{B}} T \frac{f_{5/2}(z)}{f_{3/2}(z)}. \tag{N.69b}$$

$$f_\nu^+(e^y) \approx \frac{y^\nu}{\Gamma(\nu+1)} \left(1 + 2\nu \sum_{j=1,3,5,\cdots} (\nu-1)\cdots(\nu-j) \left(1-2^{-j}\right) \frac{\zeta(j+1)}{y^{j+1}} \right) \tag{N.70}$$

$$\frac{C}{N} = \frac{\pi^2}{2} k_{\mathrm{B}} \frac{k_{\mathrm{B}} T}{\epsilon_{\mathrm{F}}} \tag{N.71a}$$

$$A = N k_{\mathrm{B}} T \left(\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)} \right) \tag{N.71b}$$

Bosons

$$\Omega = \prod_\epsilon \frac{1}{1 - z e^{-\beta\epsilon}} \tag{N.72}$$

$$P\beta = \frac{1}{\lambda^3} g_{5/2}(z) \tag{N.73}$$

$$U = \frac{3}{2} k_{\mathrm{B}} T \frac{V}{\lambda^3} g_{5/2}(z) \tag{N.74}$$

$$N_e = N - N_0 = N \left(\frac{T}{T_c} \right)^{3/2} \tag{N.75}$$

For $T < T_c$, $z = 1$.

$$g_\nu(1) = \zeta(\nu). \tag{N.76}$$

$$\sum_{n_k = 0}^{\infty} e^{-\beta(\epsilon_k - \mu) n_k} = \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}} \tag{N.77}$$

$$f_\nu^-(e^{-\alpha}) = \frac{\Gamma(1-\nu)}{\alpha^{1-\nu}} + \cdots \tag{N.78}$$

$$\begin{aligned}\rho\lambda^3 &= g_{3/2}(z) \\ &\le \zeta(3/2) \\ &\approx 2.612\end{aligned} \tag{N.79a}$$

$$k_B T_c = \left(\frac{\rho}{\zeta(3/2)}\right)^{2/3} \frac{2\pi\hbar^2}{m} \tag{N.79b}$$

BEC

$$\rho = \rho_{\mathbf{k}=0} + \frac{1}{\lambda^3} g_{3/2}(z) \tag{N.80a}$$

$$\rho_0 = \rho\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right) \tag{N.80b}$$

$$\frac{E}{V} \propto (k_B T)^{5/2} \tag{N.81a}$$

$$\frac{C}{V} \propto (k_B T)^{3/2} \tag{N.81b}$$

$$\frac{S}{N k_B} = \frac{5}{2}\frac{g_{5/2}}{g_{3/2}} - \ln z \Theta(T - T_c) \tag{N.81c}$$

Density of states Low velocities

$$N_1(\epsilon) = V \frac{m\hbar}{\hbar^2\sqrt{2m\epsilon}} \tag{N.82a}$$

$$N_2(\epsilon) = V \frac{m}{\hbar^2} \tag{N.82b}$$

$$N_3(\epsilon) = V\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2}\sqrt{\epsilon} \tag{N.82c}$$

relativistic

$$\mathcal{D}_1(\epsilon) = \frac{2L}{ch}\frac{\sqrt{\epsilon^2 - \left(mc^2\right)^2}}{\epsilon} \tag{N.83a}$$

$$\mathcal{D}_2(\epsilon) = \frac{2\pi A}{(ch)^2} \frac{\epsilon^2 - \left(mc^2\right)^2}{\epsilon} \tag{N.83b}$$

$$\mathcal{D}_3(\epsilon) = \frac{4\pi V}{(ch)^3} \frac{\left(\epsilon^2 - \left(mc^2\right)^2\right)^{3/2}}{\epsilon} \tag{N.83c}$$

O

MATHEMATICA NOTEBOOKS.

These Mathematica notebooks, some just trivial ones used to generate figures, others more elaborate, and perhaps some even polished, can be found in

https://github.com/peeterjoot/mathematica/tree/master/phy452/.

The free Wolfram CDF player, is capable of read-only viewing these notebooks to some extent.

- Dec 25, 2012 atleeJackson1_13.nb
- Jan 1, 2013 kittelCh2Fig1App.nb

  Use the labeling app for a figure
- Jan 1, 2013 kittelCh2Fig1.nb

  Output of kittelCh2Fig1App.nb
- Jan 10, 2013 lecture2Figures.nb

  Plots for lecture 2
- Jan 10, 2013 lecture2Fig7.nb

  Generated notebook for plot for lecture 2, figure 7
- Jan 13, 2013 normalizationCentralLimitTheoremVsBinomialLimitCheck.nb

  Check normalization of central limit theorem binomial fair coin result vs result given in class ... these are off by a factor of two
- Jan 19, 2013 attemptAtProblemSet2Problem1iiIntegrals.nb

  Plots and integrals for problem set II.
- Jan 30, 2013 statMechProblemSet3.nb

  problem set 3 calculations and figures

- Feb 2, 2013 shoPhaseSpacePlots.nb

  SHO elliptic plot. Have a Manipulate driven illustration of Liouville's theorem, showing the trajectory of an area in the phase space, allowing observation of the area invariance as it distorts around the path.

- Feb 6, 2013 binomialPlotsExactAndApprox.nb

  Plot of unfair coin binomial and the Gaussian approximation.

- Feb 10, 2013 kittelCh3Problem1Plots.nb

  Plots for chapter 3, problem 1. Used the new mathematica 9 PlotLegends, a bit better than the version 8 implementation, and now built in.

- Feb 10, 2013 cyclindrialMomenta.nb

  Jacobian transformation, for the change of vars for the volume element from Cartesian cylindrical coordinates.

- Feb 11, 2013 nVolumeTrickToCalculateAreaOfCircle.nb

  integration of $x^2 + y^2$ over a circular quadrant. Used as an example in the easy way hyper volume discussion

- Feb 11, 2013 sphericalPhaseSpaceChangeOfVars.nb

  Jacobian calculation for phase space change of vars, Cartesian to spherical. Also verifies the hand calculations for the momenta in spherical coordinates

- Feb 13, 2013 midtermQ4twoEqualMassesCollision.nb

  verify the collision of two equal masses statement made in class. Particles swap velocities. The other solution is that the final velocities equal the initial.

- Feb 23, 2013 problemSet4Problem2c.nb

  Problem set 4 stuff

- Feb 23, 2013 problemSet4Problem1.nb

  Problem set 4 stuff

- Feb 28, 2013 kittelRotationalPartition.nb

  Kittel problem 3.6 plots

- March 6, 2013 problemSet5Plots.nb

  plots and rough calculations for problem set 5

- March 6, 2013 problemSet5Problem3partD.nb

  plots and rough calculations for problem set 5

- March 10, 2013 midtermTwoQ1FinalSimplificationMu.nb

  Expand and simplify some hyperbolic products. This took a bit of coercion, surprising for a simple expression. To do the simplification, I had to use all of TrigToExp, Expand, Simplify, Numerator, Denominator, ExpandAll, ExpToTrig

- March 13, 2013 pathria_3_30.nb

  Plot and messy algebra bits for Pathria problem 3.30

- March 19, 2013 crudeAttemptsToPlotFermiOccupancy.nb

  Try to Plot the Fermi occupancy. This doesn't behave well numerically at low temperatures

- March 21, 2013 kittelZipper.nb

  Kittel zipper problem and plot. Found how to use Placed PlotLegends with Left, Top instead of Left, to get the legend into the figure for use in Save As.

- March 25, 2013 lecture16DensityPlot.nb

  Plot the period boundary conditions density. Used Mathematica Map, pure functions, Placed PlotLegends, ToString, Text, text concatonation operator

- March 27, 2013 largeTemperatureGaussianFermionDistributionIntegral.nb

  Lecture 16, Integral verification for thermal de Broglie lambda calculation.

- March 30, 2013 basicStatMechProblemSet6Problem2.nb

  Some rough calculations and plots that were discarded for ps6 p2. Mathematica functions of interest: Map, Evaluate, Flatten, pure functions, Assumptions

- April 1, 2013 basicStatMechProblemSet6Problem3.nb

  Numerical calculation for Nucleon energy

- April 2, 2013 lecture20PlotAndIntegral.nb

  Boltzmann indefinite integral

- April 3, 2013 basicStatMechProblemSet7.nb

  problem 1 Plots for occupation number averages. Another use of pure functions and Map, for both the set of functions to Plot and for the Text of the Placed PlotLegends. Problem 2 numerical calculations for Bose condensation temperatures.

- April 4, 2013 lecture21Plot.nb

  figure 2 plot

- April 4, 2013 huang93relativisiticGas.nb

  Lots of stuff, calculations and plots, for Huang 9.3 problem: relativistic gas

- April 17, 2013 negativeBinomial.nb

  Verify definition of negative integer binomial coefficient for an exponent value of -2. Used pattern matching /. for the first time in this notebook

- April 28, 2013 einsteinFunctionAndLowTempApproxPlot.nb

  Plot Einstein function and approx from Pathria equation 7.3.10

- April 28, 2013 pathriaIntegralsFor7_4_phononDriftVelocity.nb

  Pathria 7.4 integrals for calculation of mean phonon drift velocity

- April 28, 2013 stirlingError.nb

  Plots showing the relative error of a Stirling approximation

- April 30, 2013 spinZeroBoseCondensation.nb

  Plot for spinZeroBoseCondensation.tex, final exam reflection, problem 2

- Feb 18, 2019 lecture19f32Fig1.nb

  Plot lecture19f32Fig1

INDEX

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