
PHY452H1S Basic Statistical Mechanics. Problem Set 5: Temperature

1.1 Disclaimer

This is an ungraded set of answers to the problems posed.

Exercise 1.1 Polymer stretching - “entropic forces” (2013 problem set 5, 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).

- Using this, find the entropy of this polymer as $S = k_B \ln \Omega$. 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.
- Find the change in free energy of this polymer if we stretch this polymer from its end being at X to a larger distance $X + \Delta X$.
- 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 1.1

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

$$P_N(Y) = \begin{cases} \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N-Y}{2}\right)! \left(\frac{N+Y}{2}\right)!} & \text{if } Y \text{ and } N \text{ have same parity} \\ 0 & \text{otherwise} \end{cases} \quad (1.1)$$

For an individual coin tosses we have averages $\langle Y_1 \rangle = 0$, and $\langle Y_1^2 \rangle = 1$, so the central limit theorem provides us with a large N Gaussian approximation for this distribution

$$P_N(Y) \approx \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{Y^2}{2N}\right). \quad (1.2)$$

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

$$P_N(Y) = \frac{\Omega(N, Y)}{2^N}, \quad (1.3)$$

From this, the total number of configurations that have, say, length $X = |Y|$, in the large N Gaussian approximation, is

$$\Omega(N, X) = 2^N (P_N(+X) + P_N(-X)) = \frac{2^{N+2}}{\sqrt{2\pi N}} \exp\left(-\frac{X^2}{2N}\right). \quad (1.4)$$

The entropy associated with a one dimensional polymer of length X is therefore

$$S_N(X) = -k_B \frac{X^2}{2N} + k_B \ln \frac{2^{N+2}}{\sqrt{2\pi N}} = -k_B \frac{X^2}{2N} + \text{constant}. \quad (1.5)$$

Writing S_0 for this constant the free energy is

$$F = U - TS = U + k_B T \frac{X^2}{2N} + S_0 T. \quad (1.6)$$

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

$$\begin{aligned} \Delta F &= F(X + \Delta X) - F(X) \\ &= \frac{k_B T}{2N} ((X + \Delta X)^2 - X^2) \\ &= \frac{k_B T}{2N} (2X\Delta X + (\Delta X)^2) \end{aligned} \quad (1.7)$$

If ΔX is assumed small, our constant temperature change in free energy $\Delta F \approx (\partial F / \partial X)_T \Delta X$ is

$$\Delta F = \frac{k_B T}{N} X \Delta X. \quad (1.8)$$

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

$$F = U - TS, \quad (1.9a)$$

$$dU = TdS - PdV. \quad (1.9b)$$

The differential of the free energy is

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= -PdV - SdT \\ &= \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV. \end{aligned} \quad (1.10)$$

Forming the wedge product with dT , we arrive at the two form

$$\begin{aligned} 0 &= \left(\left(P + \left(\frac{\partial F}{\partial V}\right)_T \right) dV + \left(S + \left(\frac{\partial F}{\partial T}\right)_V \right) dT \right) \wedge dT \\ &= \left(P + \left(\frac{\partial F}{\partial V}\right)_T \right) dV \wedge dT, \end{aligned} \quad (1.11)$$

This provides the relation between free energy and the “pressure” for the system

$$P = - \left(\frac{\partial F}{\partial V}\right)_T. \quad (1.12)$$

For a system with a constant cross section ΔA , $dV = \Delta A dX$, so the force associated with the system is

$$f = P\Delta A = -\frac{1}{\Delta A} \left(\frac{\partial F}{\partial X}\right)_T \Delta A, \quad (1.13)$$

or

$$f = - \left(\frac{\partial F}{\partial X}\right)_T. \quad (1.14)$$

Okay, now we have a relation between the force and the rate of change of the free energy

$$f(X) = -\frac{k_B T}{N} X. \quad (1.15)$$

Our temperature dependent “entropic spring constant” in analogy with $f = -kX$, is therefore

$$k = \frac{k_B T}{N}. \quad (1.16)$$

Exercise 1.2 Independent one-dimensional harmonic oscillators (2013 problem set 5, p2)

Consider a set of N independent classical harmonic oscillators, each having a frequency ω .

- 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.)
- Using this, derive the mean energy and the specific heat at temperature T .
- 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 $n = 0, 1, 2, \dots$. Hence, find the canonical partition function for N independent distinguishable quantum oscillators, and find the mean energy and specific heat at temperature T .
- 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.
- 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 1.2

Part a. Classical partition function For a single particle in one dimension our partition function is

$$Z_1 = \frac{1}{h} \int dpdq e^{-\beta(\frac{1}{2m}p^2 + \frac{1}{2}m\omega^2q^2)}, \quad (1.17)$$

with

$$a = \sqrt{\frac{\beta}{2m}} p \quad (1.18a)$$

$$b = \sqrt{\frac{\beta m}{2}} \omega q, \quad (1.18b)$$

we have

$$\begin{aligned} Z_1 &= \frac{1}{h\omega} \sqrt{\frac{2m}{\beta}} \sqrt{\frac{2}{\beta m}} \int dadb e^{-a^2 - b^2} \\ &= \frac{2}{\beta h\omega} 2\pi \int_0^\infty r e^{-r^2} \\ &= \frac{2\pi}{\beta h\omega} \\ &= \frac{1}{\beta h\omega}. \end{aligned} \quad (1.19)$$

So for N distinguishable classical one dimensional harmonic oscillators we have

$$Z_N(T) = Z_1^N = \left(\frac{k_B T}{\hbar\omega} \right)^N. \quad (1.20)$$

Part b. Classical mean energy and heat capacity From the free energy

$$F = -k_B T \ln Z_N = N k_B T \ln(\beta \hbar \omega), \quad (1.21)$$

we can compute the mean energy

$$\begin{aligned} U &= \frac{1}{k_B} \frac{\partial}{\partial \beta} \left(\frac{F}{T} \right) \\ &= N \frac{\partial}{\partial \beta} \ln(\beta \hbar \omega) \\ &= \frac{N}{\beta}, \end{aligned} \quad (1.22)$$

or

$$U = N k_B T. \quad (1.23)$$

The specific heat follows immediately

$$C_V = \frac{\partial U}{\partial T} = N k_B. \quad (1.24)$$

Part c. Quantum partition function, mean energy and heat capacity For a single one dimensional quantum oscillator, our partition function is

$$\begin{aligned} Z_1 &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} \\ &= e^{-\beta \hbar \omega / 2} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} \\ &= \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \\ &= \frac{1}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} \\ &= \frac{1}{\sinh(\beta \hbar \omega / 2)}. \end{aligned} \quad (1.25)$$

Assuming distinguishable quantum oscillators, our N particle partition function is

$$Z_N(\beta) = \frac{1}{\sinh^N(\beta \hbar \omega / 2)}. \quad (1.26)$$

This time we don't add the $1/\hbar$ correction factor, nor the $N!$ indistinguishability correction factor. Our free energy is

$$F = N k_B T \ln \sinh(\beta \hbar \omega / 2), \quad (1.27)$$

our mean energy is

$$\begin{aligned}
 U &= \frac{1}{k_B} \frac{\partial F}{\partial \beta} \\
 &= N \frac{\partial}{\partial \beta} \ln \sinh(\beta \hbar \omega / 2) \\
 &= N \frac{\cosh(\beta \hbar \omega / 2) \hbar \omega}{\sinh(\beta \hbar \omega / 2) 2},
 \end{aligned} \tag{1.28}$$

or

$$U(T) = \frac{N \hbar \omega}{2} \coth \left(\frac{\hbar \omega}{2 k_B T} \right). \tag{1.29}$$

This is plotted in fig. 1.1.

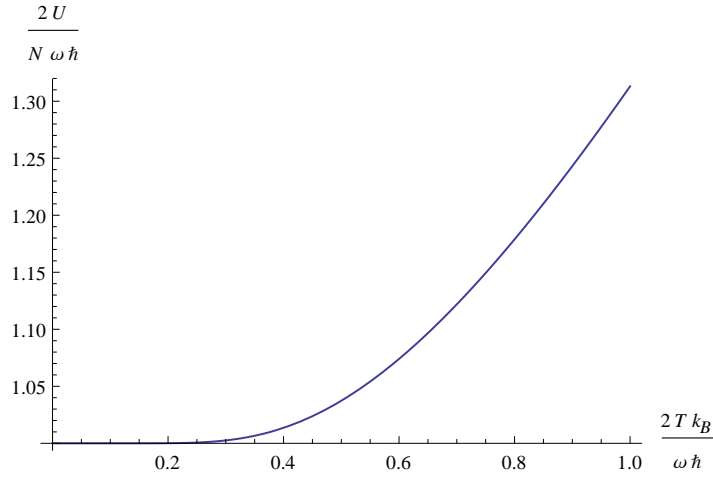


Figure 1.1: Mean energy for N one dimensional quantum harmonic oscillators

With $\coth'(x) = -1/\sinh^2(x)$, our specific heat is

$$\begin{aligned}
 C_V &= \frac{\partial U}{\partial T} \\
 &= \frac{N \hbar \omega}{2} \frac{-1}{\sinh^2 \left(\frac{\hbar \omega}{2 k_B T} \right)} \frac{\hbar \omega}{2 k_B} \left(\frac{-1}{T^2} \right),
 \end{aligned} \tag{1.30}$$

or

$$C_V = N k_B \left(\frac{\hbar \omega}{2 k_B T \sinh \left(\frac{\hbar \omega}{2 k_B T} \right)} \right)^2. \tag{1.31}$$

Part d. Classical limits In the high temperature limit $1 \gg \hbar\omega/k_B T$, we have

$$\cosh\left(\frac{\hbar\omega}{2k_B T}\right) \approx 1 \quad (1.32)$$

$$\sinh\left(\frac{\hbar\omega}{2k_B T}\right) \approx \frac{\hbar\omega}{2k_B T}, \quad (1.33)$$

so

$$U \approx N \frac{\hbar\omega}{2} \frac{2k_B T}{\hbar\omega}, \quad (1.34)$$

or

$$U(T) \approx Nk_B T, \quad (1.35)$$

matching the classical result of eq. (1.23). Similarly from the quantum specific heat result of eq. (1.31), we have

$$C_V(T) \approx Nk_B \left(\frac{\hbar\omega}{2k_B T \left(\frac{\hbar\omega}{2k_B T} \right)} \right)^2 = Nk_B. \quad (1.36)$$

This matches our classical result from eq. (1.24). We expect this equivalence at high temperatures since our quantum harmonic partition function eq. (1.26) is approximately

$$Z_N \approx \frac{2}{\beta\hbar\omega}, \quad (1.37)$$

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 ($C_V = Nk_B$), 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

$$\begin{aligned} \lim_{T \rightarrow 0} C_V &= Nk_B \lim_{x \rightarrow \infty} \frac{x^2}{\sinh^2 x} \\ &= Nk_B \lim_{x \rightarrow \infty} \frac{2x}{2 \sinh x \cosh x} \\ &= Nk_B \lim_{x \rightarrow \infty} \frac{1}{\cosh^2 x + \sinh^2 x} \\ &= Nk_B \lim_{x \rightarrow \infty} \frac{1}{\cosh(2x)} \\ &= 0. \end{aligned} \quad (1.38)$$

We also see this in the plot of fig. 1.2.

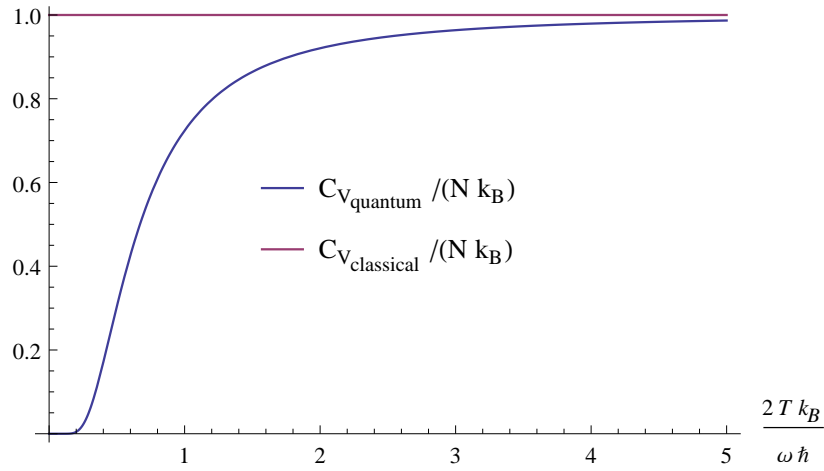


Figure 1.2: Specific heat for N quantum oscillators

Exercise 1.3 Quantum electric dipole (2013 problem set 5, 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

$$H = \frac{\mathbf{L} \cdot \mathbf{L}}{2I} - \mu \mathcal{E} L_z, \quad (1.39)$$

where I is the moment of inertia, and we have assumed an electric field $\mathcal{E} = \mathcal{E} \hat{z}$. This Hamiltonian has eigenstates described by spherical harmonics $Y_{l,m}(\theta, \phi)$, with m taking on $2l + 1$ possible integral values, $m = -l, -l + 1, \dots, l - 1, l$. The corresponding eigenvalues are

$$\lambda_{l,m} = \frac{l(l+1)\hbar^2}{2I} - \mu \mathcal{E} m \hbar. \quad (1.40)$$

(Recall that l is the total angular momentum eigenvalue, while m is the eigenvalue corresponding to L_z .)

- Schematically sketch these eigenvalues as a function of \mathcal{E} for $l = 0, 1, 2$.
- Find the quantum partition function, assuming only $l = 0$ and $l = 1$ contribute to the sum.
- Using this partition function, find the average dipole moment $\mu \langle L_z \rangle$ 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.
- Estimate the temperature above which discarding higher angular momentum states, with $l \geq 2$, is not a good approximation.

Answer for Exercise 1.3

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

$$\lambda_{0,0} = 0. \quad (1.41)$$

$l = 1$ For $l = 1$ we have

$$\frac{l(l+1)}{2} = 1(2)/2 = 1, \quad (1.42)$$

so we have

$$\lambda_{1,0} = \frac{\hbar^2}{I} \quad (1.43a)$$

$$\lambda_{1,\pm 1} = \frac{\hbar^2}{I} \mp \mu\mathcal{E}\hbar. \quad (1.43b)$$

$l = 2$ For $l = 2$ we have

$$\frac{l(l+1)}{2} = 2(3)/2 = 3, \quad (1.44)$$

so we have

$$\lambda_{2,0} = \frac{3\hbar^2}{I} \quad (1.45a)$$

$$\lambda_{2,\pm 1} = \frac{3\hbar^2}{I} \mp \mu\mathcal{E}\hbar \quad (1.45b)$$

$$\lambda_{2,\pm 2} = \frac{3\hbar^2}{I} \mp 2\mu\mathcal{E}\hbar. \quad (1.45c)$$

These are sketched as a function of \mathcal{E} in fig. 1.3.

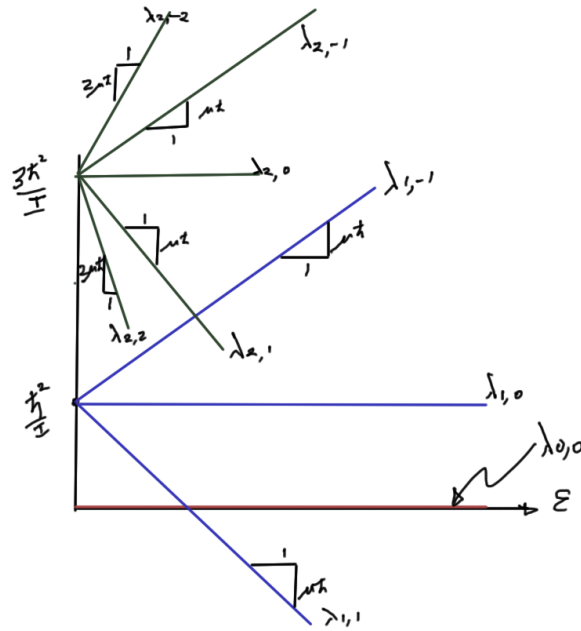


Figure 1.3: Energy eigenvalues for $l = 0, 1, 2$

Part b. Partition function Our partition function, in general, is

$$\begin{aligned}
 Z &= \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-\lambda_{l,m}\beta} \\
 &= \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \sum_{m=-l}^l e^{m\mu\hbar\mathcal{E}\beta}.
 \end{aligned}
 \tag{1.46}$$

Dropping all but $l = 0, 1$ terms this is

$$Z \approx 1 + e^{-\hbar^2\beta/4I} \left(1 + e^{-\mu\hbar\mathcal{E}\beta} + e^{\mu\hbar\mathcal{E}\beta}\right),
 \tag{1.47}$$

or

$$Z \approx 1 + e^{-\hbar^2\beta/4I} (1 + 2 \cosh(\mu\hbar\mathcal{E}\beta)).
 \tag{1.48}$$

Part c. Average dipole moment For the average dipole moment, averaging over both the states and the partitions, we have

$$\begin{aligned}
Z \langle \mu L_z \rangle &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \langle lm | \mu L_z | lm \rangle e^{-\beta \lambda_{l,m}} \\
&= \sum_{l=0}^{\infty} \sum_{m=-l}^l \mu \langle lm | m \hbar | lm \rangle e^{-\beta \lambda_{l,m}} \\
&= \mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I}\right) \sum_{m=-l}^l m e^{\mu m \hbar \mathcal{E} \beta} \\
&= \mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I}\right) \sum_{m=1}^l m \left(e^{\mu m \hbar \mathcal{E} \beta} - e^{-\mu m \hbar \mathcal{E} \beta}\right) \\
&= 2\mu \hbar \sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2 \beta}{2I}\right) \sum_{m=1}^l m \sinh(\mu m \hbar \mathcal{E} \beta).
\end{aligned} \tag{1.49}$$

For the cap of $l = 1$ we have

$$\begin{aligned}
\langle \mu L_z \rangle &\approx \frac{2\mu \hbar}{Z} \left(1(0) + e^{-\hbar^2 \beta / I} \sinh(\mu \hbar \mathcal{E} \beta)\right) \\
&\approx 2\mu \hbar \frac{e^{-\hbar^2 \beta / I} \sinh(\mu \hbar \mathcal{E} \beta)}{1 + e^{-\hbar^2 \beta / I} (1 + 2 \cosh(\mu \hbar \mathcal{E} \beta))},
\end{aligned} \tag{1.50}$$

or

$$\langle \mu L_z \rangle \approx \frac{2\mu \hbar \sinh(\mu \hbar \mathcal{E} \beta)}{e^{\hbar^2 \beta / I} + 1 + 2 \cosh(\mu \hbar \mathcal{E} \beta)}. \tag{1.51}$$

This is plotted in fig. 1.4.

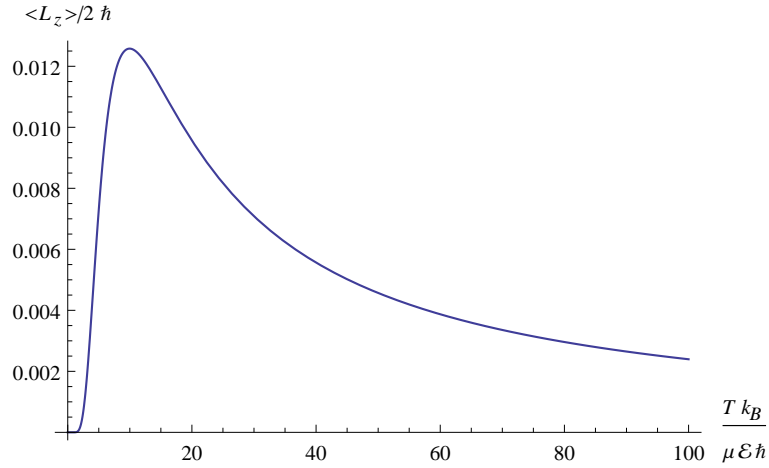


Figure 1.4: Dipole moment

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

$$\begin{aligned} \langle \mu L_z \rangle &\approx 2\mu\hbar \frac{\frac{\mu\hbar\mathcal{E}}{k_B T}}{4 + \frac{\hbar^2}{Ik_B T} + \left(\frac{\mu\hbar\mathcal{E}}{k_B T}\right)^2} \\ &= \frac{2(\mu\hbar)^2 \mathcal{E} k_B T}{4(k_B T)^2 + \hbar^2 k_B T / I + (\mu\hbar\mathcal{E})^2} \\ &\approx \frac{(\mu\hbar)^2 \mathcal{E}}{4k_B T}. \end{aligned} \tag{1.52}$$

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. 1.5.

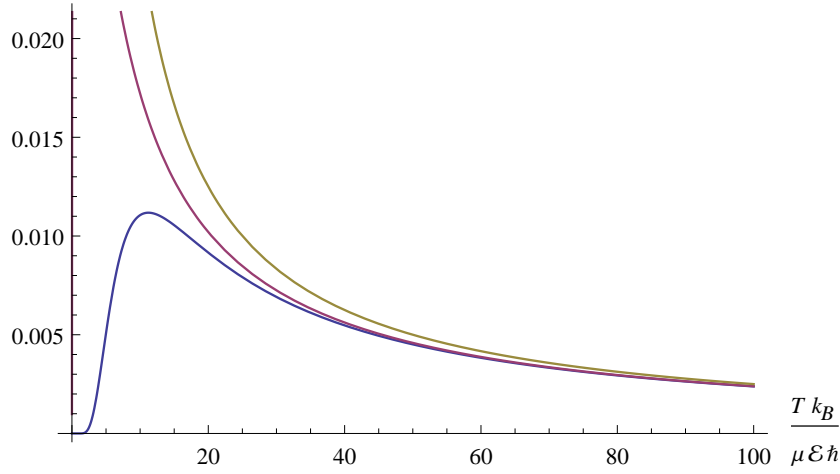


Figure 1.5: High temperature approximations to dipole moments

For low temperatures $k_B T \ll \mu\hbar\mathcal{E}$, where $\mu\hbar\mathcal{E}\beta \gg 1$ we have

$$\begin{aligned} \langle \mu L_z \rangle &\approx \frac{2\mu\hbar e^{\mu\hbar\mathcal{E}\beta}}{e^{\hbar^2\beta/I} + e^{\mu\hbar\mathcal{E}\beta}} \\ &= \frac{2\mu\hbar}{1 + e^{(\hbar^2\beta/I - \mu\hbar\mathcal{E})/k_B T}}. \end{aligned} \tag{1.53}$$

Provided the electric field is small enough (which means here that $\mathcal{E} < \hbar/\mu I$) this will look something like fig. 1.6.

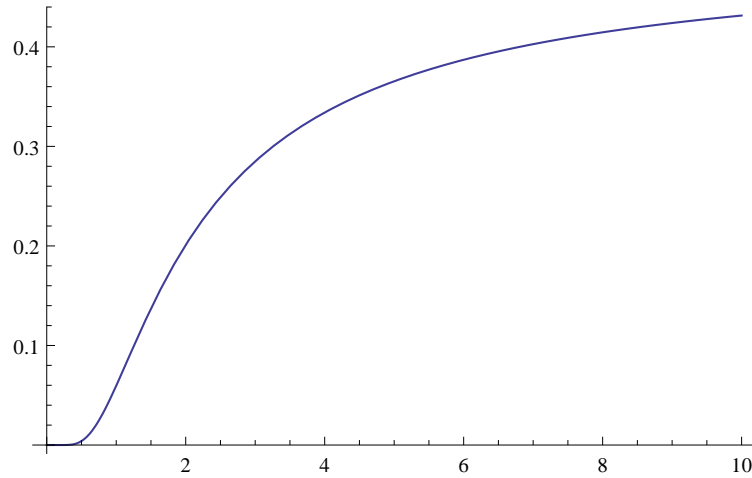


Figure 1.6: Low temperature dipole moment behavior

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 $n = m + l$

$$\begin{aligned}
 \sum_{m=-l}^l a^m &= a^{-l} \sum_{n=0}^{2l} a^n \\
 &= a^{-l} \frac{a^{2l+1} - 1}{a - 1} \\
 &= \frac{a^{l+1} - a^{-l}}{a - 1} \\
 &= \frac{a^{l+1/2} - a^{-(l+1/2)}}{a^{1/2} - a^{-1/2}}.
 \end{aligned} \tag{1.54}$$

With a substitution of $a = e^b$, we have

$$\sum_{m=-l}^l e^{bm} = \frac{\sinh(b(l + 1/2))}{\sinh(b/2)}. \tag{1.55}$$

Now we can sum the azimuthal exponentials for the dipole moment. This sum is of the form

$$\begin{aligned}
\sum_{m=-l}^l ma^m &= a \left(\sum_{m=1}^l + \sum_{m=-l}^{-1} \right) ma^{m-1} \\
&= a \frac{d}{da} \sum_{m=1}^l (a^m + a^{-m}) \\
&= a \frac{d}{da} \left(\sum_{m=-l}^l a^m - 1 \right) \\
&= a \frac{d}{da} \left(\frac{a^{l+1/2} - a^{-(l+1/2)}}{a^{1/2} - a^{-1/2}} \right). \tag{1.56}
\end{aligned}$$

With $a = e^b$, and $1 = adb/da$, we have

$$a \frac{d}{da} = a \frac{db}{da} \frac{d}{db} = \frac{d}{db}, \tag{1.57}$$

we have

$$\sum_{m=-l}^l me^{bm} = \frac{d}{db} \left(\frac{\sinh(b(l+1/2))}{\sinh(b/2)} \right). \tag{1.58}$$

With a little help from Mathematica to simplify that result we have

$$\sum_{m=-l}^l me^{bm} = \frac{l \sinh(b(l+1)) - (l+1) \sinh(bl)}{2 \sinh^2(b/2)}. \tag{1.59}$$

We can now express the average dipole moment with only sums over radial indices l

$$\begin{aligned}
\langle \mu L_z \rangle &= \mu \hbar \frac{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \sum_{m=-l}^l me^{\mu\hbar\mathcal{E}\beta}}{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \sum_{m=-l}^l e^{m\mu\hbar\mathcal{E}\beta}} \\
&= \mu \hbar \frac{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \frac{l \sinh(\mu\hbar\mathcal{E}\beta(l+1)) - (l+1) \sinh(\mu\hbar\mathcal{E}\beta l)}{2 \sinh^2(\mu\hbar\mathcal{E}\beta/2)}}{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \frac{\sinh(\mu\hbar\mathcal{E}\beta(l+1/2))}{\sinh(\mu\hbar\mathcal{E}\beta/2)}}. \tag{1.60}
\end{aligned}$$

So our average dipole moment is

$$\langle \mu L_z \rangle = \frac{\mu \hbar}{2 \sinh(\mu\hbar\mathcal{E}\beta/2)} \frac{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) (l \sinh(\mu\hbar\mathcal{E}\beta(l+1)) - (l+1) \sinh(\mu\hbar\mathcal{E}\beta l))}{\sum_{l=0}^{\infty} \exp\left(-\frac{l(l+1)\hbar^2\beta}{2I}\right) \sinh(\mu\hbar\mathcal{E}\beta(l+1/2))}. \tag{1.61}$$

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. 1.7.

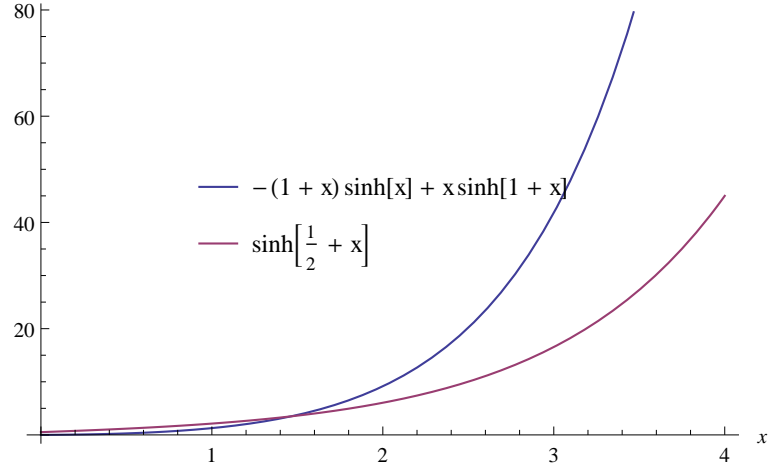


Figure 1.7: Hyperbolic sine plots for dipole moment

Let's look at the order of these hyperbolic sines for large arguments. For the numerator we have a difference of the form

$$\begin{aligned}
 x \sinh(x+1) - (x+1) \sinh(x) &= \frac{1}{2} \left(x (e^{x+1} - e^{-x-1}) - (x+1) (e^x - e^{-x}) \right) \\
 &\approx \frac{1}{2} \left(x e^{x+1} - (x+1) e^x \right) \\
 &= \frac{1}{2} (x e^x (e-1) - e^x) \\
 &= O(x e^x).
 \end{aligned} \tag{1.62}$$

For the hyperbolic sine from the partition function we have for large x

$$\sinh(x+1/2) = \frac{1}{2} \left(e^{x+1/2} - e^{-x-1/2} \right) \approx \frac{\sqrt{e}}{2} e^x = O(e^x). \tag{1.63}$$

While these hyperbolic sines increase without bound as l increases, we have a negative quadratic dependence on l in the 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

$$\frac{l(l+1)\hbar^2}{2Ik_B T} \gg 1, \tag{1.64}$$

or

$$T \ll \frac{l(l+1)\hbar^2}{2Ik_B T}. \tag{1.65}$$

Observe that the RHS of this inequality, for $l = 1, 2, 3, 4, \dots$ satisfies

$$\frac{\hbar^2}{Ik_B} < \frac{3\hbar^2}{Ik_B} < \frac{6\hbar^2}{Ik_B} < \frac{10\hbar^2}{Ik_B} < \dots \quad (1.66)$$

So, for small electric fields, our approximation should be valid provided our temperature is constrained by

$$T \ll \frac{\hbar^2}{Ik_B}. \quad (1.67)$$