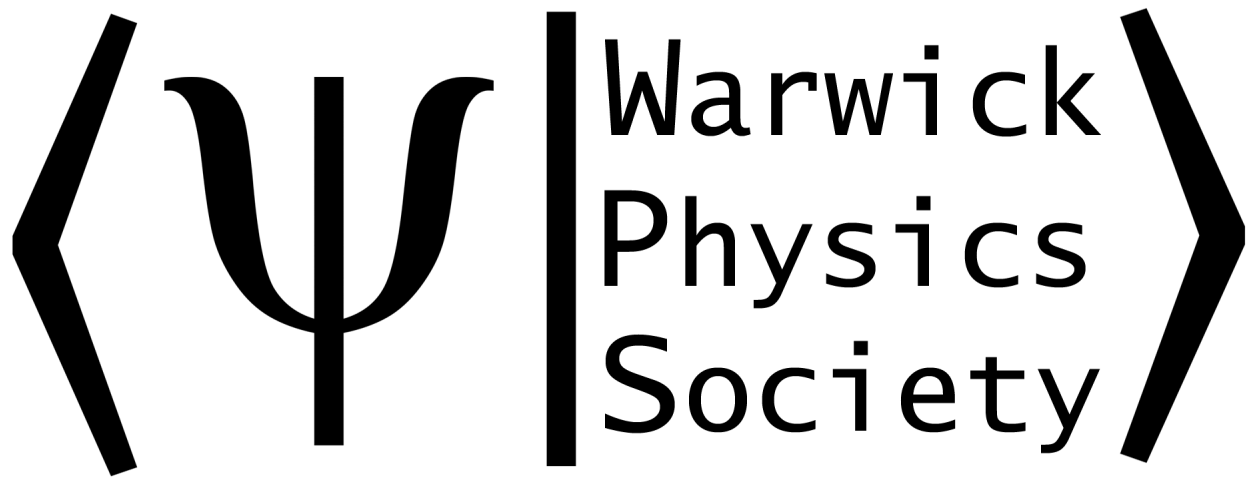


# PX265 - Thermal Physics II



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December 2013*

## Disclaimer

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# 1 Exact Differentials

The differential  $df = A(x, y)dx + B(x, y)dy$  is said to be an **exact differential** if there exists a function  $f(x, y)$  which changes according to the above when its independent variables are changed.

I.e we must have:  $A(x, y) = \frac{\partial f}{\partial x}$  and  $B(x, y) = \frac{\partial f}{\partial y}$ . Most compactly:

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \text{ is an exact differential if:} \quad (1)$$

$$a) \left(\frac{\partial}{\partial y} \left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y}\right)_x\right)_y \quad b) F(B) - F(A) = \int_A^B dF \quad c) \oint dF = 0 \quad (2)$$

We use the notation  $d$  prefixing an **exact differential** and the  $\delta$  prefixing a **not exact differential**. E.g  $dU$  - is an exact differential but  $\delta Q$  is not.

An **Integrating Factor** is a factor which creates an exact differential. E.g  $\delta F_1 = ydx - xdy$  then  $\left(\frac{\partial F_1}{\partial x}\right)_y = y$  and  $\left(\frac{\partial F_1}{\partial y}\right)_x = -x$ . Then  $\left(\frac{\partial}{\partial y} \left(\frac{\partial F_1}{\partial x}\right)_y\right)_x = 1 \neq -1 = \left(\frac{\partial}{\partial x} \left(\frac{\partial F_1}{\partial y}\right)_x\right)_y$ . So  $\delta F_1$  is not an exact differential. However,  $dF_2 = \frac{1}{y}dx - \frac{x}{y^2}dy$  is an exact differential. (Check this for yourself). As the only different between  $\delta F_1$  and  $dF_2$  is the factor  $\frac{1}{y^2}$ , so the factor  $\frac{1}{y^2}$  is said to be the **integrating factor**.

# 2 Closed Systems and the Microcanonical Ensemble

## 2.1 Basic Definitions

Here are some definitions worth remembering:

**Closed System** - Is a system which does not share Heat or Particles with it's environment.

**Macrostate** - Is a state of a many-body system defined by a set of thermodynamic functions (T, ρ, N, U). In general they have very few variables.

**Microstate** - Is any microscopic configuration of the system's particles consistent with restrictions. In general there are loads of variables.<sup>2</sup>

Some examples of microstates are: Velocity and momentum for a classical particle. Also the wavefunctions  $\phi(s)$  for a quantum particle. Where s is a full set of variables such as position and spin.

An important notion to keep in mind is that many different *microstates* can lead to the same *macrostate*.

**Extensive Quantities** - are proportional to the amount of matter present

**Intensive State Functions** - are independent of the amount of matter present

These aren't really explained, so I will delve a bit deeper into this.

An intensive quantity is something that doesn't change, something that regardless of how much you take away or add it stays the same. A good example I found was that of the hardness of a diamond. If we cut a diamond, regardless of how small, the hardness does not change. We therefore call the hardness an intensive property.

An extensive property is the exact opposite, as it depends on the amount you have. Again with the diamond example, the mass of the diamond you have changes, also the volume. Therefore, mass and volume are said to be extensive quantities. (For more information on intensive/extensive functions I refer you to the wikipedia page: [here](#))

## 2.2 Thermodynamics of closed systems

The central quantity in which we are concerned in this case is the **Internal Energy**  $U$ . Remember the relation  $dU = \delta Q + \delta W$  and for a gas, which is quasi-static  $dU = TdS - pdV$  Notice here, that  $U$  has an

<sup>1</sup>The notation  $\left(\frac{\partial F}{\partial x}\right)_y$  means the partial derivative of F wrt x keeping y constant. This notation will turn up everywhere in Thermodynamics, so it's worth remembering

<sup>2</sup>For a good qualitative description of Macro and Micro -states I recommend you watch the video found [here](#)

exact differential however, Q and W are not. This implies that entropy, S and volume, V are independent variables.

Also U is a **thermodynamic potential** IN THE VARIABLES S AND V!! (For examples U(T,V) exists, but this is not a thermodynamic potential). Calling U a **Thermodynamic potential** means that if you are given S, V you can get the full thermodynamics of the system from U(S,V).

### 2.2.1 Maxwell Relations

Now, recall that U is an exact differential in S,V. Therefore we can find some **Maxwell Relations** As U(S,V) is an exact differential that means that it's mixed derivatives must commute.

I.e  $\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_S\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right)_V$ . Now taking  $U(S, V) = TdS - pdV$  we can see that  $\left(\frac{\partial U}{\partial S}\right)_V = T$  and that  $\left(\frac{\partial U}{\partial V}\right)_S = -p$ . So now applying that U's mixed derivatives must commute we get that:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (3)$$

Equation 3 is known as a Maxwell Relation. Also, you may notice, that  $\left(\frac{\partial U}{\partial S}\right)_V = T$  acts as a definition for temperature!

### 2.2.2 Stability of the Thermal Equilibrium

**Stability Criterion:** The first and second law of thermodynamics imply that for a closed system at thermal equilibrium then  $\delta Q = 0$  and  $\delta W = 0$ . The second law implies states that:  $\delta Q \leq TdS$ . Now combining the two leads to the fact that  $TdS \geq 0 \implies dS \geq 0$ . Now at thermal equilibrium we have that  $\delta Q = TdS \implies dS = 0$ .

Therefore, S is a maximum in equilibrium and  $S \rightarrow S_{\max}$  otherwise.

### 2.2.3 Fundamental Assumptions and Definitions of the Statistical Description

**Equipartition Theorem:** All microstates of a closed system (i.e E,N fixed) are equally likely to occur in the state of equilibrium.

This serves as a definition for equilibrium also.

**Average of a quantity, A:** The average of A is given by the following formula:  $\langle A \rangle = \frac{1}{\Omega(E,N)} \sum_i A_i$  where  $\Omega(E, N)$  is the total number of configurations and  $A_i$  is the value of the quantity A if the system is in microstate i.

**A quick example:** Imagine there are 3 particles in a particle trap, these particles have energies:  $0, \hbar\omega, 2\hbar\omega$ . And the system energy is  $E = U = 2\hbar\omega$ . So, there are 3! configurations as there are 3 different energies and 3 particles.<sup>3</sup> So, what is the average energies of the particles? I.e set  $A = E$  in the equation above. So we consider one particle, A, and consider what energies can it have in different states. So if the other two particles, B,C, have no energy, then particle A has energy  $2\hbar\omega$ , if one of the particles, B/C has energy of  $\hbar\omega$ , then particle A has energy  $\hbar\omega$  also. And otherwise it must have zero energy. So plugging these into the equation we end up with:

$$\langle E \rangle = \frac{1}{\Omega(E, N)} \sum_i A_i = \frac{1}{6}(2 + 1 + 1 + 0 + 0 + 0)\hbar\omega = \frac{4}{6}\hbar\omega = \frac{2}{3}\hbar\omega$$

**Probability for a specific state:**  $p_A = \frac{1}{\Omega(E,N)}$  - this is from the equipartition theorem!

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<sup>3</sup>These particles are distinguishable - this assumption will be questioned later.

### 3 The Micro-Canonical Ensemble

In the microcanonical ensemble, the following are kept constant:

- The number of particles,  $N$
- The volume,  $V$
- The internal energy,  $U$

To link Thermodynamics and Statistical physics, the connection that  $U = E$  is not enough!

The additional connection is what Boltzmann came up with:  $\boxed{S^{\text{thermal}} = S^{\text{statistical}} = k_b \ln(\Omega)}$ .

This is a postulate, something Boltzmann found to work from experiments, and requires no proof.

The arguments for the formula  $S = k_b \ln(\Omega)$  are:

i) IT WORKS! <sup>4</sup>

ii) It has similarities with other quantities such as:

- a)  $S$  increases with heat input -  $\Omega$  increases with the energy available.  $dS \geq \frac{\delta Q}{T}$
- b) Heat tends to disorder the system  $\implies$  heat causes more accessible states  $\rightarrow p_i$  decreases.
- c)  $S$  is a measure of disorder  $\implies \Omega$  is related to disorder  $\implies S = f(\Omega)$

It turns out this  $f$  is  $\boxed{S(\mathbf{E}) = k \ln(\Omega(\mathbf{E}))}$

Where  $k$  is Boltzmann's Constant, and  $\Omega(E)$  is the total number of states of the system at energy  $E$ . And this equation is consistent with the first and second law of thermodynamics and the equilibrium condition ( $T_1 = T_2$ ).

#### 3.1 Counting Microstates for a given $E$ and $N$

In general this is very problematic! However, it turns out for special cases, more precisely where the system has discrete energies, it is a lot easier.

##### 3.1.1 Notation

- $\Omega(\mathbf{E}, N)$  - Number of microstates with energy  $E$  and number of particles  $N$
- $\omega_N(N_1)$  - Number of all microstates with  $E, N$  under the restriction that  $N_1$  particles are in the state  $E_1$
- $\omega_N(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_j)$  - Number of all microstates with  $E, N$  and  $n_i$  particles in state  $E_i$ . ( $\sum_k n_k = N$ )
- $p_v$  - Probability of microstate  $p_v = \frac{1}{\Omega}$
- $p(N_1)$  - Probability to find  $N_1$  particles in the special state, e.g  $E_1$
- $p_N(\mathbf{n}_1, \dots, \mathbf{n}_j)$  - Probability to find  $N_1$  particles in  $E_1$ ,  $N_2$  particles in  $E_2$  ... etc.

##### 3.1.2 Counting States

If we have  $N$  independent particles which can each occupy  $M$  states, the number of microstates is:  $\Omega(E, N) = \underbrace{M \cdots M}_{N \text{ times}} = M^N$ , this is because each particle can choose from  $M$  states regardless of the other particles choice <sup>5</sup>. This implies that:  $w_N(N_1) = \frac{N!}{N_1!(N-N_1)!}$ . Or If we have splitting of the system multiple times

$$w_N(n_1, \dots, n_j) = \frac{N!}{\prod_k n_k!}$$

and therefore we have that the probability for this setup is:

$$p_N(n_1, \dots, n_j) = \frac{N!}{\prod_k n_k!} p_1^{n_1} p_2^{n_2} \cdots p_j^{n_j}$$

<sup>4</sup>A lot of physics is found in this way, a perfect example is the Schrödinger's equation. Schroödinger originally found from his calculations an equation called the Klein-Gordon equation, but he rejected it because it gave the wrong energies. So he then devised one that "worked" and that is what we know today as the Schrödinger equation.

<sup>5</sup>This does not always hold for a realistic situation, for example electrons (and fermions in general) obey the Pauli exclusion principle and this means that if an electron has chose one of the states, another cannot occupy the same state.

The conditions to be held are as follows:

- $\Omega = \sum_{n_k} w_N(n_1, \dots, n_j)$ . All this is saying is that the sum of all the states for each setup is equal to total number of states for the system.
- $\sum_k n_k = N$ . The sum of all the collection of particles in each energy level, is equal to the total number of particles in the entire system.
- $\sum_{n_k=0}^N p_N(n_1, \dots, n_j) = 1$ . This is a statement that all probabilities must sum to be equal to 1. You met a similar concept in Quantum Mechanics:  $\int \|\psi^2\| d\tau = 1$ . You can use the same understanding here.

## 4 The Canonical Ensemble

### 4.1 Systems in heat contact to environment

This is thought of as a system with a heat contact to a large reservoir, but with no particle exchange. I.e energy can be transferred between the two, but the particle number stays the same for each system (reservoir and system in question). From this we can determine that the system is at constant temperature (From the 0th Law of Thermodynamics).

Now, because we have changed the situation, we need a new thermodynamic potential! This is because,  $U$  is no longer constant, internal energy of the system can change due to the energy flux from the reservoir. So this cannot be the thermodynamic potential. Instead we use the **Helmholtz Free Energy** which is defined by:  $F = U - TS$ <sup>6</sup>.

Lets now look at the thermodynamics. The exact differential of the Helmholtz Free Energy is as follows:

$$dF = dU - d(TS) = dU - SdT - TdS \quad (4)$$

Now we know that  $dU = TdS - pdV$ , so plugging this back into the equation (4) to give the following:

$$dF = -SdT - pdV \quad (5)$$

Therefore we can see that the independent variables for this thermodynamics potential are  $T$  and  $V$ .

Now lets come up with a Maxwell relation for the Helmholtz free energy:

First Derivatives

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \& \quad \left(\frac{\partial F}{\partial V}\right)_T = -p \quad (6)$$

Now using these first derivatives, let find the maxwell relation:

Maxwell Relation

$$\begin{aligned} \left(\frac{\partial}{\partial F} \left(\frac{\partial T}{\partial V}\right)_V\right)_T &= \left(\frac{\partial}{\partial F} \left(\frac{\partial V}{\partial T}\right)_T\right)_V \\ \implies \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \end{aligned}$$

There are 3 more Maxwell equation, you should have a go at calculating them.

Equilibrium Condition

Lets now look at the stability of the Helmholtz free energy. Consider changes to state of the system that require no work. So we have that  $\delta W = 0$ , therefore this implies the following:

<sup>6</sup>The arrival at this expression is due to Legendre Transformations, which are beyond the scope of this course.

$$dU = \delta Q \leq TdS \leftarrow \text{This is from the fundamental law.}$$

$$\leq d(TS) \leftarrow \text{This is because } T \text{ is constant in this setting.}$$

Therefore we have the following equation:

$$d(U - TS) \leq 0$$

$$dF \leq 0 \quad (7)$$

Therefore, this tells us that the Helmholtz free energy tends to a minimum at equilibrium. I.e  $F \rightarrow F_{min}$ .

## 4.2 The Canonical Ensemble

It is used for systems in heat contact to and environment (reservoir) In the canonical ensemble,  $T$  - Temperature,  $V$  - Volume and  $N$  - number of particles are all kept constant.

So the reservoir and system are isolated and there is no particle exchange.

$$\text{Ratio of probabilities} = \frac{P(E_1)}{P(E_2)} = \frac{\Omega(E - E_2)}{\Omega(E - E_1)}$$

But  $S_R[E_j] = k_B \ln(\Omega(E - E_j)) \implies \Omega(E - E_j) = e^{S_R/k_B}$ . Therefore:

$$\frac{P(E_1)}{P(E_2)} = \exp[(S_R[E_2] - S_R[E_1])/k_B] \quad (8)$$

Also, as  $dN_R = 0$  due to there being no particle exchange and  $|pdV_R| \ll dU_R$ , as  $|pdV_R| \approx 10^{-25}$  for gases Therefore,  $\Delta S_R = \frac{1}{T} \Delta U_R$ . As  $\Delta U_R = U_R(E_2) - U_R(E_1)$  and that  $E = E_R + E_s = E = U_R + E_s \implies U_R = E - E_s$ . Therefore, we have that  $\Delta S_R = \frac{1}{T}((E - E_2) - (E - E_1)) = \frac{1}{T}(E_1 - E_2) = \frac{1}{T}(E_2 - E_1)$

Therefore using that  $S_R[E_2] - S_R[E_1] = \frac{1}{T}(E_2 - E_1)$  into (8), this gives us:

$$\frac{P(E_1)}{P(E_2)} = e^{-(E_2 - E_1)/k_B T} = \frac{e^{-\beta E_2}}{e^{-\beta E_1}}$$

So the ratio of probabilities is just the ratio of Boltzmann factors. Neat huh?

So we can see that:

$$\frac{P(E_1)}{\exp(-\beta E_1)} = \frac{P(E_2)}{\exp(-\beta E_2)} = \text{constant} = \frac{1}{Z}$$

$$\implies P(E_j) = \frac{1}{Z} e^{-\beta E_j} \quad (9)$$

But what is this  $Z$ ?

Well,  $P(E_j)$  is the probability to find system in state  $E_j$ . We know that the sum over all the probabilities must be unity (one). Therefore:

$$1 = \sum_j P(E_j) = \frac{1}{Z} \sum_j e^{-\beta E_j} \quad (10)$$

Which then, after some rearranging gives:  $Z = \sum_{\text{states}} e^{-\beta E_j} \leftarrow \text{is the Partition Function}$

## Helmholtz Free Energy

Considering the internal energy  $U = \langle E \rangle = \sum_j E_j P(E_j) = -\frac{\partial}{\partial \beta} (\ln(Z))$  So  $Z$  describes a thermodynamic quantity, however,  $U$  is not the potential for the canonical ensemble.

We are going to show that:

$$\boxed{F = -k_B T \ln(Z)} \quad (11)$$

is a potential for this ensemble.

We can and will demonstrate that:

i)  $F \sim \ln(Z)$

ii)  $F = U - TS$  holds with the upper relation.

So for i) Consider two systems with no interaction. (independent systems)

$$\implies E_{1+2} = E_1 + E_2 \text{ and that } Z_{1+2} = Z_1 \cdot Z_2 \text{ (Prove this yourself! )}$$

$$\implies F_{1+2} = -k_B T \ln(Z_{1+2}) = -k_B T \ln(Z_1 \cdot Z_2) = -k_B T \ln(Z_1) + (-k_B T \ln(Z_2)) = F_1 + F_2$$

For ii) thermodynamics:  $dF = dU + SdT$

$$\implies \left(\frac{\partial F}{\partial T}\right)_V = -S = \frac{F-U}{T} \iff F = U - TS$$

Manipulating statistic sides:

$$\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T}[-k_B T \ln(Z)] = \underbrace{-k_B \ln(Z)}_{\textcircled{1}} - \underbrace{k_B T \frac{\partial}{\partial T}(\ln(Z))}_{\textcircled{2}}$$

① This form is going to be okay to deal with,

② We need to resolve the  $\frac{\partial}{\partial T} \ln(Z)$ .

$$\frac{\partial}{\partial T} \ln(Z) = \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \frac{\partial}{\partial T} \sum_j e^{-\beta E_j} = \frac{1}{Z} \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \sum_j e^{-\beta E_j}$$

using that  $\beta = \frac{1}{k_B T} \implies$

$$= \frac{1}{Z} \left[ \frac{-1}{k_B T^2} \right] \sum_j -E_j e^{-\beta E_j}$$

$$= \frac{1}{k_B T^2} \sum_j E_j \frac{e^{-\beta E_j}}{Z}$$

using that  $\frac{e^{-\beta E_j}}{Z} = p(E_j) \implies$

$$= \frac{1}{k_B T^2} \sum_j E_j p(E_j) = \frac{1}{k_B T^2} \langle E \rangle$$

therefore we have that

$$\frac{\partial}{\partial T}(\ln(Z)) = \frac{U}{k_B T^2} \quad (12)$$

### 4.3 Energy Fluctuations in the Canonical Ensemble

Fluctuations are defined by  $\sigma_A^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 = \langle (\delta A)^2 \rangle$  and the standard deviation of  $A$  is just  $\sigma_A = \sqrt{\sigma_A^2}$ .

#### Energy Fluctuations

$$\boxed{\sigma_E^2 \stackrel{(a)}{=} -\frac{\partial \langle E \rangle}{\partial \beta} \stackrel{(b)}{=} k_B T^2 c_V} \quad (13)$$



Where  $C_V = \frac{\partial U}{\partial T}$ .

We will show that both (a) and (b) hold:

(a)  
Consider

$$\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \sum_s E_s \exp(-\beta E_s) \right) \quad (14)$$

$$= \frac{1}{Z} \sum_s E_s \exp(-\beta E_s) (-E_s) \quad - \frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \sum_s E_s \exp(-\beta E_s) \quad (15)$$

$$= \frac{-1}{Z} \sum_s E_s^2 \exp(-\beta E_s) \quad - \underbrace{\frac{1}{Z} \frac{\partial Z}{\partial \beta}}_{\langle E \rangle} \frac{1}{Z} \sum_s E_s \exp(-\beta E_s) \quad (16)$$

$$= -\langle E^2 \rangle \quad - \frac{\partial \ln(Z)}{\partial \beta} \langle E \rangle \quad (17)$$

If we notice that:  $\langle E \rangle = \frac{1}{Z} \sum_s E_s \exp(-\beta E_s) = -\frac{\partial \ln(Z)}{\partial \beta}$ , then we have that:

$$\frac{\partial \langle E \rangle}{\partial \beta} = \langle E \rangle^2 - \langle E^2 \rangle = -\langle (\delta E)^2 \rangle \quad (18)$$

Therefore we have that:

$$\sigma_E^2 = -\frac{\partial \langle E \rangle}{\partial \beta} \quad (19)$$

(b)

Now lets consider the following approach:

$$-\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial T}{\partial \beta} \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial T}{\partial \beta} \frac{\partial U}{\partial T} = \frac{\partial T}{\partial \beta} C_V \quad (20)$$

Now look at

$$\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial \beta} \left( \frac{1}{k_B \beta} \right) = \frac{-1}{k_B \beta^2} = \frac{-k_B^2 T^2}{k_B} = -k_B T^2$$

So we have that:

$$-\frac{\partial \langle E \rangle}{\partial \beta} = -(-k_B T^2) C_V = k_B T^2 C_V \quad (21)$$

And this is the form we were looking for.

Now we ask how does the energy fluctuations scale with particle number?

We now notice that  $c_V$  is an extensive quantity. Where  $C_V$  is the **heat capacity**. Defined as follows:  $C_V = \frac{\partial U}{\partial T}$ . First of all, we have that  $C_V = c_V^3 N$ , where  $c_V$  is the **specific heat capacity**. All we need to know from this relation is that  $C_V$  scales with  $N$ .

This implies that  $\sigma_E^2 = \langle (\delta E)^2 \rangle \sim N$ , so  $\sigma_E \sim \sqrt{N}$ . And therefore we have that:

$$\frac{\sigma_E}{E} = \frac{\sigma_E}{N \cdot \epsilon} \sim \frac{1}{\sqrt{N}} \quad (22)$$

Where  $\epsilon$  is the average energy per particle.

## 5 Mixing Entropy and Gibbs Paradox

Consider a container split into two parts:

Gas A	Gas B
$P_A, T_A$	$P_B, T_B$
$N_A, V_A$	$N_B, V_B$

At equilibrium  $P_A = P_B$  and  $T_A = T_B$ . Now, to make things easier, that  $N_A = N_B = N$  and that  $V_A = V_B = V$ . Now if we remove the wall separating gas A and B:

i) **Calculate the entropy before removing the wall**

$$S_{\text{initial}} = S_A + S_B = Nk_B(\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_A + \frac{3}{2}) + Nk_B(\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_B + \frac{3}{2})$$

ii) **Calculate the Entropy After Mixing**  $S_{\text{mixing}} = S_A(2V) + S_B(2V) = S_{\text{initial}} + 2Nk_B \ln(2)$

So we have an entropy increase of  $2Nk_B \ln(2)$ . This is called the mixing entropy.

**Gibb's Paradox** is that we have specified a specific gas. Therefore, if we set gas A = gas B, i.e mix the same gas. Then we still end up with an entropy increase. Even though the gas is technically fully fixed. As the pressure, temperature, etc, are all the same either side of the wall. So by constructing and deconstructing this imaginary partition which doesn't do anything we can continually increase the entropy. This is **very** unrealistic!

### 5.1 Solution!

The solution is to recognise that we can have *distinguishable* and *indistinguishable* particles. I.e

State 1) 

+
-

      State 2) 

-
+

 ← Here the states are different, so we have 2 States.

Now imagine the following situation:

State 1) 

•
•

      State 2) 

•
•

 ← You cannot tell whether the system has changed or not. So the states are the same. So you only have 1 state.

So now suppose we have N gas particles, that are indistinguishable. Therefore we have N! ways of swapping the particles without altering the state. This then leads us to a new partition function:  $Z_N = \frac{1}{N!} Z_1^N$

### 5.2 Correct Thermodynamics for an Ideal Gas

Using our new partition function:  $Z_N = \frac{1}{N!} Z_1^N$  for a gas. Rerunning through the steps we get:

**Helmholtz Free Energy:**

$$F = -k_b T \ln Z = -Nk_B T \left[ \ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + 1 \right]$$

Now  $F$  is *extensive* because:  $\ln V - \ln N = \ln \frac{V}{N}$  - which is constant if you double V and double N.

**Entropy**

$$S = - \left( \frac{\partial F}{\partial T} \right)_T = Nk_B T \ln Z + Nk_B T \frac{3}{2} \frac{\partial}{\partial T} (\ln T) = Nk_B \left[ \ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

**Internal Energy**

$U = F + TS$ , now notice that all the terms cancel except for the constant terms. So we end up with  $U = \frac{3}{2} Nk_B T$

**Pressure**

$p = - \left( \frac{\partial F}{\partial V} \right)_T = Nk_B T V^{-1}$ . So the pressure is unchanged.

**What about the Paradox?**

Assume we are "mixing" two identical gases just like before. Then we now end up with:

The partition is now:  $Z_{NA} = \frac{1}{N!} Z_A^N = \frac{1}{N!} Z_B^N$  and that implies that:

$$S_{\text{initial}} = S_A + S_B = 2Nk_B \left[ \ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

Now after mixing we have:  $Z_{\text{mix}} = \frac{1}{2^N} Z^{2N}$  and that implies that:  
 $S_{\text{mix}} = 2Nk_B [\ln 2V - \ln 2N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2}]$ , However,  $\ln 2V - \ln 2N = \ln \frac{2V}{2N} = \ln \frac{V}{N} = \ln V - \ln N$   
 So we now have that  $S_{\text{initial}} = S_{\text{mix}}$ . So the paradox has been resolved!

## 6 The Grand - Canonical Ensemble

The grand canonical ensemble is for an open system. This is when energy and particle number are allowed to be transferred to the environment. The 1<sup>st</sup> law of thermodynamics for this system is as follows:

1<sup>st</sup> Law:  $dU = TdS - pdV + \sum_j \mu_j dN_j$  where  $\mu$  is called the chemical potential and can be defined as:

$\mu_j = \left( \frac{\partial U}{\partial N_j} \right)_{S,V}$ , which is not a very enlightening definition. Or it can be defined as  $\mu = \frac{G}{N}$  where G is the

Gibbs free energy. This means the *chemical potential is the Gibbs free energy per particle*. But what's the Gibbs free energy? Well let  $U = TS - pV + \sum_j \mu_j N_j$  then rearrange to have the following:

$\sum_j \mu_j N_j = U - TS + pV \equiv G$ . So these definitions of G and  $\mu$  are conceptually better in my opinion.

### 6.0.1 Thermodynamics of an Open system

We have arrived at a problem, in previous cases, U, F and now G all depend on N. But N can now fluctuate. The trick to solving this problem is to swap from N to  $\mu$ <sup>7</sup> So what is the new thermodynamic potential for this system.

#### *Grand - Canonical Thermodynamics potential*

$$\Omega_{gr} = U - TS - \mu N \quad (23)$$

As  $U = TS - pV + \mu N$ , this gives that  $\Omega_{gr} = -pV$ . Which also means that  $d\Omega_{gr} \leq 0$ . So this thermodynamic potential tends to a minimum at equilibrium. I would also point out that the natural variables for this potential are  $\mu$ , T and V.

### 6.0.2 Gibbs Factor

The Gibbs factor derivation is similar to that of the Boltzmann factor but we have an extra term in the 1<sup>st</sup> law of thermodynamics. The Gibbs factor has the form:

$$p(E_i, N_i) \propto \exp[-\beta(E_i - \mu N_i)] \quad (24)$$

To get this into an equality we use the same trick as for finding the equality for the Boltzmann factor. We use the fact that  $\sum_{E_i, N_i} p(E_i, N_i) = 1$ . So if  $p(E_i, N_i) = C_i \exp[-\beta(E_i - \mu N_i)]$ , then we have that, (if we let  $\sum_i C_i = C$ ), then

$$\frac{1}{C} = \sum_{E_i, N_i} \exp[-\beta(E_i - \mu N_i)] = Z_{gr} \quad (25)$$

This is known as the **Grand Partion Function**

This is often written in a different way. If we define the **fugacity** as  $z = e^{\beta\mu}$ . Then we can write the grand partition function as so:

$$Z_{gr} = \sum_N z^N Z_{can} \quad (26)$$

Where  $Z_{can}$  is the Canonical Partition Function.

At this point, you may have noticed we've missed a fair bit of physics in this ensemble. Such as the degeneracy of states and the distinguishability of the particles. But there is a clever trick to rectify this. We put all the desired physics into the canonical partition function.

<sup>7</sup>This is done by a Legendre Transformation, which is a technique beyond this course. So don't worry about it ;)

### 6.0.3 Thermodynamic Relation

Now we have the grand partition function we can retrieve all the thermodynamics from it. So we need to find a function such that  $\Omega_{gr} = f(Z_{gr})$ . This function is as follows:

$$\Omega_{gr} = -k_B T \ln(Z_{gr}(T, \mu, V)) \quad (27)$$

There is a summary of all the ensembles and their properties at the end of this guide.

## 7 Fermions, Bosons and their technicalities

A **Fermion** is a particle with spin  $s = n + 1/2$  for  $n \in \mathbb{Z}$

A **Boson** is a particle with integer spin.  $s = n$  for  $n \in \mathbb{Z}$

To determine whether a composite particle, such as protons and elements of the periodic table, you count the number of basic fermions.

If the number of basic fermions is even you have a Boson

If the number of basic fermions is odd you have a Fermion

### 7.1 Energy Distributions for Fermions and Bosons

#### 7.1.1 Fermions

All we are given to begin with is the probability of each state,  $p(E, N)$ , they obey the Pauli exclusion principle and they are indistinguishable. From this we are looking to find an energy distribution for a system of Fermions.

We start off by thinking of the system micro-canonically. If we let  $\Omega$  be the number of different states of the system,  $G$  to be the number of different states each particle can occupy and  $N$  to be the number of Fermions we have.

Therefore as they obey the Pauli exclusion principle. We know that  $G \geq N$  and we also know that there must be  $N$  occupied states and  $G - N$  unoccupied states. Therefore we know that:

$$\Omega = \frac{G!}{N!(G - N)!} \quad (28)$$

Now that we have this, we then consider every single energy state  $E_j$  and the probability of this state. When the state is unoccupied, the energy of this state is zero, i.e  $E = 0$  When the state is occupied by  $N$  particles the energy of the state is,  $E = N \cdot E_j$ . However, Pauli's exclusion principle states that no two fermions can occupy the same state, therefore  $N = 0$  or  $N = 1$ .

With this we can calculate the probabilities using  $p(N) = \frac{1}{Z_{gr}} \exp[-\beta(E - \mu N)] = \frac{1}{Z_{gr}} \exp[-\beta N(E_j - \mu)]$  So we need to figure out  $Z_{gr}$  in order to find the probabilities. We do this by using the formula we saw earlier:  $Z_{gr} = \sum_E \sum_N \exp[-\beta(E - \mu N)]$ . As we are only considering the single state  $E_j$  the sum over energies becomes redundant, and using Pauli's Exclusion principle we know  $N = 0$  or  $N = 1$ . This gives us the following.  $Z_{gr} = 1 + \exp[-\beta(E_j - \mu)]$

Now using these we can calculate the average number density,  $\langle N \rangle$  as follows:

$$\langle N \rangle = \sum_{N=0,1} N p(N) = 0p(0) + p(1) \quad (29)$$

$$= \frac{\exp[-\beta(E_j - \mu)]}{1 + \exp[-\beta(E_j - \mu)]} \quad (30)$$

This approach works for all energies  $E_j$ , so we can now define the **Fermi-Dirac Distribution**: I

$$f_{FD}(E) = \langle n_{FD}(E) \rangle = \frac{1}{1 + \exp[\beta(E - \mu)]} \quad (31)$$

### 7.1.2 Bosons

When dealing with bosons we know that from other fields of physics that they do not obey the Pauli exclusion principle. So if we begin by treating the system of bosons micro-canonically. We have the number of states,  $\Omega$ , for a system with  $G$  states and  $N$  bosons. Now similar to fermions, bosons are indistinguishable, so our classical model of  $\Omega = G^N$  does not hold. So we have to think about this slightly, and I will redirect you to a very useful website I found, it can be found [here](#). And referring to the webpage, for bosons we have combinations with repetitions. For Bosons we can think of the ice cream machine as you, the flavours of ice cream as distinct states and the scoops as placements of bosons. Then we end up with the following formula:

$$\Omega = \frac{(N + G - 1)!}{N!(G - 1)!} \quad (32)$$

Now that we have the number of states we can proceed to consider a single energy state,  $E_j$  and try to calculate the probability that this state is occupied by  $N$  bosons.

So if  $N$  bosons are in the state  $E_j$  then the total energy is  $E = N \cdot E_j$ . Now using the formula from before:  $p(N) = \frac{1}{Z_{gr}} \exp(-\beta N(E_j - \mu))$ . Next we plug this into the partition function,  $Z_{gr} = \sum_N \exp(-\beta N(E_j - \mu)) = 1 + \exp(-\beta(E_j - \mu)) + \exp(-2\beta(E_j - \mu)) + \dots$ . Now if we treat  $x = \exp(-\beta(E_j - \mu))$ , then we can say that  $Z_{gr} = 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x}$  as long as  $|x| < 1$ . So we have that  $Z_{gr} = (1 - \exp(-\beta(E_j - \mu)))^{-1}$ .

So we now need to find the average number of particles in each state  $E_j$ , so as before this is done by  $\langle N \rangle = \sum_N N \cdot p(N) = p(1) + 2p(2) + 3p(3) + \dots$ . So now if make this a bit easier to write and put  $\bar{x} = \beta(E_j - \mu)$ , then we have that  $\langle N \rangle = \sum_N N \frac{1}{Z_{gr}} \exp(-N\bar{x})$

So  $\langle N \rangle = \frac{-1}{Z_{gr}} \sum_N \frac{d}{d\bar{x}} e^{-N\bar{x}} = -\frac{1}{Z_{gr}} \frac{d}{d\bar{x}} \sum_N e^{-N\bar{x}}$ . Now using the fact that  $Z_{gr} = \sum_N e^{-N\bar{x}}$  we have that:  $\langle N \rangle = -\frac{1}{Z_{gr}} \frac{d}{d\bar{x}} Z_{gr}$ . Now using the result we arrived at earlier,  $Z_{gr} = 1 - e^{-\bar{x}}$ . We have the following:

$$\langle N \rangle = -(1 - e^{-\bar{x}}) \frac{d}{d\bar{x}} [1 - e^{-\bar{x}}]^{-1} \quad (33)$$

$$= -(1 - e^{-\bar{x}})(-1)[1 - e^{-\bar{x}}]^{-2} e^{-\bar{x}} \quad (34)$$

$$= \frac{e^{-\bar{x}}}{1 - e^{-\bar{x}}} = \frac{1}{e^{\bar{x}} - 1} \quad (35)$$

This method work for all energies  $E_j$ , so we can now define the ***Bose-Einstein Distribution***

$$f_{BE}(E) = \langle n_{BE}(E) \rangle = \frac{1}{\exp[\beta(E - \mu)] - 1} \quad (36)$$

## 8 Classical Limit

So we have found new distributions for fermions and bosons, however we do see physics based on Boltzmann's formulation. So where does Boltzmann statistics become applicable? So a short list of cases when it does apply and when:

1) For distinguishable particles. One example useful to remember for 3<sup>rd</sup> year is this applies for atoms in a lattice. Particularly solids.

2) A gas can have Boltzmann statistics if  $\beta\mu = \ln(n\Lambda^3)$

The Boltzmann stats apply also if we have  $e^{\beta\mu} \gg 1 \iff n\Lambda^3 \ll 1$ . So you can think of this statement as "low densities" or "high temperatures" as  $n = \frac{N}{V}$  and  $\Lambda \sim T^{\frac{1}{2}}$

A gas of fermions can be treated classically when  $E \gg \mu$ . then  $f_{FD}$

## Micro-Canonical Ensemble / Closed Systems

- Thermodynamics

The internal energy,  $U$ , is the thermodynamic potential. In This ensemble the number  $N$  is held constant and also the energy,  $E$ , is held constant but also  $E = U$ . The natural variables for this case are  $S$ ,  $V$  and  $N$

- Thermodynamic Relation

$$S = k_B \ln(\Omega)$$

- Equilibrium

The entropy  $S$ , tends to its maximum. I.e  $S \rightarrow S_{max}$

## Canonical Ensemble

- Thermodynamics

The thermodynamic potential is the Helmholtz free energy,  $F$ , and  $F = U - TS$ . In this ensemble the number,  $N$ , is kept constant. But this time  $E$  fluctuates, and the temperature of the system is given by the heat bath that is attached. The natural variables for this case are  $T$ ,  $V$  and  $S$

- Thermodynamic Relation

$$F = -k_B T \ln(Z_{can})$$

- Equilibrium

The Helmholtz energy tends to a minimum at equilibrium. I.e  $F \rightarrow F_{min}$

## Grand-Canonical Ensemble

- Thermodynamics

The thermodynamic potential is the Grand Canonical Thermodynamic Potential,  $\Omega_{gr}$ . With  $\Omega_{gr} = -pV$ . In this ensemble the number,  $N$ , and energy,  $E$ , can fluctuate. The natural variables for this are  $T$ ,  $\mu$  and  $V$

- Thermodynamic Relation

$$\Omega_{gr} = -k_B T \ln(Z_{gr})$$

- Equilibrium

The grand canonical potential tends to its minimum. I.e  $\Omega_{gr} \rightarrow \Omega_{max}$