

---

**PHY452H1S Basic Statistical Mechanics. Lecture 10: Continuing review of thermodynamics. Taught by Prof. Arun Paramekanti**

---

1.1 Disclaimer

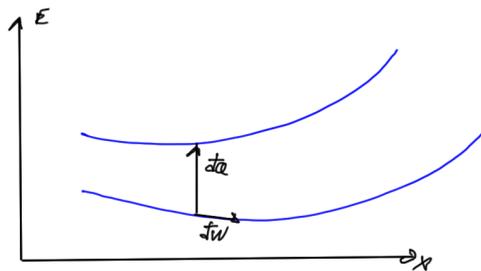
Peeter's lecture notes from class. May not be entirely coherent.

1.2 Continuing review of thermodynamics

We have energy conservation split into two types of energy

$$dE = \underbrace{\text{d}W}_{\text{Organized macroscopic variable } X} + \underbrace{\text{d}Q}_{\text{disorganized}} \quad (1.1)$$

In fig. 1.1 we plot changes that are adiabatic processes ( $\text{d}Q = 0$ ) and heating and cooling processes (with  $\text{d}W = 0$ ).



**Figure 1.1: Adiabatic and heating processes**

Given a dimensionality of  $d_w + 1$ , a cyclic change is that for which we have

$$\{X_{\text{initial}}\} \rightarrow \{X_{\text{final}}\} \quad (1.2a)$$

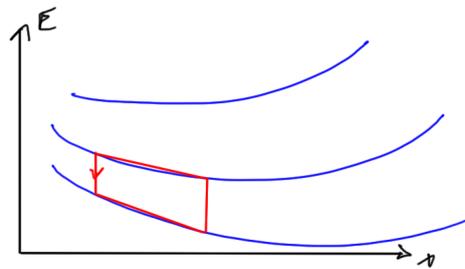
$$E_{\text{initial}} \rightarrow E_{\text{final}} \tag{1.2b}$$

$$\Delta W \neq 0 \tag{1.2c}$$

$$\Delta Q \neq 0 \tag{1.2d}$$

$$\Delta E = 0 \tag{1.2e}$$

Such a cyclic process could be represented as in fig. 1.2.



**Figure 1.2:** Cyclic process

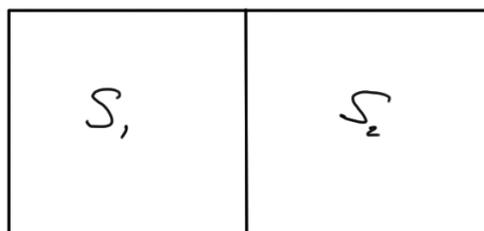
Here we've labeled the level curves with a parameter  $\sigma$ , as yet undefined. We call  $\sigma$  the thermodynamic entropy and say that

$$(\sigma, \{x_i\}), \tag{1.3}$$

specifies the state of the system.

*Example:* Pushing a block against a surface with friction.

*Equilibrium* Considering two systems in contact as in fig. 1.3.



**Figure 1.3:** Two systems in contact

We require

1. Mechanical equilibrium.

requires balance of the forces  $f_i$

$$\frac{\partial E}{\partial x_i} = f_i, \quad (1.4)$$

(Note the neglect of the sign here, the direction of the force isn't really of interest).

and

$$\frac{\partial E_1}{\partial x_i} = \frac{\partial E_2}{\partial x_i} \quad (1.5)$$

2. Thermal stability

$$\frac{\partial E_1}{\partial \sigma} = \frac{\partial E_2}{\partial \sigma} \quad (1.6)$$

We must have some quantity that characterizes the state of the system in a non-macroscopic fashion. The identity (1.6) is a statement that we have equal temperatures.

We define temperature as

$$T \equiv \frac{\partial E}{\partial \sigma}. \quad (1.7)$$

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  $\sigma$  in a specific way. The definition (1.7) effectively defines this non-macroscopic parameter  $\sigma$  (the entropy) in the simplest possible way.

*Cyclic state variable verses non-state variables*

$$\{x_i\}, \sigma \rightarrow \text{“state variable”} \quad (1.8)$$

A non-cyclic process changes these, whereas a cyclic process takes  $\sigma, \{x_i\}$  back to the initial values. This is characterized by

$$\oint d\sigma = 0 \quad (1.9a)$$

$$\oint dx_i = 0. \quad (1.9b)$$

This doesn't mean that the closed loop integral of other qualities, such as temperature are necessarily zero

$$\oint T d\sigma = \oint \delta Q \neq 0 \quad (1.10a)$$

$$\oint f_i dx_i = \oint \delta W \neq 0. \quad (1.10b)$$

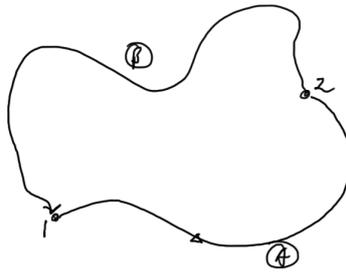
Note that the identification of  $\delta Q = T d\sigma$  follows from our definition

$$\left(\frac{\partial E}{\partial \sigma}\right)_x = T \quad (1.11)$$

so that with  $\delta W = 0$  we have

$$dE = T \delta \sigma \quad (1.12)$$

Graphically we have for a cyclic process fig. 1.4.



**Figure 1.4: Cyclic process**

We have

$$\delta W_{\rightarrow} = -\delta W_{\leftarrow} \quad (1.13a)$$

$$\delta Q_{\rightarrow} = -\delta Q_{\leftarrow} \quad (1.13b)$$

so that

$$\Delta Q_{12}^{(A)} + \Delta Q_{21}^{(B)} \neq 0, \quad (1.14)$$

or

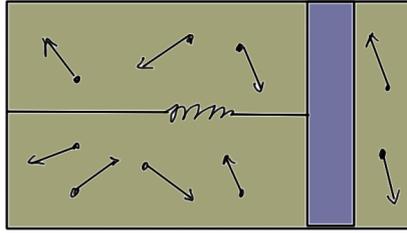
$$\Delta Q_{12}^{(A)} \neq \Delta Q_{12}^{(B)}. \quad (1.15)$$

*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. 1.5.

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

$$\text{Energy}_1 \rightarrow \text{Energy}_2 \quad (1.16a)$$

$$\text{Work} \rightarrow \text{Heat} \quad (1.16b)$$



**Figure 1.5:** Heat loss and irreversibility

but not all

Heat  $\rightarrow$  Work.

(1.17)