

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 ... 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.

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

$$\tilde{F} = -k_B T \ln(z) \Rightarrow \left|\frac{\partial \tilde{F}}{\partial T}\right| = -k_B \ln(z) - k_B T \frac{\partial}{\partial T} \ln(z)$$

$$= -k_B \ln(z) + \frac{1}{T} \frac{\partial}{\partial B} \ln(z)$$

We are also theoretically able to derive

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

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

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

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

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

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

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