

PHYS 427

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# Chapter 1

## PHYS427

I did a bunch of stat mech in my silly research group I'm assuming this won't be the end of the world.

Much of this course builds on PHYS213

Homework has to be physically printed and put in a bin so I have to steal a ton of paper.

Just do textbook problems if you don't understand any part of the material.

She seems like she enjoys this course.

# Chapter 2

## Probability and Multiplicity

### 2.1 Microstates

Complete description of the system.

Knowing the position/momentum of every molecule in a box (unrealistic).

### 2.2 Macrostates

Gas pressure, volume, temperature, etc.

#### 2.2.1 Ex: Polymer

Imagine a polymer

The microstate would be the state of every single portion of the polymer.

A macrostate could be the end-to-end extension of the polymer.

#### 2.2.2 Ex: Magnet

Microstate: the configuration of every single electron spin in the entire magnet.

Macrostate: magnetization of the magnet (average spin value)

### 2.3 Particles In a Box

Imagine a box with  $N$  particles distributed in both the left half and the right half.

Microstate: Configuration of all  $N$  particles in either the right or left half.

Macrostate: Total number of particles in the left box.

### 2.3.1 Number of Possible Microstates

consider  $n_L$  as the macrostate which is the number of particles in the left box.

### 2.3.2 $\Omega(n_L, N)$

$\Omega(n_L, N)$  is the number of microstates given 1 possible macrostate.

- Consider  $N = 1$  and  $n_L = 0$ . This means that only 1 particle has to be in the right box, so  $\Omega(0, 1) = 1$ .  
if  $n_L = 1$ , then the 1 particle has to be in the left side, so  $\Omega(1, 1) = 1$ .
- What about  $N = 2$ ?  
if  $n_L = 0$ , then all particles have to be in the right side, so  $\Omega(0, 2) = 1$ .  
if  $n_L = 1$ , then either particle  $A$  can be on the left side, or particle  $B$  can be on the left side, so  $\Omega(1, 2) = 2$ .  
if  $n_L = 2$ , then all particles have to be in the left side, so  $\Omega(2, 2) = 1$ .
- $N = 3$   $n_L = 0 \rightarrow \Omega(0, 3) = 1$ .  
 $n_L = 1 \rightarrow \Omega(1, 3) = 3$ .  
 $n_L = 2 \rightarrow \Omega(2, 3) = 3$ .  
 $n_L = 3 \rightarrow \Omega(3, 3) = 1$ .

For this example, the number of possible microstates grows exponentially.

the total number of microstates is known as the ensemble of microstates.

The total number of microstates grows like  $2^n$ .

The total number of macrostates grows like  $n$

For large  $n$  the number of microstates becomes unreasonably big.

### 2.3.3 General Formula for $\Omega$ ?

I think you just use combinatorics.

For  $n_L$  particles on the left side, there are  $N - n_L$  particles on the right side.

for the first particle going to  $L$ , you have  $N$  choices.

for the second particle going to  $L$ , you have  $N - 1$  choices.

for the third particle going to  $L$ , you have  $N - 2$  choices.

go all the way until you have  $n_L$  particles in the left bin.

Then you remove all permutations that are the same as each other by dividing by  $n_L!$



$$\frac{N(N-1)(N-2)\dots(N-n_L+1)}{n_L!} \Rightarrow$$

$$\frac{N!}{(N-n_L)!n_L!} = \binom{N}{n_L}$$

That's just the binomial coefficient.

If we consider  $p$  and  $q$  as the right and left sides of the box, then we can derive another formula.

For this box,  $p = 1$  and  $q = 1$  because there is 1 left side and 1 right side.

$$(p+q)^N = \sum_{n=0}^N \binom{N}{n} p^n q^{N-n}$$

$$2^N = \sum_{n=0}^N \binom{N}{n} = \sum_{n=0}^N \Omega(n, N)$$

## 2.4 Probability of a Macrostate

An assumption we make is that each microstate is equally likely. This is true for microstates, but **not true** for macrostates.

If a macrostate has many many many possible microstates, then it is more likely than a macrostate with fewer possible microstates.

Let  $p(n_L, N)$  be the probability of getting a certain macrostate

$$p(n_L, N) = \frac{\Omega(n_L, N)}{\sum_{n=0}^N \Omega(n, N)} = \frac{\Omega(n_L, N)}{2^N} = \frac{\binom{N}{n_L}}{2^N} = \frac{N!}{n_L!(N-n_L)!} \cdot \frac{1}{2^N}$$

Graph this and you will see a spike for large  $N$ 's

This means that there is a better and better defined macrostate that becomes overwhelmingly likely given the probabilities and microstates.

This very likely macrostate is the equilibrium state.

For  $N \rightarrow 6.022 * 10^{23} \approx \infty$ , you get very well defined equilibrium states.

## 2.5 Averages

To work with the probabilities of macrostates, we have to normalize the function.

$$\sum_{n=0}^N p(n, N) = 1$$

This is easy to check (see lecture note 1)

### 2.5.1 Expectation Value

$$\langle n_L \rangle = \frac{N}{2}$$

So to find the average of a function that takes  $n_L$ ,

$$f(n_L) \rightarrow \langle f(n_L) \rangle = \sum_{n=0}^N f(n_L) \cdot p(n_L, N) \rightarrow \langle n_L^2 \rangle = \sum_{n=0}^N n_L^2 \cdot p(n_L, N)$$

$$\langle n_L \rangle = \sum_{n=0}^N n_L \cdot p(n_L, N) = \sum_{n=0}^N n_L \frac{N!}{n_L!(N-n_L)!} \left(\frac{1}{2}\right)^N = \dots = \frac{N}{2}$$

Everything is dependent on the probability distribution of your macrostates.

### 2.5.2 Math Trick

$$(p + q)^N = \sum_{n=0}^N \binom{N}{n_L} p^{n_L} q^{N-n_L}$$

$$\left(p \frac{\partial}{\partial p}\right) p^{n_L} = n_L p^{n_L}$$

$$\langle n_L \rangle = \sum_{n=0}^N \binom{N}{n_L} n_L p^{n_L} q^{N-n_L} =$$

$$\left(p \frac{\partial}{\partial p} \sum_{n=0}^N \binom{N}{n_L} p^{n_L} q^{N-n_L}\right) = p \frac{\partial}{\partial p} (p + q)^N = N p (p + q)^{N-1}$$

$$p = q = \frac{1}{2}$$

$$\Rightarrow \langle n_L \rangle = \frac{N}{2}$$

## 2.6 Variance

$$\begin{aligned}\sigma_{n_L}^2 &= \langle n_L - \langle n_L \rangle \rangle^2 = \langle n_L^2 - 2n_L \langle n_L \rangle + \langle n_L \rangle^2 \rangle = \\ &\langle n_L^2 \rangle - 2\langle n_L \rangle^2 + \langle n_L \rangle^2 = \langle n_L^2 \rangle - \langle n_L \rangle^2\end{aligned}$$

## 2.7 Discussion 1

All microstates are equally likely.

$\Omega$  is the number of microstates in a given macrostate.

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

The general entropy equation can be written as

$$S = -k_B \sum_i p_i \ln(p_i)$$

### 2.7.1

Compute the average number of successful experiments given a binomial distribution of probability  $p$ .

$$\langle n \rangle = \sum_{n=0}^N P_p(n, N) n \quad P_p(n, N) = \binom{N}{n} p^n (1-p)^{N-n}$$

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

$$\sum_{n=0}^N P_p(n, N) n = \sum_{n=0}^N \binom{N}{n} p^n (1-p)^{N-n} n = \sum_{n=0}^N \frac{N! * n}{n!(N-n)!} p^n (1-p)^{N-n}$$

$$\sum_{n=0}^N n = \frac{N(N+1)}{2} \quad \sum_{n=0}^N p^n = p^0 + p^1 + p^2 + p^3$$

I give up I'm stupid

Supposedly the answer is  $Np$  and that makes sense but I have no idea how to get to it.

The given answer is

$$\langle n \rangle = p \frac{\partial}{\partial p} ((p + q)^N) = Np(p + q)^{N-1} \quad p + q = 1$$

$$\langle n \rangle = Np$$

Stirling's approximation is

$$\ln(N!) = N \ln(N) - N \quad N \rightarrow \infty$$

## 2.7.2 Paramagnet

Consider a lattice of  $N$  particles with energy

$$U = -\mu B(N_{\uparrow} - N_{\downarrow})$$

a) Calculate the entropy for very large  $N$  specifically with just  $U$ ,  $N$ , and  $B$

Supposedly the answer is given by

$$\Omega = \frac{(N_{\uparrow} - N_{\downarrow})}{N_{\uparrow}! N_{\downarrow}!} \quad U = -\mu B(N_{\uparrow} - N_{\downarrow}) \quad N_{\uparrow} + N_{\downarrow} = N$$

$$\Omega = \frac{N!}{(\frac{N}{2} - \frac{U}{2\mu B})! (\frac{N}{2} + \frac{U}{2\mu B})!} \quad S = k_B \ln(\Omega)$$

Do some log stuff and **use Stirling's Approximation** and then you get a decent number.

b) Compute the energy of the system at temperature  $T$

Okay so we can solve for temperature, and then we can replace parts of the equation for  $T$  to get the energy as a function of  $T$ .

$$\frac{1}{T} \equiv \frac{\partial S}{\partial U} \quad S = k_b \ln \left( \frac{N!}{(\frac{N}{2} - \frac{U}{2\mu B})! (\frac{N}{2} + \frac{U}{2\mu B})!} \right)$$

## 2.8 Probability Width

We talked about for  $n_L$  when  $\langle n_L \rangle = N/2$ , as  $N$  gets large, there is a significant peak in probability at  $N/2$ . However, we do not know the width of the peak.

$$\sigma_{n_L}^2 = \langle n_L^2 \rangle - \langle n_L \rangle^2 \quad \langle n_L^2 \rangle = \frac{N(N+1)}{4}$$

With derivation

$$\left(p \frac{\partial}{\partial p}\right)^2 p^{n_L} = n_L^2 p^{n_L}$$

$$p \frac{\partial}{\partial p} \left(p \frac{\partial}{\partial p}\right) p^{n_L} \rightarrow p \frac{\partial}{\partial p} (p \cdot n_L p^{n_L-1}) \rightarrow p \frac{\partial}{\partial p} (n_L p^{n_L}) = n_L^2 p^{n_L}$$

Now we can determine the average of the square

Remember that  $p = q = 1/2$

$$\langle n_L^2 \rangle = \sum_{n_L=0}^N n_L^2 \binom{N}{n_L} p^{n_L} q^{N-n_L} \rightarrow$$

$$\left(p \frac{\partial}{\partial p}\right)^2 \sum_{n_L=0}^N \binom{N}{n_L} p^{n_L} q^{N-n_L} = \left(p \frac{\partial}{\partial p}\right)^2 (p+q)^N$$

$$\langle n_L^2 \rangle = \sum_{n_L} n_L^2 P(n_L, N)$$

$$p \frac{\partial}{\partial p} (Np(p+q)^{N-1}) = Np(p+q)^{N-1} + N(N-1)p^2(p+q)^{N-2}$$

$$\langle n_L^2 \rangle = \sum_{n_L=0}^N \binom{N}{n_L} n_L^2 \left(\frac{1}{2}\right)^N \equiv \frac{N}{2} + \frac{N(N-1)}{4} = \frac{N(N+1)}{4}$$

$$\sigma_{n_L}^2 = \langle n_L^2 \rangle - \langle n_L \rangle^2 = \frac{N(N+1)}{4} - \left(\frac{N}{2}\right)^2 = \frac{N}{4}$$

$$\sigma_{n_L} = \frac{\sqrt{N}}{2}$$

The standard deviation increases, but it increases less quickly than  $N$  and  $\langle n_L \rangle$ , so the ratio of width to number of particles decreases

$$\frac{\sigma_{n_L}}{\langle n_L \rangle} = \frac{1}{\sqrt{N}} \xrightarrow{N \rightarrow \infty} 0$$

## 2.9 Physical Systems

We know that

$$\Omega = \text{Multiplicity}$$

But how does this look for real systems?

### 2.9.1 Closed System

Energy is conserved. Also known as an isolated system.

No change in  $E, U, N$

So we're trying to find  $\Omega(U, N)$

### 2.9.2 Einstein Solid

Imagine a lattice of particles connected via strings.

$N$  identical independent quantum harmonic oscillators.

The quantum harmonic oscillators have energy levels of the form

$$E = \hbar\omega(s_i + \frac{1}{2}), s_i = \mathbb{N}$$

This is derived from the Schrodinger Equation

$$H\Psi(x, t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x, t) + m\omega^2 x^2\Psi(x, t) = \epsilon_i\Psi(x, t)$$

But this is not actually important for the material.

Given  $N$  oscillators

$$U = \sum_{i=0}^N \epsilon_i = \hbar\omega(n + \frac{N}{2}) \quad n = \sum_i^N s_i$$

$n$  is the number of energy quanta that you have.

The  $+\frac{1}{2}$  in energy does not affect the statistics whatsoever, so we can ignore it.

To get the multiplicity, we have to know the number of microstates for the same amount of energy in  $N$  oscillators.

How many ways are there to have different  $\sum s_i$  such that they all yield the same quantum number  $n$ .

Oh my good we're doing stars and bars.

$\cdot$  is a quanta and  $|$  is the positions between the oscillators.

$$\cdot | \cdots | | \cdots \cdot | \cdot | \dots$$

represents  $s_1 = 1, s_2 = 3, s_3 = 0, s_4 = 4$

There are always  $n$  dots and  $N - 1$  bars going into  $n + (N - 1)$  slots.

Therefore, the total number of ways to distribute it is.

$$\Omega(U, N) = \binom{n + N - 1}{n} = \frac{(n + N - 1)!}{n!(N - 1)!}$$

### 2.9.3 Stirling's Approximation

This is literally the more important thing in the entirety of statistical mechanics.

$$\ln(N!) \underset{N \rightarrow \infty}{\approx} N \ln(N) - N$$

The approximation works from a sum from 1 to large  $N$  being similar to a continuous integral.

## 2.10 Entropy

The entropy involves the log of the multiplicity, so we can calculate that for our Einstein solid.

$$\begin{aligned} \ln(\Omega(U, N)) &\approx \ln((n + N)!) - \ln(N!) - \ln(n!) && \text{Use Stirling's Approx.} \\ &\approx (n + N) \ln(n + N) - (n + N) - N \ln(N) + N - n \ln(n) + n \\ &= (n + N) \ln(n + N) - N \ln(N) - n \ln(n) \end{aligned}$$

### 2.10.1 High Temperature Limit

This is known as the high temperature limit because we're assuming that  $n \gg N$ , meaning there are many possible energy states for each particle.

$$\ln(n + N) = \ln\left(n \left(1 + \frac{N}{n}\right)\right) = \ln(n) + \ln\left(1 + \frac{N}{n}\right)$$

$$\ln(1 + x) \approx x : x \ll 1$$

$$\ln(n + N) \approx \ln(n) + \frac{N}{n}$$

We then plug this result back into our original expressions

$$\begin{aligned}
(n + N) \ln(n + N) - N \ln(N) - n \ln(n) &\approx \\
(n + N) \left( \ln(n) + \frac{N}{n} \right) - N \ln(N) - n \ln(n) &= \\
(n + N) \ln(n) + (n + N) \frac{N}{n} - N \ln(N) - n \ln(n) &= \\
n \ln(n) + N \ln(n) + (n + N) \frac{N}{n} - N \ln(N) - n \ln(n) &= \\
N(\ln(n) - \ln(N)) + \left( N + \frac{N^2}{n} \right) &= \\
N \ln\left(\frac{n}{N}\right) + N\left(1 + \frac{N}{n}\right) &\approx N \ln\left(\frac{n}{N}\right) + N
\end{aligned}$$

You can then re-exponentiate that expression.

$$\Omega(U, N) = e^{\ln(\Omega(U, N))} = \left(e \frac{n}{N}\right)^N = \left(\frac{eU}{N\hbar\omega}\right)^N$$

$$\Omega \sim U^N$$

For an ideal gas,  $\Omega \sim U^f$ ,  $f \sim N$

## 2.10.2 Entropy Property

For two independent systems:

$$\Omega_{A+B} = \Omega_A \Omega_B \Rightarrow \sigma_{A+B} = \sigma_A + \sigma_B$$

For changing system size

$$\sigma = N \ln\left(\frac{eU}{N\hbar\omega}\right)$$

If both  $N$  and  $U$  double in size

$$N \rightarrow 2N \quad U \rightarrow 2U$$

$$\sigma = N \ln\left(\frac{eU}{N\hbar\omega}\right)$$

The variance is independent of system size.

Intensive quantities are independent of system size  $T, p$

$\sigma$  goes up logarithmically with  $U$



### 2.10.3 Not High Temperatures

All of this **only works because of the high temperature approximation**

$$U \gg N\hbar\omega$$

So the limit

$$\sigma(U \rightarrow 0) = -\infty$$

is wrong because it ignore the approximation we made.

$$\sigma(U \rightarrow 0) \rightarrow \ln(1) = 0$$

That is what actually happens at low temperatures.

## 2.11 Paramagnet

Imagine a paramagnetic with  $N$  independent spins of both  $\uparrow$  and  $\downarrow$ .

$$N = n_{\uparrow} + n_{\downarrow}$$

The paramagnet has a magnetic moment given by

$$\vec{\mu} = g \frac{q}{2m} \vec{s}$$

$$\epsilon = -\vec{\mu} \cdot \vec{B} = -\mu_z B$$

The general solution for magnetic moment in this case is

$$\mu_z = g \frac{q\hbar}{2m} m_s \quad m_s = -s, -s+1, \dots, s-1, s$$

$$m_s = \frac{1}{2} \text{ or } \frac{-1}{2} \quad g \approx 2$$

$$\mu_B = \frac{e\hbar}{2m_e} \quad \text{Bohr Magnetron}$$

$$\epsilon = -\mu B, \epsilon = +\mu B$$

$$U = n_{\uparrow}(-\mu B) + n_{\downarrow}(\mu B) = -\mu B(n_{\uparrow} - n_{\downarrow}) = -\mu B(2n_{\uparrow} - N)$$

For a binary system, we get

$$\Omega(n_{\uparrow}, N) = \binom{N}{n_{\uparrow}} = \frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!}$$

$$\Omega(U, N) = \frac{N!}{\left(\frac{N}{2} - \frac{U}{2\mu B}\right)! \left(\frac{N}{2} + \frac{U}{2\mu B}\right)!}$$

Use Stirling Approximation and put the terms together.

After everything is said, we should get

$$\ln(\Omega(U, N)) = N \ln(N) - (N - n_{\uparrow}) \ln((N - n_{\uparrow})) - n_{\uparrow} \ln(n_{\uparrow})$$

$$\sigma = \ln(\Omega(U, N)) =$$

$$N \ln(N) - \left(\frac{N}{2} - \frac{U}{2\mu B}\right) \ln\left(\frac{N}{2} - \frac{U}{2\mu B}\right) - \left(\frac{N}{2} + \frac{U}{2\mu B}\right) \ln\left(\frac{N}{2} + \frac{U}{2\mu B}\right)$$

The variance to energy graph looks like a circle because the lowest variances are at 2 edges where all is up or all is down.

You can calculate  $\sigma(U = 0, N)$  by just plugging in the numbers, and you get  $N \ln(2)$ .

## 2.12 Discussion 2

In thermal equilibrium, a closed system is equally likely to be in any of the microstates available to it.

$\Omega$  = total # of microstates available

$$S = k_b \ln \Omega$$

### 2.12.1 Mini Equation Sheet

$$\frac{1}{T} \equiv \left( \frac{\partial}{\partial U} \right)_{N,V}$$

$$\text{chemical potential} = \mu \equiv -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

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

These are Lagrange Multipliers which I don't remember

$$\Omega(U, N) = \sum_i \delta_k(U - U_i) \delta_k(N - N_i)$$

$$\delta_{i,k}(x) = \begin{cases} 1 & \text{if } x = 0 \\ 0 & \text{otherwise} \end{cases}$$

The kronecker delta enforces boundary conditions.

$$\delta(ax) = \delta(x) : a \neq 0$$

$$\sum_m \sum_n g(m, n) \delta(P(m, n)) = \sum_m g(m, n = n^*(m))$$

$$n * (m) \Rightarrow P(m, n^*) = 0$$

### 2.12.2 Stars and Bars

$$\Omega(n, N) = \binom{N + n - 1}{n}$$

Imagine a bunch of stars and bars

$$\cdot \cdot || \cdot | \cdot \cdot | \cdot || \cdot$$

each section between 2 bars is a certain classification, and each star in between the bars is an item that is a part of that classification.

### 2.12.3 Questions

Find the entropy for multiplicity

$$\Omega(U, N, V) = \frac{V^N (CU)^{3N/2}}{N! (3N/2)!}$$

So you do the thing

$$\begin{aligned}
S &= k \ln \left( \frac{V^N (CU)^{3N/2}}{N! (3N/2)!} \right) = \ln \left( V^N (CU)^{3N/2} \right) - \ln(N! (3N/2)!) \\
&\ln(V^N) + \ln((CU)^{3N/2}) - \ln(N!) - \ln((3N/2)!) \\
&N \ln(V) + 3N/2 \ln(CU) - N \ln(N) + N - 3N/2 \ln((3N/2)) + 3N/2 \\
&N \ln(V) + 3N/2 \ln(CU) - N \ln(N) + N - 3N/2 (\ln((N)) + \ln(3/2)) \\
&+ 3N/2
\end{aligned}$$

You just do a bunch of math and it works.

It's not hard everything is fine

## 2.12.4 Determining Multiplicity Functions

Consider

$$U = \hbar\omega n \quad \epsilon = \hbar\omega(n_x + n_y + n_z)$$

Where  $n_i = 0, 1, 2, \dots, \infty$

I think we're just gonna do stars and bars but with 3.

there is a total energy  $N$  that needs to be split 3 different ways for the energy to be in  $n_x, n_y$ , or  $n_z$ .

# Chapter 3

## Temperature

### 3.1 Thermal Contact

Imagine a box  $A$  and a box  $B$  that are able to interact with each other. Each box has multiplicity  $\Omega_A$  and  $\Omega_B$

The multiplicity and energy of the combined boxes is

$$\Omega_{AB} = \Omega_A \cdot \Omega_B \quad U_{AB} = U_A + U_B$$

$U_A$  and  $U_B$  can change, but the combined energy is fixed.

To write everything in terms of just a single box, we can say that

$$\Omega_{tot} = \sum_{U_A} \Omega_A(U_A) \cdot \Omega_B(U - U_A)$$

We know that approximately

$$\Omega_A(U_A) \sim U_A^N$$

We find that the total multiplicity has a peak centered at the average  $1/U_A$  and with a relative width of  $1/\sqrt{N}$ .

Consider the natural log  $\ln(\Omega)$ . We also know that at the peak

$$\frac{d\Omega}{dU} = 0 \quad \frac{d \ln(\Omega)}{dU} = \frac{1}{\Omega} \frac{d\Omega}{dU} = 0$$

We look for  $U_A$  where

$$\frac{\partial \ln(\Omega_A(U_A)\Omega_B(U - U_A))}{\partial U_A} = 0$$

So we do some calculations

$$\ln(\Omega_A(U_A)\Omega_B(U - U_A)) = \ln(\Omega_A(U_A)) + \ln(\Omega_B(U - U_A))$$

So our equation is

$$\frac{\partial}{\partial U_A} (\ln(\Omega_A(U_A))) + \frac{\partial}{\partial U_A} (\ln(\Omega_B(U - U_A))) = 0$$

Know the derivative

$$\frac{\partial \ln(U^N)}{\partial U} = \frac{1}{U^N} \cdot N(U^{N-1}) = \frac{N}{U}$$

This solves to

$$\begin{aligned} \frac{N_A}{\bar{U}_A} - \frac{N_B}{U - \bar{U}_A} &= 0 \rightarrow \frac{U}{\bar{U}_A} - 1 = \frac{N_B}{N_A} \\ \bar{U}_A &= \frac{U}{1 + \frac{N_B}{N_A}} \quad \bar{U}_B = \frac{U}{1 + \frac{N_A}{N_B}} = U - \bar{U}_A \end{aligned}$$

Notice that from our equations we get

$$\frac{\bar{U}_A}{N_A} = \frac{\bar{U}_B}{N_B} = \frac{U}{N_A + N_B}$$

So our peak multiplicity is found where

$$\bar{U}_A = \frac{U}{1 + \frac{N_B}{N_A}}$$

The energy per particle is the same in both  $A$  and  $B$  and it is equal to

$$\frac{U}{N} = \frac{U}{N_A + N_B}$$

### 3.1.1 Peak Sharpness

We are trying to find how sharp the multiplicity peak is

$$N_A = N_B \Rightarrow \bar{U}_A = \frac{U}{2} \quad \bar{U}_B = \frac{U}{2}$$

For an Einstein solid, we can do a small perturbation and then take a taylor expansion around that point to find the equation

$$U_A = \bar{U}_A + \delta U$$

Our energy function is given as

$$\Omega(U) = \left( \frac{eU}{N\hbar\omega} \right)^N = \Omega_A(U_A) + \Omega_B(U - U_A)$$

We can do a taylor expansion around this to get

$$\begin{aligned} & \Omega_A(U_A) + \Omega_B(U - U_A) \\ &= 2N + N \ln \left( \frac{U_A + \delta U}{N\hbar\omega} \right) + N \ln \left( \frac{U_A - \delta U}{N\hbar\omega} \right) \\ &= 2N - 2N \ln(N\hbar\omega) + N \ln \left( \bar{U}_A^2 - (\delta U)^2 \right) \\ &= 2N \ln \left( \frac{eU_A}{N\hbar\Omega} \right) + N \ln \left( 1 - \frac{\delta U^2}{\bar{U}_A^2} \right) \end{aligned}$$

Use a  $\ln(1+x) \approx x$  approximation to get

$$2N \ln \left( \frac{eU_A}{N\hbar\Omega} \right) - N \frac{\delta U^2}{\bar{U}_A^2}$$

So now we have

$$\begin{aligned} \Omega &= \Omega_A(U_A)\Omega_B(U - U_A) \approx \left( \frac{eU_A}{N\hbar\Omega} \right)^{2N} \exp \left( -\frac{N\delta U^2}{\bar{U}_A^2} \right) \\ &\approx \left( \frac{eU_A}{N\hbar\Omega} \right)^{2N} \exp \left( -\frac{\delta U^2}{2\sigma^2} \right) \end{aligned}$$

So our variance and standard deviation are given by

$$\sigma_{U_A} = \frac{\bar{U}_A}{\sqrt{2N}}$$

And the fractional width is given by

$$\frac{\sigma_{U_A}}{\overline{U}_A} = \frac{1}{\sqrt{2N}}$$

The multiplicity can again be written as

$$\Omega_{tot} = \sum_{U_A} \Omega_A(U_A) \Omega_B(U - U_A) \approx \Omega_A(\overline{U}_A) \Omega_B(U - \overline{U}_A)$$

This works almost perfectly for large  $N$  ( $N \approx 10^{20}$ )

## 3.2 Thermal Equilibrium

The entropy equation is

$$\sigma \equiv \ln(\Omega)$$

When systems  $A$  and  $B$  are in thermal contact at  $t = 0$ , then

$$\sigma_{tot} = \sigma_A(U_A) + \sigma_B(U - U_A)$$

initially, let's say that  $U_A > U_B$ . Then, over time,  $U_A$  will decrease and  $U_B$  will increase until both reach  $\overline{U}_A$  and  $\overline{U}_B$ .

The entropy of  $\sigma_A$  might decrease, but the total entropy of the two systems will always increase when going towards equilibrium.

Thermal equilibrium is reached when total entropy is maximized.

To maximize total entropy, we find a critical point

$$\frac{\partial \sigma_{tot}}{\partial U_A} = 0 = \frac{\partial \sigma_A}{\partial U_A} + \frac{\partial \sigma_B}{\partial U_B} = \frac{\partial \sigma_A}{\partial U_A} + \frac{\partial \sigma_B}{\partial U_B} \cdot \frac{\partial U_B}{\partial U_A}$$

So at equilibrium

$$\frac{\partial \sigma_A}{\partial U_A} = \frac{\partial \sigma_B}{\partial U_B}$$

At thermal equilibrium there is a fundamental temperature  $\tau$

$$\frac{1}{\tau} = \left( \frac{\partial \sigma}{\partial U} \right)_N \Rightarrow \tau_A = \tau_B$$

### 3.2.1 0th Law of Thermodynamics

If system  $A$  is in thermal equilibrium with systems  $B$  and  $C$ , then  $B$  is in thermal equilibrium with  $C$ .

This is just the transitive property but with equilibrium.



### 3.2.2 Conversions

$\tau$  is a form of energy. The absolute temperature is  $T$  in regular temperature units (Kelvin)

$$\tau \equiv k_B T \quad k_B = 1.371 * 10^{-23} \frac{J}{K}$$

The regular entropy you are used to is

$$S \equiv k_B \ln(\Omega) \quad \frac{1}{T} \equiv \left( \frac{\partial S}{\partial U} \right)_N$$

So for the einstein solid example we were talking about, the initial parameters lead to

$$\left. \frac{\partial S}{\partial U_A} \right|_{U_A(t=0)} < \left. \frac{\partial S}{\partial U_B} \right|_{U_B(t=0)=U-U_A(t=0)}$$

So

$$T_A > T_B$$

$S_{tot}$  increases when  $U_A$  goes down and  $U_B$  goes up. Entropy flows from the hotter system to the cooler system.

### 3.2.3 How Much Energy is Transferred?

$$S_{tot} = \Delta S_A + \Delta S_B = \frac{\partial S}{\partial U_A} \cdot \Delta U_A + \frac{\partial S}{\partial U_B} \cdot \Delta U_B$$

$$= \frac{1}{T_A} \Delta U_A + \frac{1}{T_B} \Delta U_B \quad \Delta U_B = -\Delta U_A$$

$$\Delta S_{tot} = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A$$

So if  $T_A > T_B$ , then

$$\left( \frac{1}{T_A} - \frac{1}{T_B} \right) < 0$$

So for entropy to increase,  $\Delta U_A < 0$ . Energy flows from hot to cold. This energy transfer is heat  $Q$ .

$$\Delta U_A = T_A \Delta S_A = -\Delta U_B = -T_B \delta S_B$$

### 3.2.4 Einstein Solid

$$\Omega \simeq U^N$$

$$S = k_B \ln(\Omega) = k_B N \ln(U) + \text{terms independent of } U$$

Let's take the derivative with respect to  $U$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = N k_B \frac{\partial}{\partial U} \ln(U) = \frac{N k_B}{U} \rightarrow U = N k_B T$$

Many systems have multiplicities of the form

$$\Omega = U^f \quad f \propto N \Rightarrow k_B T \sim \frac{U}{f}$$

## 3.3 Heat Bath/Reservoir

Consider a very large room  $A$  with temperature  $T_A$  connected to your experimental system  $B$  with temperature  $T_B$ .  $U_A \gg U_B$  and  $N_A \gg N_B$ .

Because of those, any change in  $B$  should not affect the reservoir, so  $T_A$  does not change.

Temperature is defined as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_N$$

All the information about heat baths is given in lecture 3.

For an einstein solid of the form

$$\Omega \sim U^f$$

For a paramagnet, the entropy-energy curve has 2 separate zero-points. It looks like a semicircle, and the two zero-points are all spin-up and all spin-down.

If you take the derivative of that graph to get temperature, you see that temperature is positive on the spin-up side of the graph, but negative for the spin-down part of the graph.

At the apex, temperature goes to infinity because  $1/T \rightarrow 0$

Let's let an unstable ( $T_A \rightarrow 0$ ) paramagnet be in contact with a system.

We know that entropy increases on average, so which direction does energy move from entropy to increase?

$$\begin{aligned} \Delta S_{tot} &= \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial U_A} \Delta U_A + \frac{\partial S_B}{\partial U_B} \Delta U_B \quad \Delta U_B = -\Delta U_A \\ &= \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A \end{aligned}$$

We can do something to get rid of  $1/T_A$  so that we get

$$\Delta S_{tot} = -\frac{1}{T_B} \Delta U_A \geq 0$$

$$T_A \rightarrow \infty \quad T_B > 0 \quad \Delta U_A \leq 0$$

Now let's consider  $T_A < 0$  and  $T_B > 0$

$$\Delta S_{tot} = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A = \left( -\frac{1}{|T_A|} - \frac{1}{|T_B|} \right) \Delta U_A \geq 0$$

$$U_A < 0$$

## 3.4 Entropy of an Ideal Gas

Consider a particle in a box of volume

$$V = L_x L_y L_z$$

And you have a multiplicity function with inputs

$$\Omega(U, N)$$

The hamiltonian operator of an ideal gas is given as

$$H(\Psi(\vec{r}, t)) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) = \epsilon \Psi(\vec{r}, t)$$

$$\Psi(\vec{r}, t) = \frac{1}{\sqrt{v}} e^{i\vec{k}\vec{r} - i\omega t} \quad \epsilon = \frac{p^2}{2m} = \frac{\hbar^2}{2m} |\vec{k}|^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

$$k_x = \frac{\pi}{L_x} n_x \quad n = 1, 2, 3, \dots$$

This looks like a quantum harmonic oscillator. The discrete set of energy eigenstates are given in the form

$$\epsilon = \frac{\hbar^2 \pi^2}{2m} - \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$\vec{k}$  can be written in the form

$$\vec{k} = \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

So now our multiplicity function can be written as

$$\Omega(\epsilon, N)$$

So if we consider a large lattice of potential states, each quantum state is represented by a point on the lattice.

The axes are  $k_x, k_y, k_z$ , and each interval is  $\pi/L$

The number of possible quantum states for a certain energy is given by all points that intersect a **shell** of radius  $|\vec{k}|$ . The energy is given in the form  $\epsilon = \hbar^2 |\vec{k}|^2 / 2m$ .

This cannot be solved trivially, but to start, we can find all the points that are inside a **sphere** of radius  $|\vec{k}|$ .

We only consider the shell in a **single octant**, so we divide our volume by 8.

each state space occupies a point in a box with volume

$$\frac{\pi}{L_x} \frac{\pi}{L_y} \frac{\pi}{L_z} = \frac{\pi^3}{V}$$

So we can just divide that volume by our sphere

$$\frac{\# \text{ state with energy } \leq \epsilon}{\text{volume of box each state occupies}} = \Psi(\epsilon)$$

And the number of microstates with energy  $\leq \epsilon$  can be written as

$$\frac{\text{volume of sphere with radius } r = |\vec{k}| = \sqrt{\frac{2m\epsilon}{\hbar^2}}}{\text{volume per state}}$$

This can be written in the form

$$\Phi(\epsilon) = \frac{\frac{4}{3} \frac{\pi |\vec{k}|^3}{8}}{\frac{\pi^3}{V}} = \frac{V}{6\pi^2} |\vec{k}|^3 = \frac{V}{6\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{3/2}$$

This approximation is good for

$$|\vec{k}| \gg \Delta k = \frac{\pi}{L} \quad \text{or} \quad \epsilon \gg \Delta \epsilon = \frac{\pi^2 \hbar^2}{2mV^{2/3}}$$

If the energy of the particle is much larger than the spacing between each energy level.

Now, to find the amount of microstate for a **specific** energy, we give our sphere a small change in radius, and we see the resulting change in number of microstates from that

$$\Omega(\epsilon, \epsilon + \delta\epsilon) = \Phi(\epsilon + \delta\epsilon) - \Phi(\epsilon) \approx \frac{\partial\Phi}{\partial\epsilon}\delta\epsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}\delta\epsilon$$

This is the same answer as getting the volume of the shell and dividing it by the volume of each state

$$\frac{V_{shell}}{V_{state}} = \frac{\frac{4\pi|\vec{k}|^2}{8}\delta k}{\frac{\pi^3}{V}} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}\delta\epsilon$$

### 3.4.1 2D Ideal Gas in an Area $A$

We have a state area

$$\frac{\pi}{L_x} \frac{\pi}{L_y} = \frac{\pi^2}{A}$$

Now you see how many state volumes fit in the quarter circle of a certain energy level.

$$\Phi_{2d}(\epsilon) = \frac{\frac{1}{4}\pi|\vec{k}|^2}{\left(\frac{\pi^2}{A}\right)} \quad k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

You now perform the same perturbation math to get

$$\Omega(\epsilon, \epsilon + \delta\epsilon) = \frac{\partial\Phi}{\partial\epsilon}\delta\epsilon = \frac{A}{4\pi} \left(\frac{2m}{\hbar^2}\right) \delta\epsilon$$

## 3.5 Density of States

The number of states per energy interval

$$D(\epsilon) = \frac{\partial\Phi}{\partial\epsilon} \quad \text{or} \quad \int_0^\epsilon d\epsilon' D(\epsilon') = \Phi(\epsilon)$$

$$\Omega(\epsilon, \epsilon + \delta\epsilon) = D(\epsilon)\delta\epsilon$$

## 3.6 2 Particles in a Box

Consider 2 particles in a box. Energy is given by

$$U = \epsilon_1 + \epsilon_2 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} = \frac{\hbar^2 k^2}{2m^2}$$

And our energy space is now given by

$$k = \sqrt{k_{x1}^2 + k_{y1}^2 + k_{z1}^2 + k_{x2}^2 + k_{y2}^2 + k_{z2}^2}$$

The states are particles in a lattice in a 6-dimensional  $k$ -space  
Now, each quantum state is in a box of volume

$$V_{state} = \left(\frac{\pi^3}{V}\right)^2$$

So all states with energy  $\epsilon < U$  occupies a volume of  $(1/8)^2$  of the 6D hypersphere.

So our multiplicity  $\Omega(\epsilon, \epsilon + \delta\epsilon)$

Are all the states in between  $\epsilon$  and  $\epsilon + \delta\epsilon$  that occupy  $1/2^6$  of the hypersphere.

### 3.6.1 $N$ Particles

All states with energy  $\epsilon \leq U$  occupy a volume that's  $1/2^{3N}$  of a  $3N$  dimension hypersphere. So to find all the states, in a shell, it's the same volume partition, but with a shell.

Ignore geometric factors and constants.

$$k \sim \sqrt{U} \quad (k \sim \sqrt{\epsilon})$$

$$N = 1 \quad \Phi_1(U) \sim V k^3 \sim V U^{3/2}$$

$$\Omega_1(U_1, U + \delta U) \sim V k^2 dk \sim V \sqrt{U} dU$$

$$N = 2 \quad \Phi_2(U) \sim V^2 k^6 \sim V^2 U^3$$

$$\Omega_2(U_2, U + \delta U) \sim V^2 k^5 dk \sim V^2 U^2 dU$$

$$N = N \quad \Phi_N(U) \sim V^N k^{3N} \sim V^N U^{3N/2}$$

$$\Omega_N(U_N, U + \delta U) \sim V^N k^{3N-1} dk \sim V^N U^{(3N/2)-1} dU$$

Because all the particles are identical, we divide  $\Omega_N$  by  $N!$  to make up for the different possible permutations.

$$\Omega_N(U, U + \delta U) = \frac{g_{3N}}{2^{3N} N!} \left( \frac{V}{\pi^3} \right)^N \left( \frac{2m}{\hbar^2} \right)^{3N/2} \frac{U^{(3N/2)-1}}{2} \delta U$$

$g_D$  is the solid angle of the hypershell in  $N$  dimensions

$$g_3 = 4\pi$$

Our multiplicity function can also be written as

$$\Omega_N(U, U + \delta U) = \frac{g_{3N}}{2^{3N+1} N!} \left( \frac{U}{\Delta\epsilon} \right)^{(3N/2)-1} \frac{\delta U}{\Delta\epsilon} \quad \Delta\epsilon = \frac{\hbar^2 \pi^2}{2mV^{2/3}}$$

The entropy of this system can be written as

$$\begin{aligned} S(U, U + \delta U, V) &= k_B \ln(\Omega_N) \\ &= Nk_B \ln(V) + \left( \frac{3N}{2} - 1 \right) k_B \ln(U) + k_B \ln(f(N)) + \dots \\ &\approx Nk_B \ln(V) + \left( \frac{3}{2} \right) Nk_B \ln(U) + k_B \ln(f(N)) \end{aligned}$$

## 3.7 MISSED LECTURE

## 3.8 Discussion

I microcanonical ensemble is when  $U$  and  $N$  are fixed, and it is ideal but not realistic.

$$\Omega(U, N) = \sum_i \delta(U - U_L) \delta(N - N_L)$$

A canonical ensemble is an ensemble connected to a thermostat.  $N_S$  is fixed

$$U_0 = U_R + E$$

The probability of a state having a certain energy can be written as

$$P(E_i) = \frac{\Omega_{R+S}(E_i)}{\sum_j \Omega_{R+S}(E_j)}$$

The main way to do things is find  $z$  such that

$$z = \sum_i e^{-\beta E_i}$$

And then take the derivatives of  $z$

$$U = -\frac{\partial z}{\partial \beta}$$

## 3.9 Equipartition Theorem

Imagine a gas coupled to a reservoir.

$$\epsilon_1 = \frac{\hbar^2}{2m}(k_x^2 - k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} - \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$z_1 = \sum e^{-\frac{\epsilon_1}{k_B T}} = \sum e^{-\frac{\left( \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} - \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \right)}{k_B T}}$$

$$z_1(t) = \left( \sum_{nx=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} \frac{n_x^2}{L_x^2 k_B T}} \right) \left( \sum_{ny=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} \frac{n_y^2}{L_y^2 k_B T}} \right) \left( \sum_{nz=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} \frac{n_z^2}{L_z^2 k_B T}} \right)$$

Let's consider just one of these parts

$$\sum_{nx=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} \frac{n_x^2}{L_x^2 k_B T}} = \sum_{nx=1}^{\infty} e^{-\alpha_x n_x^2}$$

This works for low temperatures. For high temperatures (many  $n \in N$ ), we get a different answer. Large  $T$  means  $k_B T \gg \hbar^2 \pi^2 / (2m L_x^2)$  for  $x, y, z$ . It can also be written as  $k_B T \gg \Delta \epsilon = \hbar^2 \pi^2 / (2m V^{2/3})$

$$\sum_{nx=1}^{\infty} e^{-\alpha_x n_x^2} \approx \int_0^{\infty} dn_x e^{-\alpha_x n_x^2} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha_x}}$$

$$z(\text{high } T) \approx \frac{\pi^{3/2}}{2^3 (\alpha_x \alpha_y \alpha_z)^{1/2}} L_x L_y L_z = \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} * V$$

This looks similar to a density times a volume.

Let  $k_B T = 1/\beta$ . For  $N$  particles in a box at the high temperature limit, we can describe it with



$$\begin{aligned}
z_{tot} &= \frac{z_1^N}{N!} & U &= -\frac{\partial}{\partial \beta} \ln(z_{tot}) = -\frac{\partial}{\partial \beta} \ln(z_1^N) = -N \frac{\partial}{\partial \beta} \ln(z_1) \\
&= -N \frac{\partial}{\partial \beta} \left( \ln(\beta^{-3/2}) + f(\text{not } \beta) \right) \\
U &= \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T & k_B T &\gg \Delta \epsilon
\end{aligned}$$

Now we can go back to our density

$$z_1 = \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} * V \quad n_{\emptyset} \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \quad z_1(T) = n_{\emptyset}(T) * V$$

$n_{\emptyset}$  is known as the quantum density.  $\lambda = h/p$  is the De Broglie Wavelength and  $p = \hbar/k$ . For an ideal gas, our energy is described as

$$\langle \epsilon \rangle \frac{3}{2} k_B T = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} \quad h = 2\pi \hbar$$

And the expected value of  $\lambda$  is

$$\langle \lambda \rangle = \frac{h}{\sqrt{2m \langle \epsilon \rangle}} = \sqrt{\frac{4\pi^2 \hbar^2}{3m k_B T}}$$

So with this, we can describe  $n_{\emptyset}$

$$n_{\emptyset} = \frac{\text{const} O(1)}{\langle \lambda \rangle^3}$$

If you have a density of particles on the order of the quantum density, then you cannot ignore quantum effects.

### 3.9.1 Example

Consider Helium at 300K.

$$\begin{aligned}
n_{\emptyset} &\approx 0.8 * 10^{25} \frac{1}{\text{cm}^3} = \frac{1}{0.5 \text{\AA}^3} \\
n_{He} &= 2.5 * 10^{19}
\end{aligned}$$

So we are in the classical limit.

# Chapter 4

## Equipartition Theorem

A diatomic ideal gas can not only be translated around, but also rotated to change its potential state. The energy of this atom can be written as

$$\epsilon_{mol} = \epsilon_{trans} + \epsilon_{vib} + \epsilon_{rot}$$

$$z_{mol} = \sum_{allstates} e^{-\beta\epsilon_{mol}} = \left( \sum_{\epsilon_{trans}} e^{-\beta\epsilon_{trans}} \right) \left( \sum_{\epsilon_{vib}} e^{-\beta\epsilon_{vib}} \right) \left( \sum_{\epsilon_{rot}} e^{-\beta\epsilon_{rot}} \right)$$

$$\epsilon_{transl} = \frac{\hbar^2 k^2}{2m} \quad z_{transl} = n_{\emptyset}(T) \cdot V \quad U_{transl} = \frac{3}{2} N k_B T$$

We can figure out rotational energy in quantum mechanics in the form of angular momentum

$$J = |\vec{J}| = \sqrt{j(j+1)\hbar} \quad j \in \mathbb{N}$$

$$J_z = m_z \hbar \quad m_z = -j, -j+1, \dots, j-1, j$$

$$\epsilon_{rot} = \frac{|\vec{J}|^2}{2I} = \frac{j(j+1)\hbar^2}{2I} = \epsilon * j(j+1) \quad j \in \mathbb{N}$$

$$z_{rot} = \sum_{J, J_z} e^{-\beta\epsilon_{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{\frac{\epsilon j(j+1)}{k_B T}}$$

For low temperature  $T$ , then

$$z_{rot} = 1 + 3e^{-2\beta\epsilon} + 5e^{-6\beta\epsilon} + 7e^{-12\beta\epsilon} + \dots$$

The  $\dots$  corresponds to excited states that are "frozen out", or they don't contribute to the physics.

For the high temperature limit, we can make some approximations

$$z_{rot} \approx \int_0^\infty dj (2j+1) e^{\frac{\epsilon_j(j+1)}{k_B T}} \quad x = \beta \epsilon(j(j+1)) dx = \beta \epsilon(2j+1) dj$$

$$z_{rot} = \frac{1}{\beta \epsilon} \int_0^\infty dj e^{-x} = \frac{1}{\beta \epsilon}$$

$$U_{rot} = -\frac{\partial}{\partial \beta} \ln(z_{rot}) = \frac{1}{\beta} = k_B T$$

Now we can calculate the vibrational degrees of freedom

$$\epsilon_{vib} = \hbar \omega \left(n + \frac{1}{2}\right) \quad n \in \mathbb{N}$$

$$z_{vib} \sum_n e^{-\beta \epsilon_{vib}} = e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^\infty e^{-\beta \hbar \omega * n}$$

We can use a geometric series

$$\sum x^n = \frac{1}{1-x} \quad e^{-\beta \hbar \omega} = x$$

$$z_{vib} = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$\begin{aligned} U_{vib} &= \langle \epsilon_{vib} \rangle = -\frac{\partial}{\partial \beta} \ln(z_{vib}) \\ &= +\frac{\partial}{\partial \beta} \left( \frac{1}{2} \hbar \omega \beta + \ln(1 - e^{-\beta \hbar \omega}) \right) \\ &= \hbar \omega \left( \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right) = \hbar \omega \left( \langle n \rangle + \frac{1}{2} \right) \end{aligned}$$

We can also find the average

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

In the low temperature limit  $k_B T \ll \hbar \omega$ , we get

$$\frac{1}{e^{\beta \hbar \omega} - 1} \approx e^{-\beta \hbar \omega} \rightarrow U_{vib} \approx \hbar \left( e^{-\beta \hbar \omega} + \frac{1}{2} \right)$$

In the high temperature limit, we can take a taylor expansion to get

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \approx \frac{1}{1 + \beta \hbar \omega - 1} = \frac{1}{\beta \hbar \omega}$$

$$U_{vib} = \hbar \omega \left( \langle n \rangle + \frac{1}{2} \right) \approx \hbar \omega \left( \frac{k_B T}{\hbar \omega} + \frac{1}{2} \right) = k_B T + \frac{\hbar \omega}{2} \approx k_B T$$

## 4.1 Heat Capacity

Heat capacity is defined as

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad U_{tot} = U_{transl} + U_{rot} + U_{vib}$$

$$C_V = C_V^{transl} + C_V^{rot} + C_V^{vib}$$

For Helium the heat capacity over temperature is a step function.

Each of the different degrees of freedom become relevant at different times, so the specific heat capacity changes depending on the temperature.

## 4.2 Equipartition Theorem

This theorem helps us figure out the high temperature limit of systems very easily.

$$U \propto \alpha \cdot N k_B T \quad k_B T \gg \Delta \epsilon$$

This can be found with

$$z = \sum_i e^{\epsilon_i / k_B T}$$

$$A \int dq_1 \int dq_2 \int dq_3 \dots e^{-\beta \epsilon(q_1, q_2, q_3, \dots, q_N)}$$

$$p(\epsilon_i) = \frac{e^{-\beta \epsilon_i}}{z}$$

$$\langle \epsilon_{qi} \rangle = \langle a_i q_i \rangle$$

$$\langle \epsilon_{qi} \rangle = \frac{1}{2} k_B T$$

## 4.3 Discussion

Consider a system with a bath  $R$  connected to a system  $D$  with parameters

$$U_R = U_0 - \epsilon \quad T_R = T_D = \text{fixed}$$

We can try to find the extrema in the systme  $S$

$$dS_{R+D} = 0 = dS_R + dS_D$$

$$\frac{dU_R}{T_R} + dS_D = 0 \rightarrow dU_R = d(U_0 - U_D) = -dU_D$$

$$0 = \frac{-dU_D}{T} + dS_D \rightarrow \frac{-1}{T}d(U_D - TS_D) = 0$$

$$F \equiv U - TS$$

That is an extremum of  $S$  in the canonical ensemble. It is also known as the Helmholtz Free energy.

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

$$\begin{aligned} \tilde{F} = -k_B T \ln(z) &\Rightarrow \left|\frac{\partial \tilde{F}}{\partial T}\right| = -k_B \ln(z) - k_B T \frac{\partial}{\partial T} \ln(z) \\ &= -k_B \ln(z) + \frac{1}{T} \frac{\partial}{\partial B} \ln(z) \end{aligned}$$

We are also theoretically able to derive

$$\frac{\partial \tilde{F}}{\partial T} = \frac{\tilde{F} - U}{T}$$

$$\tilde{F}(T=0) = -\lim_{T \rightarrow 0} k_B T \ln(z) = -\lim_{T \rightarrow 0} k_B T \ln\left(\sum_i e^{\epsilon_i/k_B T}\right)$$

$$z(T=0) = e^{-\epsilon_0/k_B T} + e^{-\epsilon_1/k_B T} \approx e^{-\epsilon_0/k_B T}$$

$$\tilde{F}(T=0) = -\lim_{T \rightarrow 0} k_B T \ln\left(e^{\epsilon_0/k_B T}\right) = \epsilon_0$$

$$F(T=0) = U(T=0)$$

$$-\frac{\partial}{\partial B} \ln(z(T \rightarrow 0)) = -\frac{\partial}{\partial B} \ln(e^{-B\epsilon_0}) = \epsilon_0$$

$$F = -k_B \ln(z)$$

## 4.4 Equipartition Theorem

$$\langle \epsilon_{q1} \rangle = \langle a_1 q_1^2 \rangle = \frac{1}{2} k_B T$$

This is true for each degree of freedom at the high temperature limit. This means that for a particle with 3 degrees of freedom, then the expected value of the energy is

$$\langle U \rangle = \frac{3}{2} k_B T$$

We have a function  $z(T)$  that can be written as

$$z(T) = A \int_{-\infty}^{\infty} dq_1 * \dots * \int_{-\infty}^{\infty} dq_N e^{-\beta \epsilon(q_1, \dots, q_N)}$$

$$\epsilon = a_1 q_1^2 + a_2 q_2^2 + \dots + a_N q_N^2$$

And the probability of getting a certain energy is

$$p(\epsilon_1) = \frac{A dq_1 \dots dq_N e^{-\beta \epsilon(q_1, \dots, q_N)}}{A \int_{-\infty}^{\infty} dq_1 \dots \int_{-\infty}^{\infty} dq_N e^{-\beta \epsilon(q_1, \dots, q_N)}}$$

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} dq_1 \dots \int_{-\infty}^{\infty} dq_N a_1 q_1^2 e^{-\beta \epsilon(q_1, \dots, q_N)}}{\int_{-\infty}^{\infty} dq_1 \dots \int_{-\infty}^{\infty} dq_N e^{-\beta \epsilon(q_1, \dots, q_N)}} = \frac{\int_{-\infty}^{\infty} dq_1 a_1 q_1^2 e^{-\beta \epsilon_{q_1}}}{\int_{-\infty}^{\infty} dq_1 e^{-\beta \epsilon_{q_1}}}$$

$$\langle \epsilon_1 \rangle = \frac{\int_{-\infty}^{\infty} dq_1 \epsilon_{q_1} e^{-\beta \epsilon_{q_1}}}{\int_{-\infty}^{\infty} dq_1 e^{-\beta \epsilon_{q_1}}} = -\frac{\partial}{\partial \beta} \ln \left( \int_{-\infty}^{\infty} dq_1 e^{-\beta a_1 q_1^2} \right) = -\frac{\partial}{\partial \beta} \ln \left( \sqrt{\frac{\pi}{\beta a_1}} \right)$$

$$\langle \epsilon_1 \rangle = -\frac{\partial}{\partial \beta} \left( \ln \left( \frac{1}{\sqrt{\beta}} \right) \right) + f(\text{not } \beta)$$

$$\langle \epsilon_1 \rangle = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

This works in the high temperature limit for systems of quadratic energy  $\epsilon = q_1^2 + \dots$

An ideal gas in 3 dimensions has an expected total system energy of

$$\langle \epsilon \rangle = N \frac{3}{2} k_B T$$

A 1d harmonic oscillator has energy

$$\epsilon = \frac{p_1^2}{2m} + \frac{1}{2} \omega x^2 \Rightarrow \langle \epsilon \rangle = 2 \frac{1}{2} k_B T = k_B T$$

For  $N$  oscillators, the expected energy is just  $N k_B T$ .

### 4.4.1 Counterexample

A paramagnet has energy of the form

$$U = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$

So for the high temperature limit

$$U = -\frac{N\mu^2 B^2}{k_B T} \neq Nk_B T$$

Because the energy is not in the form  $k_B T$ , we **cannot** use the equipartition theorem.

### 4.4.2 Maxwell Velocity Distribution

The kinetic energy can be written as

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

This is equivalent to the energy having multiple quadratic degrees of freedom. The probability of having a specific velocity (certain components), we its

$$P(\vec{v}) = \frac{dv_x dv_y dv_z e^{-\beta\epsilon}}{\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z e^{-\beta\epsilon}}$$

If we switch from cartesian coordinates to spherical coordinates, we get

$$P(\vec{v}) = \frac{v^2 dv \sin(\theta) d\theta d\varphi e^{-\beta\epsilon}}{\int_0^\infty v^2 dv \int_0^{2\pi} d\varphi \int_0^\pi \sin(\theta) d\theta e^{-\beta\epsilon}} = \frac{v^2 dv e^{-\beta\frac{mv^2}{2}}}{\int_0^\infty v^2 dv e^{-\beta\frac{mv^2}{2}}} \frac{4\pi}{4\pi}$$

$$\int_0^\infty v^2 e^{-\alpha v^2} dv = -\frac{\partial}{\partial \alpha} \int_0^\infty e^{-\alpha v^2} dv = -\frac{\partial}{\partial \alpha} \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{4\pi} \left( \frac{2\pi k_B T}{m} \right)^{3/2}$$

$$f(v)dv = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

So we get some properties

$$v_{peak} = \sqrt{\frac{2k_B T}{m}} \quad \left( \frac{\partial f}{\partial v} \right) = 0$$

$$\langle v \rangle = \int_0^\infty dv f(v) v = \sqrt{\frac{8k_B T}{\pi m}} \quad \langle v^2 \rangle = \int_0^\infty dv f(v) v^2 = \frac{3k_B T}{m}$$

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$$

Equipartition theorem does hold.

## 4.5 Helmholtz Free Energy

Consider a system  $\phi$  with fixed  $U, N$ . It is a microcanonical ensemble, so  $U_S$  is at a maximum in equilibrium ( $dS_\phi = 0$ ).

In a canonical ensemble of fixed  $N$ , our system is connected to a larger bath, so  $U_0$  is constant, and  $T = T_0 = T_\phi$  is fixed.  $S_{R+\phi}$  is at an extremum ( $dS_{R+\phi} = 0$ )

What qualities of  $\phi$  are at an extremeum?

$$dS(U, V) = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV = \frac{1}{T} dU + \frac{p}{T} dV$$

$$dS_{R+\phi} = 0 = dS_R + dS_\phi = \frac{dU_R}{T} + dS_\phi$$

$$U_0 = U_R + U_\phi \quad dU_R = -dU_\phi$$

$$dS_{R+\phi} = -\frac{dU_\phi}{T} + dS_\phi = -\frac{1}{T} d(U_\phi - TS_\phi) = 0$$

So the Helmholtz Free energy is given by

$$FU_\phi - TS_\phi$$

$$0 = dS_{R+\phi} = -\frac{1}{T} dF$$

When the entropy is maximized (system is at equilibrium), then  $F$  is minimized.

With the Helmholtz Free Energy, we get

$$F = U_\phi - TS_\phi \quad dF = dU - T dS - S dT \quad dU = T dS - p dV$$

$$dF = -p dV - S dT \implies dF = -\left( \frac{\partial F}{\partial V} \right) dV - \left( \frac{\partial F}{\partial T} \right) dT$$

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



So now we have both momentum and entropy in terms of the Helmholtz Free Energy.

In a microcanonical ensemble, our equations are

$$S_\phi = k_b \ln(\Omega_\phi)$$

But in a canonical ensemble, we should be able to predict the free energy

$$F = -k_B T \ln(z) \quad z = \sum_{i=0}^{\infty} e^{-\beta \epsilon_i}$$

We can find this with

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

Use an ansatz

$$\tilde{F} = -k_B T \ln(z)$$

And you see that  $\tilde{F}$  fulfills the differential equation.

To make sure that there is no constant offset, you can check the term at  $T = 0$

$$\tilde{F}(T = 0) = F(T = 0)$$

## 4.6 2 Energy Levels

$\epsilon$  is either  $\Delta$  or 0. What is the entropy  $S(T)$ ? What is  $S$  for both  $T \rightarrow 0$  and  $T \rightarrow \infty$ ?

First, start with a partition function  $z$

$$z = \sum e^{-\beta \epsilon} = e^{-\beta \Delta} + e^{-\beta 0} = 1 + e^{-\beta \Delta}$$

Then find the free energy

$$F = -k_B T \ln(z) = -k_B T \ln(1 + e^{-\beta \Delta})$$

And then find the entropy

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = k_B \ln(1 + e^{-\Delta/k_B T}) + \frac{\Delta}{T} \frac{e^{-\Delta/k_B T}}{1 + e^{-\Delta/k_B T}}$$

Then you can check  $S$  for small and large  $T$

$$S(T \rightarrow 0) = k_B \ln(1) = 0 \quad S(T \rightarrow \infty) = k_B \ln(2)$$

Those both look good.

## 4.7 Summary

### 4.7.1 Microcanonical Ensemble

In a microcanonical ensemble, the system is closed, so the fixed variables are  $N, V, U$ .

The extremum is when  $S(U, V)$  is at a maximum

The system is measured with the multiplicity

$$\Omega = \sum_{\text{all states with energy } U} 1$$

And entropy is defined as

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

$$dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV$$

$$dS = \frac{1}{T} dU + \dots\dots\dots$$

### 4.7.2 Canonical Ensemble

In a canonical ensemble, the system is connected to a bath. The fixed variables are  $N, V, T$

The extremum is when  $F(T, V)$  is at a minimum

The system is defined with a partition function

$$z = \sum_{\text{all states with temperature } T} e^{-\epsilon/k_B T}$$

And free energy is defined as

$$F = -k_B T \ln(z)$$

$$dF = \left( \frac{\partial F}{\partial U} \right)_V dU + \left( \frac{\partial F}{\partial V} \right)_U dV$$

# Chapter 5

## Heat and Work

Recall the thermodynamic identities

$$\begin{aligned}dU &= T dS - p dV & dQ &= T dS & dW_{on} &= -p dV \\dU &= dQ + dW_{on}\end{aligned}$$

All types of work can be **completely** interconverted. Heat can be **partially** interconverted, but not completely. This is because of the 2nd law of thermodynamics.

### 5.1 Heat Engine

Consider a device that can completely convert heat into work

$$T_h \longrightarrow Q_H$$

Could you then use that heat to lift up a mass? Consider the 1st law of thermodynamics (conservation of energy). This requires that, for our engine,

$$Q_H = W$$

What about entropy? We are working in a closed system with a reservoir and an engine and a mass

$$\Delta S_{tot} = \Delta S_{res} + \Delta S_{eng} + \Delta S_{mass}$$

$$\Delta S_{res} = -\frac{Q_H}{T_H} < 0 \quad \Delta S_{eng} = 0 \quad \Delta S_{mass} = 0 \quad \Delta S_{tot} = -\frac{Q_H}{T_H}$$

This violates the 2nd law of thermodynamics, which means our engine absolutely cannot be perfectly efficient. However, if we imagine the opposite (work to heat), then we see that does not violate the 2nd law of thermodynamics.

Because of the first law, we get that

$$Q_H = Q_C + W$$

Because of the 2nd law, we get

$$\Delta S_{tot} \geq \quad \Delta S_{tot} = \Delta S_{H,res} + \Delta S_{C,res} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0$$

## 5.2 Efficiency

The efficiency will be denoted as  $\eta$ .

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

What is the maximum possible efficiency?

$$\Delta S_{tot} = 0 \Rightarrow \Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

The carnot efficiency is known as the maximum possible attainable efficiency, and that is done with

$$\eta_{max} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

In practice, this does not happen.

$$\Delta S_{tot} > 0 \quad \Delta S_{H,res} = -\frac{Q_H}{T_H} \quad \Delta S_{C,res} = \frac{Q_C}{T_C} + \Delta S_{i,res}$$

$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} > 0 \Rightarrow \frac{Q_C}{Q_H} > \frac{T_C}{T_H}$$

$$\eta = 1 - \frac{Q_C}{Q_H} < 1 - \frac{T_C}{T_H} = \eta_C$$

### 5.2.1 Types of Efficiency Losses

- Heat bypass: Heat moves from one system to another without being used for work
- Thermal Resistance: There's a gradient in temperature in your system
- Friction Loss: Work is turned to heat

- Irreversible gas expansion: This type of expansion requires more work to be undone so it is thermodynamically unfavorable.

All of these efficiency losses are irreversible, which means that one  $\Delta S_{loss} > 0$ , you cannot remove it.

## 5.3 Carnot Cycle

Consider a cycle with efficiency

$$\eta_C = 1 - \frac{T_C}{T_H}$$

A working substance (gas) can absorb/expel heat and turn it into work (move a piston). An isotropic/adiabatic process is a process such that entropy is fixed.

heat  $\rightarrow$  expand  $\rightarrow$  contract  $\rightarrow$  cool down

Because the piston returns to its original state and the gas cools down again, the total energy for 1 cycle is

$$\oint dU = 0 = \oint dQ + \oint dW$$

We can solve for each individual step of the Carnot cycle

$$\oint dQ = \oint dQ_1 + \oint dQ_2 + \oint dQ_3 + \oint dQ_4 = Q_H + 0 + -Q_H + 0 = 0$$

$$\oint T dS = T_H(S_2 - S_1) + 0 + T_C(S_4 - S_3) + 0 \Rightarrow$$

$$\oint dU = 0 = (T_H - T_C)(S_2 - S_1) - \oint p dV$$

$$W_{engine} = \oint p dV = (T_H - T_C)(S_2 - S_1)$$

All these number returns the maximum possible efficiency, but that is not practical or realistic. This is because reversible heating and cooling processes are too slow for real-world applications.

### 5.3.1 Realizing Carnot Cycle

for a gas, we assume ideal behavior

$$pV = nk_B T$$

There's something on the board called Sackur-Tetrode

$$S = Nk_B \left( \ln \left( \frac{n_Q V}{N} \right) + \frac{3}{2} \right)$$

### 5.3.2 Isothermal Segments

$$pV = \text{const}$$

### 5.3.3 Isotropic Segments

Knowing isotropic behavior will be useful for the homework

$$S = \text{const} = Nk_B \left( \ln(T^{3/2}) + \ln(V) \right) + \text{const}$$

$$T^{3/2} * V = \text{const} \quad T = \frac{pV}{Nk_B} \rightarrow (pV)^{3/2} * V = p^{3/2} V^{5/2} = \text{const}$$

$$pV^\gamma = \text{const} \quad \gamma = \frac{5}{3}$$

$\gamma = 5/3$  for a monatomic gas,  $7/5$  for a diatomic gas, etc etc.

$$\gamma = 1 + \frac{2}{f}$$

So the entire process that be written in terms of changes in pressure and volume

$$\xrightarrow{1} \text{isothermal} \xrightarrow{2} \text{adiabatic} \xrightarrow{3} \text{isothermal} \xrightarrow{4} \text{adiabatic}$$

### 5.3.4 Work Done

$$\oint p dV \Rightarrow W = (T_H - T_C)(S_2 - S_1)$$

## 5.4 Irreversible Processes

Consider a system with gases one just one side. Energy is constant and heat transferred is 0 and the work done is 0. Temperature is also constant.

$$\Delta S = Nk_B \ln \left( \frac{V_f}{V_i} \right) > 0$$

Because the entropy change is positive, this process is irreversible in a closed system. She said sackur tetrodi again and I have no idea what the fuck that means.

### 5.4.1 1st Law of Thermodynamics

$$dU = dQ + dW_{on}$$

For an reversible process,  $dQ = TdS$

$$dU = TdS + dW_{on}$$

For an **irreversible** process,  $TdS > dQ_{irrev}$

$$dW_{on} > dU - TdS$$

For the irreversible case, the total work done on the gas is  $W_{on} = 0$ , but in the reversible case, the gas would have to push a piston to expand, so  $W_{on} = \int pdV < 0$ .

## 5.5 Discussion

Consider a system of conserved  $U, N, B$  where  $B$  is the magnetic field.

$$dU = \left( \frac{dU}{dS} \right)_{NB} dS + \left( \frac{dU}{dN} \right)_{SB} dN + \left( \frac{dU}{dB} \right)_{SN} dB = TdS + \mu dN - MdB$$

The Helmholtz free energy is

$$F = U_S - TS_S = -k_B T \ln(Z)$$

The maxwell relations are as following

$$\frac{\partial}{\partial x} \left( \frac{\partial}{\partial y} f(x, y) \right) = \frac{\partial}{\partial y} \left( \frac{\partial}{\partial x} f(x, y) \right)$$

# Chapter 6

## Thermodynamic Potentials

Consider the Helmholtz Free Energy

$$F = U - TS$$

In equilibrium,  $F$  is minimized for fixed  $V, T$ . Consider starting with a reservoir and building a system out of energy just from that reservoir. Your system has an energy  $U$ , and you can transfer heat from the reservoir to the system. Let the system be  $S$  and the reservoir be  $R$ .

$$S_{R+S} \geq 0 \quad F_S = U_S - T_S S_S$$

$F$  can be intuitively described as the work provided to  $S$  at fixed  $T$ . It can also be the work extracted from  $R$  to  $S$ .

$$\Delta F = \Delta U - T \Delta S \quad \Delta U = 0 + W_{on} \rightarrow \Delta F = W_{on}$$

This is in ideal conditions, but in reality there are irreversible processes that happen.

$$T \Delta S > \Delta Q \Rightarrow \Delta F < W_{on}$$

### 6.1 Enthalpy and Gibbs Free Energy

consider a system  $s$  at fixed  $p, T$ .

$$U_S + pV = H \quad (\text{Enthalpy})$$

$$U_S + pV - TS = G \quad (\text{Gibbs Free Energy})$$

$G$  is the work required from the system  $s$  at fixed pressure. It is also the amount of work you can extract from the system  $s$ .



$$\Delta G = \Delta U + p\Delta V - T\Delta S = 0 + W_{on} + p\Delta V - T\Delta S \Rightarrow$$

$$\Delta G = W_{on} + p\Delta V \quad (\text{ideal conditions}) \quad \Delta G \leq W_{on} + p\Delta V$$

In equilibrium,  $G$  is at a minimum for fixed  $p, T$ .

In equilibrium,  $F$  is at a minimum for fixed  $V, T$ .

## 6.2 4 Thermodynamic Potentials

$$U = U(S, V) \quad dU = TdS - pdV = dQ + dW_{on}$$

$$F = F(T, V) = U - TS$$

$$dF = dU - TdS - SdT = TdS - pdV - TdS - SdT = -pdV - SdT$$

$$H = H(p, S) = U + pV$$

$$dH = dU + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp$$

$$G = G(p, T) = U + pV - TS = H - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$= TdS - pdV + pdV + Vdp - TdS - SdT = Vdp - SdT$$

The energy, Helmholtz Free Energy, Enthalpy, and Gibbs Free Energy are the most important potentials in statistical mechanics.

## 6.3 Maxwell Relations

All 4 potentials depend on 2 sets of 2 variables. They all contain one of  $\{S, T\}$  and one of  $\{p, V\}$ .

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V} = - \left(\frac{\partial p}{\partial S}\right)_V \quad \text{First Maxwell Relation}$$

Now I can do the same thing with the other potentials

$$dF = -pdV - SdT = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT \Rightarrow$$

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

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V$$

Now Enthalpy

$$dH = TdS + Vdp = \left(\frac{\partial H}{\partial S}\right)_T dS + \left(\frac{\partial H}{\partial p}\right)_T dp \Rightarrow$$

$$T = \left(\frac{\partial H}{\partial S}\right)_T \quad V = \left(\frac{\partial H}{\partial p}\right)_T$$

$$\left(\frac{\partial T}{\partial p}\right)_T dp = \frac{\partial^2 H}{\partial S \partial T} = \left(\frac{\partial V}{\partial S}\right)_T dS$$

And last but not least

$$dG = Vdp - SdT = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \Rightarrow$$

$$V = \left(\frac{\partial G}{\partial p}\right)_T \quad S = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$-\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial S}{\partial p}\right)_T$$

All of these relations come from the fact that  $S = S(U, V)$  and

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$

### 6.3.1 Applications

Let's say you measure a gas, and you have the temperature and volume of the gas. Let's say you want the entropy.  $S(U, V) \rightarrow S(T, V)$ .

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V$$

$$dS = \frac{C_v}{T} dT + \left( \frac{\partial p}{\partial T} \right)_V dV$$

Because we measured pressure, we can now get the entropy. The way we get the heat capacity is with the experimental data and a bunch of integrals that I don't really want to write down.

$$S_{tot} = S(T_i, p_i) + \Delta S_1 + \Delta S_2$$

$$= S(T_i, p_i) + \int_{T_s}^{T_f} dT \frac{C_v(T_0, V_i)}{T} + \int_{V_s}^{V_f} dV \left( \frac{\partial p}{\partial T} \right)_V$$

### 6.3.2 Monatomic Ideal Gas

$$U = \frac{3}{2} N k_B T \Rightarrow C_v = \frac{3}{2} N k_b = T \left( \frac{\partial S}{\partial T} \right)_V \quad T dS = dU + p dV = dU + 0$$

$$C_v = \frac{3}{2} N k_b = \left( \frac{dU}{dT} \right)_V$$

$$\Delta S_1 = \int_{T_s}^{T_f} dT \frac{C_v(T_0, V_i)}{T} = \int_{T_s}^{T_f} dT \frac{\frac{3}{2} N k_B}{T} = \frac{3}{2} N k_B \ln \left( \frac{T_f}{T_i} \right)$$

$$\Delta S_2 = \int_{V_s}^{V_f} dV \left( \frac{\partial p}{\partial T} \right)_V = \int_{V_s}^{V_f} dV \left( \frac{\partial}{\partial T} \right)_V \frac{N k_B T}{V} = \int_{V_s}^{V_f} dV \frac{N k_B}{V}$$

$$= N k_B \ln \left( \frac{V_f}{V_i} \right)$$

$$\Delta S_{tot} = \frac{3}{2} N k_B \ln \left( \frac{T_f}{T_i} \right) + N k_B \ln \left( \frac{V_f}{V_i} \right)$$

This is consistent with the Sackur-Tetrode Equation for a monatomic ideal gas.

$$S(T, V) = N k_B \ln(T^{3/2} \cdot V) + \text{const} \rightarrow \frac{3}{2} N k_B \ln(T) + N k_B \ln(V) + \text{const}$$

# Chapter 7

## Chemical Potential

Consider 2 systems that can exchange particles with each other.  $(U_1 + U_2)$ ,  $(V_1 + V_2)$ ,  $(N_1 + N_2)$  are all fixed. At equilibrium,  $S = (S_1 + S_2)$  is maximized, so  $dS_1 + dS_2 = 0$ .

$$dS_1 = \left( \frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} dU_1 + \left( \frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} dV_1 + \left( \frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} dN_1$$

Because everything is fixed, we can say that

$$\begin{aligned} dU_1 &= -dU_2 & dV_1 &= -dV_2 & dN_1 &= -dN_2 \\ \left( \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \right)_{V_1, N_1} dU_1 &+ \left( \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right)_{U_1, N_1} dV_1 + \left( \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \right)_{U_1, V_1} dN_1 \\ &= \left( \frac{1}{T_1} - \frac{1}{T_2} \right)_{V_1, N_1} dU_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right)_{U_1, N_1} dV_1 + \left( -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} \right)_{U_1, V_1} dN_1 \\ &= 0 \implies T_1 = T_2 & p_1 &= p_2 & \mu_1 &= \mu_2 \end{aligned}$$

This is the equilibrium condition for the 2 systems that can exchange particles. Because  $N_1$  and  $N_2$  are now non-constant, our equations change

$$\begin{aligned} dS &= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN & dU &= T dS - p dV + \mu dN \\ \mu &= \left( \frac{\partial U}{\partial N} \right)_{S, V} \end{aligned}$$

## 7.1 Chemical Potential

A temperature difference derived heat flow. A pressure difference derives volume change. A chemical potential difference derives particle change.

$$\mu_1 > \mu_2 \Rightarrow \mu_1 \rightarrow \mu_2$$

$$\mu = -T \frac{\partial S}{\partial N} \rightarrow \frac{\partial S_1}{\partial N_1} < \frac{\partial S_2}{\partial N_2}$$

$$dS = dS_1 + dS_2 > 0 \Rightarrow \left( \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \right) dN_1 > 0 \Rightarrow dN_1 < 0$$

Chemical potentials moves from high to low.

### 7.1.1 With a Reservoir

We have two systems  $A_1$  and  $A_2$  connected to a reservoir  $R$  at fixed  $T$ . The equilibrium state is when the Helmholtz Free Energy is minimized. Let's assume that  $dV = 0$  and  $dT = 0$ .

$$F = F_1(T, V_1, N_1) + F_2(T, V_2, N - N_1) \quad dF = dF_1 + dF_2 = 0$$

$$dF = \left( \frac{\partial F_1}{\partial N_1} \right)_{T, V_2} dN_1 + \left( \frac{\partial F_2}{\partial N_2} \right)_{T, V_2} dN_2 = \left( \frac{\partial F_1}{\partial N_1} - \frac{\partial F_2}{\partial N_2} \right)_{T, V_2} dN_1 = 0$$

$$\frac{\partial F_1}{\partial N_1} = \frac{\partial F_2}{\partial N_2}$$

Let's propose that  $\mu = \partial F / \partial N$

$$dU = TdS - pdV + \mu dN$$

$$F = U - TS \Rightarrow dF = dU - SdT + TdS = -SdT - pdV + \mu dN$$

$$dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial N} dN$$

That is the proof, so we now know chemical potential for a canonical ensemble.

## 7.2 Ideal Gas

$$\begin{aligned}
 F &= -k_B T \ln(Z) & Z_{I.D.} &= \frac{(n_Q * V)^N}{N!} \\
 F &= -k_B T N \ln(n_Q * V) + k_B T \ln(N!) \\
 &= -k_B T N \ln(n_Q * V) + k_B T N \ln(N) - k_B T N \\
 \mu &= \frac{\partial F}{\partial N} = -k_B T \ln(n_Q * V) + k_B T \ln(N) + k_B T - k_B T \\
 &= -k_B T \ln\left(\frac{n_Q * V}{N}\right) & \frac{N}{V} &= n \\
 \mu &= k_B T \ln\left(\frac{n}{n_Q}\right)
 \end{aligned}$$

For a classical ideal gas,  $n \ll n_Q$ , so the chemical potential is always negative. We also now know that the chemical potential is proportional to the log of the density.

## 7.3 Internal and External Chemical Potential

This is the Nernst Equation. Consider an ideal gas with charge. You can counteract  $\mu$  with a difference in potential energy  $U$ . The energy is given by

$$\begin{aligned}
 \epsilon_i &= \frac{p_i^2}{2m} q U_{1or2} & Z_{tot} &= \frac{1}{N_1!} \left( \sum_i e^{-\beta \epsilon_i} \right)^{N_1} = \frac{1}{N_1!} \left( e^{-\beta q U_1} \sum_i e^{-\beta \frac{p_i^2}{2m}} \right)^{N_1} \\
 &= \frac{1}{N_1!} (e^{-\beta q U_1} n_Q * V)^{N_1} & F &= -k_B T \ln(Z) \\
 F &= -N_1 k_B T \ln(e^{-\beta q U_1} n_Q V_1) + N_1 k_B T \ln(N_1) - N_1 k_B T \\
 \mu &= \frac{\partial F}{\partial N} = k_B T \ln\left(\frac{n_1}{n_Q}\right) + q U_1 = \mu_{int} + \mu_{ext}
 \end{aligned}$$

At equilibrium, the chemical potential can be written as

$$\begin{aligned}
 \mu_1 &= \mu_2 & \Delta \mu_{ext} &= q U_1 - q U_2 = -\Delta \mu_{int} = k_B T \ln\left(\frac{n_2}{n_1}\right) \\
 q U_1 - q U_2 &= k_B T \ln\left(\frac{n_2}{n_1}\right)
 \end{aligned}$$

This is known as the Nernst Equation. This equation also works for the chemical potential in a charge dilute solution.

$$\mu_{sol} = \mu_{sol0} + k_B T \ln \left( \frac{n_{sol}}{n_0} \right)$$

### 7.3.1 Atmospheric Density

$$\mu(h) = k_B T \ln \left( \frac{n(h)}{n_Q} \right) + mgh = \mu_{int} + \mu_{ext}$$

$$n(h) = n(0)e^{-\frac{mgh}{k_B T}} \quad p(h) = p(0)e^{-\frac{mgh}{k_B T}}$$

## 7.4 Discussion

$$\begin{aligned} I(\alpha) &= \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \\ I(1)^2 &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx e^{-(x^2+y^2)} = \int_0^{2\pi} d\theta \int_0^{\infty} dr \gamma e^{-\gamma^2} \\ &= 2\pi \left( -\frac{1}{2} e^{-\gamma^2} \right) \Big|_0^{\infty} = \sqrt{\pi} \end{aligned}$$

## 7.5 Gibbs Free Energy

$$G = U + pV - TS = H - TS$$

Where  $H$  is the heat (i think). Remember that

$$dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV = \frac{1}{T} dU + \frac{p}{T} dV$$

For the total system  $R + s$ , we know that

$$dS_{R+s} = 0 = dS_R + dS_s = \frac{dI_R}{T_R} + \frac{p_R}{T_R} dV_R + dS_s$$

$$U_{tot} = \text{const} = U_R + U_s \rightarrow dU_R = -dU_s$$

$$V_{tot} = \text{const} = V_R + V_s \rightarrow dV_R = -dV_s$$

Plug those things into our total entropy equation and get

$$dS_{tot} = -\frac{dI_s}{T_R} - \frac{p}{T}dV_s + dS_s = -\frac{1}{T}d(U_s + pV_s - TS_s)$$

We now have the equilibrium condition of entropy in terms of the system  $s$  alone.

$$G = U_s + pV_s - TS_s \quad dS_{tot} = 0 \Rightarrow 0 = -dG$$

To maximize entropy, you minimize  $G$ .

## 7.6 Summary

### 7.6.1 Microcanonical Ensemble

Closed system with fixed  $U, V$ .

At equilibrium, we maximize entropy  $\Delta S \geq 0$ .

### 7.6.2 Canonical Ensemble

System  $s$  coupled to reservoir  $S$  of set temperature.  $V_s$  and  $T$  are constant. For this, we use the Helmholtz Free Energy  $F$ . At equilibrium, we minimize Helmholtz Free Energy  $\Delta F_s \leq 0$ .

### 7.6.3 Fixed Pressure Reservoir

Consider a system with fixed  $p, T$  instead of fixed  $V_s, T$ .

At equilibrium, Gibbs Free Energy is minimized  $\Delta G \leq 0$ .

### 7.6.4 Math

We showed that

$$U = U(S, V) \quad F = F(T, V) = U - TS \quad G = G(T, p) = H - TS$$

$$dU = TdS - pdV + \mu dN$$

$$dF = -pdV - SdT + \mu dN$$

$$dG = -SdT + Vdp + \mu dN$$



## 7.7 Relating $G$ to $\mu$

Consider a monatomic ideal gas.

$$G = U + pV - TS$$

$$U = \frac{3}{2}k_B T \quad pV = Nk_B T \quad S = Nk_B \left( \ln\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right)$$

$$\begin{aligned} G_{idealgas} &= \frac{3}{2}Nk_B T + Nk_B T - Nk_B T \left( \ln\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right) = Nk_B T \left( \ln\left(\frac{n}{n_Q}\right) \right) \\ &= N * \mu_{ideal} = G_{ideal} \quad \mu = k_B T \ln\left(\frac{n}{n_Q}\right) \end{aligned}$$

While we proved this for the ideal gas, this is actually true in all cases. The proof is also supposedly very short.

An extensive quantity doubles if every feature doubles  $N \rightarrow 2N, V \rightarrow 2V, U \rightarrow 2U$ .

Examples are  $U, V, S, F$ .

Intensive quantities stay the same if the entire system doubles proportionally. Examples are  $T, p, n = \frac{N}{V}, \mu$

$$G = U + pV - TS$$

Because  $U, V, S$  are all extensive, then  $G$  is just a sum of extensive properties, and thus is also extensive. However  $G$  is only a condition based off of  $G(T, p, N)$ , and  $T$  and  $p$  are both intensive, so

$$G(T, p, 2N) = 2G$$

Because of this, we know that  $G$  must be proportional to  $N$  since it's the only extensive variable and  $G$  itself is extensive.

$$G \sim N * \varphi(T, p)$$

Now we have to figure out  $\varphi$

$$dG = -SdT + Vdp + \mu dN \Rightarrow \left( \frac{dG}{dN} \right)_{T,p} = \mu$$

$$dG = \left( \frac{d}{dN}(N * \varphi(T, p)) \right)_{T,p} = \varphi(T, p) = \mu$$

This does not work for the Helmholtz Free Energy  $F$  because it is dependent on 2 extensive variables  $V$  and  $N$ .

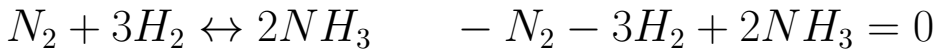
### 7.7.1 Generalizing $G_n$

This is specifically if you have  $n$  species

$$G(T, p, N_1, N_2, \dots, N_n) = \sum_{i=1}^n N_i \mu_i(T, p)$$

### 7.7.2 Chemical Equilibrium

Chemical reactions for fixed  $p, T$  can use  $G$  instead. Consider the nitrogen fixation reaction



The chemical reaction can be written as

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_n A_n = \sum_{i=1}^n \nu_i A_i = 0$$

Where  $A_i$  denotes the  $i$ th chemical species. For constants  $p, T$ , equilibrium is minimizing  $G$ .

$$dG = 0 = -SdT + VdP + \mu dN \rightarrow dG = \sum_{i=1}^n \mu_i dN_i$$

Where  $dN_i$  is the change in the number of molecules of species  $i$  in the reaction. Let  $d\hat{N}$  denote the number of reaction cycles

$$dN_{N_2} = -1 * d\hat{N} \quad dN_{H_2} = -3 * d\hat{N} \quad dN_{NH_3} = +2 * d\hat{N}$$

$$dG = 0 = -1\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3}$$

This is the condition of diffusive equilibrium.

In general, this can be written as

$$dN_i = \nu_i d\hat{N}_i \quad dG = 0 \Rightarrow \sum_{i=1}^n \mu_i \nu_i = 0$$

If we consider  $N_2, H_2, NH_3$  each as ideal gases, we can get

$$p_i = n_i k_B T \quad n_i = \frac{N_i}{V}$$

$$\mu_i = k_B T \ln\left(\frac{n_i}{n_Q(T)}\right) = k_B T \ln\left(\frac{p}{n_Q k_B T}\right) = \mu_{i0} + k_B T \ln\left(\frac{p_i}{p_0}\right)$$

$p_i$  is specifically the partial pressure of gas  $i$  in the system.

$$p_0 = 1 \text{ atm} \quad \mu_0 = k_B T \ln \left( \frac{p_0}{n_Q k_B T} \right)$$

Now we plug  $\mu_{N_2}, \mu_{H_2}, \mu_{NH_3}$  into our equilibrium equation

$$\begin{aligned} dG &= \\ &= -\mu_{N_2}^\circ - k_B T \ln \left( \frac{p_{N_2}}{p_0} \right) - 3 \left( \mu_{H_2}^\circ + \ln \left( \frac{p_{H_2}}{p_0} \right) \right) + 2 \left( \mu_{NH_3}^\circ + \ln \left( \frac{p_{NH_3}}{p_0} \right) \right) \\ &= k_B T \ln \left( \frac{p_{N_2} * (p_{H_2})^3}{(p_{NH_3})^2 * (p_0)^2} \right) = -\mu_{N_2}^\circ - 3\mu_{H_2}^\circ + 2\mu_{NH_3}^\circ \end{aligned}$$

The left side is  $\Delta G_0$  which is the standard Gibbs Free Energy of a reaction.

$$\frac{(p_{NH_3})^2 * (p_0)^2}{(p_{N_2}) * (p_{H_2})^3} = e^{-\frac{\Delta G_0}{k_B T}} = K(T) = \text{equil. constant} \quad \Delta G_0 < 0 \quad K(T) > 1$$

This is known as the law of mass action. Because  $K(T)$  is constant, you can figure out the change in resulting partial pressure if the partial pressure of the reactants changes.

If you do all the math for the water reaction  $2H_2 + O_2 = 2H_2O$ , you get

$$\frac{(p_{H_2O})^2 p_0}{(p_{H_2})^2 * (p_{O_2})^2} = e^{-\frac{\Delta G_0}{k_B T}} \equiv K(T)$$

dilute solutions have a different equations that's on the last page of lecture 11.

# Chapter 8

## Grand Canonical Ensemble (Not on Midterm 1)

Consider a reservoir  $R$  and a system  $\rho$  of  $N = N$  and  $\epsilon = \epsilon$ . The reservoir has parameters  $N_0 - N$  and  $U_0 - \epsilon$ .

$$U_0 = U_R + \epsilon = \text{const} \quad N_0 = N_R + N = \text{const}$$

For a gibbs ensemble or a grand sum ensemble. We consider the system in a single microstate and the multiplicity of the system.

$$p(N_i, \epsilon_i) = \frac{\Omega_{R+\epsilon}(N_i, \epsilon_i)}{\sum_{N_i, \epsilon_i} \Omega_{R+\rho}(N_i, \epsilon_i)}$$
$$\frac{p(N_1, \epsilon_1)}{p(N_2, \epsilon_2)} = \frac{\Omega_R(N_0 - N_1, U_0 - \epsilon_1)}{\Omega_R(N_0 - N_2, U_0 - \epsilon_2)} = \frac{e^{S_R(N_0 - N_1, U_0 - \epsilon_1)/k_B}}{e^{S_R(N_0 - N_2, U_0 - \epsilon_2)/k_B}}$$

For a reservoir  $R$ , we can do a taylor expansion around  $U_0$  for  $U_0 \gg \epsilon_1$  or  $\epsilon_2$  and  $N_0 \gg N_1$  and  $N_2$

$$S_R(N_0 - N_i, U_0 - \epsilon_i) \approx S_R(N_0, U_0) - \left. \frac{\partial S_R}{\partial N} \right|_{N_0} N_i - \left. \frac{\partial S_R}{\partial U} \right|_{U_0} \epsilon_i + \dots$$

$$= S_R(N_0, U_0) + \frac{\mu}{T} N_i - \frac{\epsilon_i}{T}$$

$$\frac{p(N_1, \epsilon_1)}{p(N_2, \epsilon_2)} = \frac{e^{(\mu N_1 - \epsilon_1)/k_B T}}{e^{(\mu N_2 - \epsilon_2)/k_B T}} \quad \sum_N \sum_{\epsilon} p(N, \epsilon) = 1$$

$$p(N_1, \epsilon_1) = \frac{e^{-(\epsilon_1 - \mu N_1)/k_B T}}{\sum_{N_j} \sum_{\epsilon_j} e^{-(\epsilon_j - \mu N_j)/k_B T}}$$

$e^{-(\epsilon_i - \mu N_i)/k_B T}$  Is known as the Gibbs Factor. The Gibbs Sum or Grand Sum

is

$$\zeta(\mu, T) = \sum_{N_j} \sum_{\epsilon_j} e^{-(\epsilon_j - \mu N_j)/k_B T}$$

I don't know what's happening anymore I don't really care I'm tired

$$\zeta(\mu, T) = \sum_N e^{-\mu N/k_B T} * \sum_{\epsilon} e^{-\epsilon/k_B T} = \sum_N \lambda^N Z(N, T) \quad \lambda = e^{\mu/k_B T}$$

$$\langle N \rangle = \frac{\sum_N \sum_{\epsilon(N)} N \lambda^N e^{-\epsilon/k_B T}}{\zeta(\mu, T)} = k_B T \frac{\partial}{\partial \mu} \ln(\zeta(\mu, T)) = \lambda \frac{\partial}{\partial \lambda} \ln(\zeta(\lambda, T))$$

$$U = \langle \epsilon \rangle = \frac{\sum_N \sum_{\epsilon(N)} \epsilon e^{-(\epsilon - \mu N)/k_B T}}{\zeta(\mu T)}$$

### 8.0.1 Example: Myoglobin

I didn't want to pay attention so I did not.

## 8.1 Multiple Species

Consider a system  $\rho$  with  $N_A, N_B, \epsilon_A, \epsilon_B$  attached to a reservoir  $R$ .

$$\frac{p_1}{p_2} = \frac{\Omega_R(N_A^\emptyset - N_{A1}, N_B^\emptyset - N_{B1}, U_0 - \epsilon_{A1} - \epsilon_{B1})}{\Omega_R(N_A^\emptyset - N_{A2}, N_B^\emptyset - N_{B2}, U_0 - \epsilon_{A2} - \epsilon_{B2})} = e^{\Delta S_R/k_B T}$$

### 8.1.1 Example: Carbon Dioxide

I don't care

# Chapter 9

## Photon Gas

Given a box of length  $L$  at temperature  $T$ . Inside the box is EM radiation.

$$|\vec{k}|^2 = k^2 = \frac{\omega^2}{c^2}$$

And an EM wave of frequency  $\omega$  has energy

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \approx \hbar\omega n$$

What is the partition function for a single mode?

$$Z = \sum_{s=0}^{\infty} e^{-\beta\epsilon_s} = \sum_{s=0}^{\infty} e^{-\beta\hbar\omega s} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

And the average energy can be calculated with

$$U = \langle\epsilon\rangle = -\frac{\partial}{\partial\beta} \ln(Z) = +\frac{\partial}{\partial\beta} \ln(1 - e^{-\beta\hbar\omega}) = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \hbar\omega\langle s\rangle$$

And  $\langle s\rangle$  is the average number of photons in the mode at temp  $T$ . For high temperatures, it starts functioning as the classical case

$$\langle s\rangle \approx \frac{k_B T}{\hbar\omega} \Rightarrow U = \langle\epsilon\rangle = k_B T$$

It follows the equipartition theorem.

### 9.0.1 Standing Waves

Standing waves are described by a discrete set of integers  $n_x, n_y, n_z$ . such that

$$\omega = c|\vec{k}| \quad \omega_n = c\sqrt{k_x^2 + k_y^2 + k_z^2} \quad k_x = \frac{n_x\pi}{L_x}$$

$$Z_{tot} = \prod_{modes} \frac{1}{1 - e^{-\beta\hbar\omega_n}} \quad U_{tot} = \sum_{modes=n} \frac{\hbar\omega_n}{e^{\beta\hbar\omega_n} - 1} = \sum_{modes=n} \hbar\omega_n \langle s_n \rangle$$

## 9.0.2 Continuum Basis

Let's assume that each particle is in an empty space of  $\pi/L_x$  by  $\pi/L_y$  by  $\pi/L_z$ . So, it occupies a volume  $\pi^3/V$ . If we consider only the quarter circle shell of points such that  $a < |\vec{k}|^2 < a + \delta$ .

What we're trying to solve is

$$\begin{aligned} \#modes : f \in [\omega, \omega + d\omega] &= \frac{V(shell)}{V(per\ k\ space)} = D(\omega)d\omega \\ &= 2 * \frac{\frac{4\pi k^2}{8} dk}{\frac{\pi^3}{V}} = \frac{V}{\pi^2} k^2 dk = \frac{V}{\pi^2} \frac{\omega^2 d\omega}{c^3} \end{aligned}$$

Remember that there are 2 polarizations per mode (hence the beginning 2 coefficient). To find energy, we calculate

$$\begin{aligned} U_{tot} &= \sum_n \langle \epsilon_n \rangle = \sum_n \frac{\hbar\omega}{e^{\beta\hbar\omega_n} - 1} \approx \int_0^\infty d\omega D(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega_n} - 1} \\ &= \int_0^\infty d\omega \frac{V}{\pi^2} \frac{\omega^2}{c^3} \frac{\hbar\omega}{e^{\beta\hbar\omega_n} - 1} \quad \frac{U_{tot}}{V} = \mu_{tot} = \int_0^\infty d\omega \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega_n} - 1} \\ \mu(\omega) &= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega_n} - 1} \end{aligned}$$

$\mu(\omega)$  is the energy density in the frequency band  $[\omega, \omega + d\omega]$ .

This is known as the **Planck Radiation Law**

You can graph it to get a black body radiation something

$$\begin{aligned} x = \beta\hbar\omega &= \frac{\hbar\omega}{k_B T} \quad \frac{d}{dx} \frac{x^3}{e^x - 1} \stackrel{!}{=} 0 \\ \frac{d}{dx} \frac{x^3}{e^x - 1} &= \frac{3x^2}{e^x - 1} - \frac{x^3 e^x}{(e^x - 1)^2} = \left( \frac{x^2}{e^x - 1} \right) \left( 3 - \frac{x e^x}{e^x - 1} \right) \end{aligned}$$

This equation has trivial solution  $x = 0$  and nontrivial solution:

$$3 = \frac{x e^x}{e^x - 1} \Rightarrow 3(1 - e^{-x}) = x$$

This can be solved numerically, and the numerical solution is known as **Wien's Law**.

## 9.0.3 Wien's Law

$$2.82 = x_{max} = \beta\hbar\omega_{max} = \frac{\hbar\omega_{max}}{k_B T} \Rightarrow \hbar\omega_{max} = 2.82 k_B T$$

### 9.0.4 Def: Black Body

Idealized object that absorbs all EM radiation. In thermal equilibrium at temp  $T$ , a black body emits radiation with spectrum  $\mu(\omega)$ .

### 9.0.5 Example: Cosmic Microwave Background

$\mu(\omega)$  at  $T = 273K \rightarrow \lambda_{peak} = \text{microwave}$ .

## 9.1 Low Temperature Limit (Ultraviolet Catastrophe)

Let  $\hbar\omega \ll k_B T$

$$\mu(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \approx \frac{\hbar\omega^3}{\pi^2 c^3} \frac{k_B T}{\hbar\omega} \quad e^x \approx 1 + x + \dots$$

$$\mu(\omega) = \omega^2 \frac{k_B T}{\pi^2 c^3} \propto \omega^2 k_B T$$

This is the Raleigh-Jeans Law. This is the classical limit without quantum mechanics. However, this breaks everything because the total energy diverges  $\int_0^\infty d\omega \mu(\omega) = \infty$  (which is bad). This catastrophe is what caused us to think of photons and discover quantum mechanics.

## 9.2 Stefan-Boltzmann Law

$$\mu_{tot} = \int_0^\infty d\omega \mu(\omega) = \int_0^\infty d\omega \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \quad x = \beta\hbar\omega = \frac{\hbar\omega}{k_B T}$$

$$\mu_{tot} = \frac{(k_B T)^4}{\pi^2 (\hbar c)^3} \int_0^\infty dx \frac{x^3}{e^x - 1} \propto T^4$$

This is dramatically different from an ideal gas where  $U \propto T$ . We can solve the integral and plug it in to get

### 9.2.1 Stefan-Boltzmann Law

$$\mu_{tot} = \frac{\pi^2 (k_B T)^4}{15 (\hbar c)^3}$$



We can do shenanigans with entropy now.

$$dU = TdS - pdV = TdS \Rightarrow dS = \frac{1}{T}dU = \alpha V \frac{4T^3 dT}{T}$$

$$dS = 4\alpha VT^2 dT \quad S = \int dS = \int 4\alpha VT^2 dT = \frac{4\alpha}{3} VT^3 + C \quad (C = 0)$$

$$S(V, T) = \frac{4\alpha}{3} VT^3 + C \quad S(U, V) = \frac{4}{3}(\alpha V)^{1/4} U^{3/4} \quad S \propto U^{3/4}$$

Very different from an ideal gas.

## 9.3 Discussion (october 14th)

It looks like we're just reviewing the different ensembles

Micro-canonical ensembles mean no reservoir, constant  $N, V, U$ , and they are governed by

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

Canonical ensembles have a reservoir and thus constant  $N, V, T$  with the small system having energy  $\epsilon$ . It is governed by

$$Z = \sum_i e^{-\beta \epsilon_i} \quad F = k_B T \ln(Z) = U - TS$$

The Grand Canonical or Gibbs ensemble allows particles to move so what's constant is  $\mu, U, T$  with small system energy  $\epsilon$  and the equations are

$$\zeta(\mu, T) = \sum_N \sum_{\epsilon(N)} e^{-(\epsilon - \mu N)/k_B T} = \sum_N \lambda^N Z(N, T) \quad \lambda \equiv e^{\mu/k_B T}$$

$$\Phi = G = U - TS - \mu \langle N \rangle \quad \langle N \rangle = \sum_N \sum_{\epsilon(N)} N e^{-(\epsilon - \mu N)/k_B T} = \lambda \frac{\partial}{\partial \lambda} \zeta(\lambda, T)$$

$$\Phi = G = -k_B T \ln(\zeta)$$

$$\langle \epsilon \rangle = \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \zeta - \frac{\partial}{\partial \beta} \ln(\zeta)$$

# Chapter 10

## Debye Model

Instead of looking at a photon gas, we look at lattice vibrations within a solid (**phonons**). I remember talking about these in the quantum + chips summer school and that's about it.

Consider a 3D lattice of atoms that are elastically coupled (Let's call them springs), and the lattices takes up a volume  $V$ .

At high temperature

$$\epsilon_i = \frac{p_i^2}{2m} + \frac{1}{2}kx_i^2 \quad U_{tot}N * 3 * 2 * \frac{1}{2}k_B T = 3Nk_B T$$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V = 3Nk_B T$$

(3 \* 2 comes from 3 translational degrees of freedom + kinetic energy + potential energy)

At low temperature, we have to consider quantum shenanigans

$$\epsilon_s = \hbar\omega \left( s + \frac{1}{2} \right)$$

This looks very similar to an Einstein Solid, which has a calculated energy of

$$U_1 = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad U_N = 3N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$
$$C_v = \left( \frac{\partial U_{tot}}{\partial T} \right)_V = \left( \frac{\hbar\omega}{k_B T} \right)^2 k_B \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

for high temperature  $k_B T \gg \hbar\omega$ , we use the taylor series  $e^x \approx 1 + x + \dots$  to get

$$U_{tot} = 3N \frac{\hbar\omega}{1 + \beta\hbar\omega - 1} = 3N \frac{1}{\beta} = 3Nk_B T \quad C_v = \left( \frac{\partial U_{tot}}{\partial T} \right)_V = 3Nk_B$$

At low temperature  $k_B T \ll \hbar\omega$ , we get

$$U_{tot} \approx 3N\hbar\omega e^{-\beta\hbar\omega} \quad C_v = 3Nk_B \left( \frac{\hbar\omega}{k_B T} \right)^2 e^{-\hbar\omega/k_B T}$$

Experimentally, we see that the specific heat capacity starts at 0 for  $T = 0K$ , and it goes up to an asymptote  $3Nk_B$  as  $T$  gets higher.  $C_V$  goes up linearly with  $T^2$  in experiments at low  $T$ .

For an insulator we calculate  $C_V = AT^3$ , and for a metal,  $C_V = \gamma T + AT^3$ . These are both wrong, so we have to figure out what's up with the Einstein model to get the experimental result of  $T^2$ . The biggest issue with the Einstein model is that it assumes that every atom has the same frequency  $\omega$ .

## 10.1 Debye Model

Atoms are **not** independent oscillators. Consider atoms of a lattice spacing  $a$ .

The force on a single atom is given by

$$F_i = \kappa(r_{i+1} - r_i - a) - \kappa(r_i - r_{i-1} - a) = m \frac{d^2 r_i}{dt^2} = \kappa(r_{i+1} - 2r_i + r_{i-1})$$

$$\frac{df}{dx} \lim_{a \rightarrow 0} \frac{f(x+a) - f(x)}{a} \Rightarrow \frac{d^2 f}{dx^2} = \lim_{a \rightarrow 0} \frac{f(x+a) - 2f(x) + f(x-a)}{a^2}$$

$$\frac{r_{i+1} - 2r_i + r_{i-1}}{a^2} \approx \frac{d^2 r}{dx^2} \approx \frac{m}{\kappa a^2} \frac{d^2 r}{dt^2} \quad \frac{m}{\kappa a^2} = \frac{1}{C_s^2}$$

$C_s$  is the speed of sound in the lattice. We can just treat the set of lattices as a wave equation.

$$\tau(x, t) \approx e^{ikx - i\omega t} \quad \omega = c_s k$$

This approximation is valid for  $\lambda = \frac{2\pi}{k} \gg a$  so there's a long wavelength. The Debye model assumes that  $\omega = c_s k$  is always valid. Atoms move either parallel or perpendicular to the wave propagation direction, and there's 1 parallel and 2 perpendicular directions. The speed of sound in the lattice  $c_s$  could depend on the polarization of the wave. All we know is that we should get

$$U_{tot} = ? \quad C_v = \left( \frac{\partial U_{tot}}{\partial T} \right)_V \simeq T^3$$

## 10.2 1D Chain

Let's consider a 1d chain bounded at distance  $L_x$  from each other. The standing waves will have the following forms

$$\lambda = 2L_x \quad k_x = \frac{2\pi}{\lambda} = \frac{\pi}{L_x} \quad \lambda = L_x \quad k_x = \frac{2\pi}{L_x} \quad \lambda = \frac{2}{3}L_x \quad k_x = \frac{3\pi}{L_x}$$

etc etc, and the maximum standing wave will be of the form

$$k_{max} = \frac{\pi}{a} = \frac{N_x \pi}{L_x} \quad k_x = \frac{n_x \pi}{L_x} \quad n_x = 1, 2, 3, \dots, N_x$$

And it's the same for  $y$  and  $z$ .

With this, the total number of modes as be written as

$$\#(modes)_{tot} = 3N_x N_y N_z = 3N$$

And there 3 is because of the polarization states of the waves.

### 10.2.1 Photon Gas

For a photon gas, we have

$$\omega = ck$$

You are always 2 transverse polarizations

$$k_{x,y,z} = n_{x,y,z} \frac{\pi}{L_{x,y,z}} \quad n_{x,y,z} = 1, 2, 3, \dots, \infty \quad 2 \sum_{n_x, n_y, n_z} \rightarrow \infty$$

### 10.2.2 Phonon Gas

and phonon gas, we have

$$\omega = c_s k : \lambda \gg a$$

You are always 2 transverse and 1 longitudinal polarization.

$$k_{x,y,z} = n_{x,y,z} \frac{\pi}{L_{x,y,z}} \quad n_{x,y,z} = 1, 2, 3, \dots, N_{x,y,z} \quad 3 \sum_{n_x, n_y, n_z} = 3N$$

## 10.3 Phonon Energy

$$U_{tot} = \sum_{n=1}^{3N} \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1}$$

Where  $n$  is shorthand for  $n_x, n_y, n_z$ . The way to do this is by transforming it into an integral with large  $N$ .

$$\#modes(\omega \in [\omega, \omega + d\omega]) = \#polarizations$$

The easiest way to do this is the spherical shell method that we used in lecture 13 or for the derivation of the ideal gas.

$$D(\omega)d\omega = 3 \frac{\frac{4\pi k^2 dk}{\frac{\pi^3}{V}}}{2\pi^2} = \frac{3V}{2\pi^2} k^2 dk = \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{c_s^3}$$

$$U_{tot} = \sum_{n=1}^{3N} \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1} = \int_0^? d\omega D(\omega) = \int_0^? d\omega D(\omega) \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1}$$

Let's assume that instead of a square of  $L_x, L_y, L_z$ , we instead have a sphere of radius  $r$  such that there is an equal amount of modes as the cube which is  $\#modes = 3N$ .

$$3N = 3 \frac{\frac{4}{3}\pi \frac{k_D^3}{8}}{\frac{\pi^3}{V}} = \frac{V}{2\pi^2} k_D^3 = \frac{V}{2\pi^2} \left( \frac{\omega_D}{c_s} \right)^3 \Rightarrow \omega_D = 6\pi^2 \left( \frac{N}{V} \right)^{1/3} c_s$$

That is known as the Debye frequency, which is the upper limit of our integral.

$$U_{tot} = \int_0^{\omega_D} d\omega D(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} = \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta \hbar \omega} - 1}$$

$$\frac{3V\hbar}{2\pi^2 c_s^3} \left( \frac{k_B T}{\hbar} \right)^4 \int_0^{x_D(T)} dx \frac{x^3}{e^x - 1}$$

that is dependent on the Debye Temperature

$$\theta_D = \frac{\hbar\omega_D}{k_B} \Rightarrow x_D = \frac{\theta_D}{T}$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \left(6\pi^2 \frac{N}{V}\right)^{1/3} \frac{\hbar c_s}{k_B} = T * x_D$$

$$U_{tot} \simeq \frac{3V\hbar}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^\infty dx \frac{x^3}{e^x - 1} \approx \frac{3V\hbar}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar}\right)^4 \frac{\pi^4}{15}$$

$$U_{tot} == \frac{3\pi^4}{5} N k_B T \left(\frac{T}{\theta_D}\right)^3$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$

This is for the low temperature limit

For the high temp limit we get

$$C_v = 3Nk_B$$

The Debye model gets the low and high temperature limits correct, but does not do as well in the middle.