

# Notes on Statistical Mechanics

Based on Pathria and PHYS404 (Lobb)

Hersh Kumar

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# 1 Chapter 1

## 1.1 Macrostates and Microstates

Suppose we have a system with  $N$  identical particles, in a space with volume  $V$ . The “thermodynamic limit” is the limit taken in the usual case, where the number of particles is very large, on the order of  $10^{23}$  generally. Thus we take  $N \rightarrow \infty$ , and also take  $V \rightarrow \infty$ , in order to maintain the value of the particle density,  $\frac{N}{V}$ . In this limit, we have two categories of properties, *intensive* and *extensive* properties. Intensive properties are independent of the size of the system (not related to the value of  $N$  or  $V$ ), while extensive properties are dependent on the size of the system.

Let us now consider the total energy of the system,  $E$ . If we assume that the particles are noninteracting, then the total energy of the system is equal to the sum of the individual energies of the particles. Since we can have particles with the same energies, let  $n_i$  be the number of particles with energy  $\epsilon_i$ . This makes the total energy:

$$E = \sum_i n_i \epsilon_i$$

Where we also have the necessary condition that adding up the multiplicity of the particles with the same energies must sum to the total number of particles:

$$N = \sum_i n_i$$

Based on quantum mechanics, the values of  $\epsilon_i$  must be discrete, and depend on the volume  $V$ . Thus, the possible values of  $E$  are also discrete. However, in the thermodynamic limit, where  $V$  is very large, the spacing between the allowed discrete values of  $E$  becomes very small, meaning that we can actually treat  $E$  as a continuous variable. This is true even if the particles are interacting, although the expression for the total energy would not be as simple.

If we are given the values of  $N$ ,  $V$ , and  $E$ , then we have defined a **macrostate** of the system. However, a specific macrostate does not necessarily define a unique system configuration, since we can think of varying sets of values of the  $\epsilon_i$ s that will all lead to the same  $E$ . As an analogy, think of being given a set amount of money, say 25 cents. There are multiple ways to create 25 cents out of coins, whether it be 25 pennies, a single quarter, 4 nickels and five pennies, et cetera. We can think of  $E$  as being the total sum of the coins, and we can have different values for  $\epsilon_i$  and  $n_i$  to get the same value of  $E$ . Another way of thinking about it is to note that if we are just given  $N$ ,  $V$  and  $E$ , we don’t know the distribution of energy to each individual particle.

Each of the different configurations that correspond to a single macrostate is known as a *microstate* (also sometimes called a complexion.) In general, the different microstates can be matched to independent solutions to the Schrodinger equation for the system,  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , which correspond to the eigenvalue  $E$  of the Hamiltonian for the system.

In general, for any given macrostate of a system, there are many different microstates that “make up” that macrostate. This leads to the fundamental assumption of statistical mechanics, the postulate of equal a priori probabilities.

### Postulate 1.1: Equal a priori probabilities

*For a system in a given macrostate, the system has an equal probability of being in any one of the microstates that correspond to the macrostate.*

The number of all possible microstates for a given macrostate (which means a given  $N$ ,  $V$ , and  $E$ ), is denoted by  $\Omega(N, V, E)$ <sup>1</sup>. It turns out that from  $\Omega$  and its dependence on  $N$ ,  $V$ , and  $E$ , we can derive the complete thermodynamics of the system. We will discuss later how to compute  $\Omega$ , for now let us see how it is related to thermodynamic quantities.

## 1.2 Significance of $\Omega$

We begin by considering thermal contact between two systems. Suppose we have two systems,  $A_1$  and  $A_2$ , each with its own set of system parameters. This means that we have  $N_1, V_1$  and  $E_1$  for system  $A_1$ , and we have  $N_2, V_2$  and  $E_2$  for system  $A_2$ . The systems are each in a particular macrostate, with microstate multiplicities given by  $\Omega_1(N_1, V_1, E_1)$  and  $\Omega_2(N_2, V_2, E_2)$ , for system  $A_1$  and  $A_2$  respectively. Note that the mathematical functions that represent  $\Omega_1$  and  $\Omega_2$  are not necessarily the same, these are dependent on the nature of each system.

Now suppose we bring the two systems into thermal contact with one another, allowing for the exchange of energy between the two. We can think of this as having a conducting wall in between the two. We disallow particle transfer, and thus the system volumes and particle counts are held constant.

In this setup, we can see that energies of the two systems can change, and they are constrained by the law of conservation of energy, the energy across both systems must sum up to the original energy in both systems:

$$E_{\text{total}} = E_1^{t=0} + E_2^{t=0}$$

Now let us look at the value of  $\Omega$  for the joint system. At any time  $t$ , the subsystem  $A_1$  is equally likely to be in any one of the  $\Omega_1(E_1)$  microstates, and similarly, the subsystem  $A_2$  is equally likely to be in any of the  $\Omega_2(E_2)$  microstates. So what is the value of  $\Omega_{\text{total}}$ ?

We can construct this by “fixing”  $A_1$  to a specific microstate. For this microstate, there are  $\Omega_2(E_2)$  different possibilities for the  $A_2$  subsystem microstate. Now we have to multiply by the different possibilities for the fixed  $A_1$  microstate, which is  $\Omega_1(E_1)$ . Thus the value of  $\Omega_{\text{total}}$  is given by

$$\Omega_{\text{total}} = \Omega_1(E_1)\Omega_2(E_2)$$

If that didn’t make sense, you can think of this as a combinatorics problem, there are  $\Omega_1(E_1)$  choices for the configuration of the first subsystem, and  $\Omega_2(E_2)$  choices for the configuration of the second subsystem. Thus the total number of configurations will be  $\Omega_1(E_1)\Omega_2(E_2)$ .

Now let us try to reparameterize this in terms of the total energy of the system. We know that  $E_2 = E_{\text{total}} - E_1$ , and thus

$$\Omega_{\text{total}} = \Omega_1(E_1)\Omega_2(E_{\text{total}} - E_1)$$

Thus we have that  $\Omega_{\text{total}}$  is a function of  $E_1$  and  $E_{\text{total}}$ .

Now let us ask the following, at what value of  $E_1$  will the composite system be in equilibrium? Speaking physically, how far will the energy exchange go in order to bring  $A_1$  and  $A_2$  into mutual equilibrium?

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<sup>1</sup>In PHYS404, Lobb uses  $g$  to denote the multiplicity function whereas here I follow Pathria’s notation. It doesn’t matter all too much, we stop dealing with the multiplicity function soon enough.

To answer this, let us make an assertion. We denote the equilibrium state of a system to be the macrostate that has the *largest* number of microstates, because a physical system left to itself will proceed in a direction that enables it to assume an increasing number of microstates, until it settles into a macrostate that has the maximum number of microstates.

Thus, in order to find the value of  $E_1$  that gives us equilibrium, we can maximize  $\Omega_{\text{total}}(E_{\text{total}}, E_1)$  by varying  $E_1$ . Let us denote the equilibrium value of  $E_1$  as  $\overline{E}_1$ , and likewise define  $\overline{E}_2$ . We can compute the partial derivative of  $\Omega_{\text{total}}$  with respect to  $E_1$ :

$$\begin{aligned}\frac{\partial \Omega_{\text{total}}}{\partial E_1} &= \left( \frac{\partial \Omega_1(E_1)}{\partial E_1} \right) \Omega_2(E_2) + \Omega_1(E_1) \left( \frac{\partial \Omega_2(E_2)}{\partial E_1} \right) \\ &= \left( \frac{\partial \Omega_1(E_1)}{\partial E_1} \right) \Omega_2(E_2) + \Omega_1(E_1) \left( \frac{\partial \Omega_2(E_2)}{\partial E_2} \right) \left( \frac{\partial E_2}{\partial E_1} \right)\end{aligned}$$

Now setting this equal to zero when we have the equilibrium state,  $E_1 = \overline{E}_1$  and  $E_2 = \overline{E}_2$ :

$$\left( \frac{\partial \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\overline{E}_1} \Omega_2(\overline{E}_2) + \Omega_1(\overline{E}_1) \left( \frac{\partial \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\overline{E}_2} \cdot \frac{\partial E_2}{\partial E_1} = 0$$

Now using the fact that  $E_{\text{total}} = E_1 + E_2$ , and  $E_{\text{total}}$  is a constant, we know that  $\frac{\partial E_2}{\partial E_1} = -1$ :

$$\left( \frac{\partial \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\overline{E}_1} \Omega_2(\overline{E}_2) - \Omega_1(\overline{E}_1) \left( \frac{\partial \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\overline{E}_2} = 0$$

#### Taking a detour

In order to simplify this, let's take a look at the derivative of the natural log of a function  $f(x, \dots)$ :

$$\frac{\partial}{\partial x} \ln f(x, \dots) = \frac{1}{f(x, \dots)} \frac{\partial f}{\partial x}$$

Now taking a look at the expression we have derived so far, we see that we can work backwards for both terms, and represent them as derivatives of the log of something.

We can rewrite this as

$$\left( \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\overline{E}_1} = \left( \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\overline{E}_2}$$

This is the equilibrium condition for the thermal contact between the two subsystems. Now let us denote the quantity on both sides as  $\beta$ :

$$\beta = \left( \frac{\partial \ln \Omega(N, V, E)}{\partial E} \right)_{N, V, E=\overline{E}}$$

So what we have found is that when the two subsystems are placed into thermal contact, the energy exchange leads to an equilibrium state that occurs when  $\beta_1 = \beta_2$ . The natural next step is to expect

Figure out  
better physics  
reasoning for  
this

that this  $\beta$  parameter is somehow related to the thermodynamic temperature,  $T$ , of the system. To determine this relationship, we can recall the relationship between  $T$  and the entropy,  $S$ :

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$

Now looking at this relationship, as well as  $\beta$ , we can write out the relationship between  $\Omega$  and  $S$ :

$$\begin{aligned} \frac{\Delta S}{\Delta(\ln \Omega)} &= \frac{1}{\beta T} \\ &= \text{const.} \end{aligned}$$

This is the correspondence that was first established by Boltzmann (and adorns his tombstone), who believed that the constant must be a universal constant. Planck was the first to write out the explicit formula:

$$S = k \ln \Omega$$

This formula is the “bridge” between the microscopic world ( $\Omega$ ) and the macroscopic world ( $S$ ). It is important to note that this formula is based on the absolute value of the entropy of a physical system, in terms of the total number of microstates accessible to it in the given macrostate. What we consider the zero point of the entropy is the state for which there is only one microstate ( $\Omega = 1$ ), which is known as the unique configuration.

This is where the idea of entropy as a measure of the “disorder” or chaos of a system comes from, as the entropy increases, the number of microstates available to the system increases. The larger the number of microstates the system can have, the less predictable the system is.

We can also rewrite  $\beta$ :

$$\beta = \frac{1}{kT}$$

Where  $k$  is generally referred to as the Boltzmann constant.

### 1.3 Statistics and Thermodynamics

Let us now take the joint system, and swap out the conducting wall with a movable conducting wall, not only can the energies of the subsystems change, but the volumes can as well. Now, we have the physically imposed boundary condition that  $V_{\text{total}} = V_1^{t=0} + V_2^{t=0}$ , along with the previously discussed energy conservation requirement. By the same argument as before, we expect the equilibrium state to occur when  $\Omega(E_{\text{total}}, V_{\text{total}}, V_1, E_1)$  is maximized.

Once again, we can derive the same equilibrium relationship for the energy:

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{N_1, V_1, E_1 = \overline{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{N_2, V_2, E_2 = \overline{E}_2}$$

But we can (through the same process as before) derive a similar relationship between the partial derivatives with respect to the volumes of the subsystems:

$$\left(\frac{\partial \ln \Omega_1}{\partial V_1}\right)_{N_1, E_1, V_1 = \overline{V}_1} = \left(\frac{\partial \ln \Omega_2}{\partial V_2}\right)_{N_2, E_2, V_2 = \overline{V}_2}$$

We then, like before, denote each side as a new variable,  $\eta$ :

$$\eta = \left( \frac{\partial \ln \Omega(N, V, E)}{\partial V} \right)_{N, E, V = \bar{V}}$$

Thus we can represent the equilibrium conditions as a set of equations that must be satisfied,  $\beta_1 = \beta_2$  and  $\eta_1 = \eta_2$ . If the wall is then allowed to be conducting, movable, and permeable, then we can derive a third condition:

$$\left( \frac{\partial \ln \Omega_1}{\partial N_1} \right)_{V_1, E_1, N_1 = \bar{N}_1} = \left( \frac{\partial \ln \Omega_2}{\partial N_2} \right)_{V_2, E_2, N_2 = \bar{N}_2}$$

And similarly to the previous two cases, we can denote a parameters  $\xi$  such that the equilibrium condition becomes  $\xi_1 = \xi_2$ .

Now as we did for  $\beta$ , we can relate these parameters to macroscopic thermodynamic quantities. We can do so by using the basic formula of thermodynamics:

$$dE = TdS - PdV + \mu dN$$

Where  $P$  is the pressure, and  $\mu$  is the chemical potential. From this, using the same reasoning as for  $\beta$ , we find that

$$\eta = \frac{P}{kT} \quad \xi = -\frac{\mu}{kT}$$

Now thinking macroscopically, we see that these equilibrium conditions that we have derived match the thermodynamic conditions. Consider the case where the wall is movable and conducting. Thermodynamics tells us that the equilibrium conditions should be

$$T_1 = T_2 \quad P_1 = P_2$$

And that is what we found, in terms of  $\Omega$ . In the case where the wall is permeable but the volume is fixed, thermodynamics tells us that

$$T_1 = T_2 \quad \mu_1 = \mu_2$$

If we allow all three variables to be free, then thermodynamics tells us that

$$T_1 = T_2 \quad P_1 = P_2 \quad \mu_1 = \mu_2$$

Which is the same as having all three of our derived conditions satisfied.

Thus we have a “recipe” of sorts for deriving the intensive properties of a system, we first compute  $\Omega(N, V, E)$  for whatever our particular macrostate is, and from this, we can obtain  $S$ :

$$S = k \ln \Omega$$

And then we can take derivatives:

$$\left( \frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{T} \quad \left( \frac{\partial S}{\partial V} \right)_{N, E} = \frac{P}{T} \quad \left( \frac{\partial S}{\partial N} \right)_{V, E} = -\frac{\mu}{T}$$

## Derivation

Let's derive the above equations, starting with

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$

To start, we know that  $S = k \ln \Omega$ , so taking a derivative with respect to  $E$ , holding  $N$  and  $V$  constant:

$$\begin{aligned} \left(\frac{\partial S}{\partial E}\right)_{N,V} &= \frac{\partial}{\partial E} [k \ln \Omega]_{N,V} \\ &= k \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \\ &= k\beta \\ &= \frac{1}{T} \end{aligned}$$

Up next, we want to show that the following relationship is true:

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}$$

We start with the definition of entropy:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{N,E} &= \frac{\partial}{\partial V} [k \ln \Omega]_{N,E} \\ &= k \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \\ &= k\eta \\ &= \frac{P}{T} \end{aligned}$$

And finally, we want to show that

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}$$

Once again starting with the definition of entropy:

$$\begin{aligned} \left(\frac{\partial S}{\partial N}\right)_{V,E} &= \frac{\partial}{\partial N} [k \ln \Omega]_{V,E} \\ &= k \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E} \\ &= k\xi \\ &= -\frac{\mu}{T} \end{aligned}$$

We can also solve for the pressure and chemical potential on their own:

$$\begin{aligned} P &= \frac{\left(\frac{\partial S}{\partial N}\right)_{V,E}}{\left(\frac{\partial S}{\partial E}\right)_{N,V}} \\ &= -\left(\frac{\partial E}{\partial V}\right)_{N,S} \end{aligned}$$

$$\begin{aligned} \mu &= \frac{-\left(\frac{\partial S}{\partial N}\right)_{V,E}}{\left(\frac{\partial S}{\partial E}\right)_{N,V}} \\ &= \left(\frac{\partial E}{\partial N}\right)_{V,S} \end{aligned}$$

And we can also invert the relationship between entropy and temperature:

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

From these derivations of thermodynamic properties, we can see that the rest of thermodynamics follows.

## 1.4 The Classical Ideal Gas

Let us now derive the properties of a classical ideal gas composed of monatomic molecules. This proves to be useful in order to examine the asymptotic limit of  $\Omega$ , as well as the result of determining  $k$  in terms of other physical constants.

Add the derivations/results for the different free energies and specific heats.