Lecture 2 – Multiplicity of physical systems

LAST TIME: introduced the multiplicity Ω to count microstates giving one macrostate.
The most likely macrostate of a system is one with highest multiplicity, and in limit that $N \gg 1$, any other macrostate is extremely unlikely.

TODAY: Multiplicity in real physical systems
What does the multiplicity look like for a real physical system? What parameters define the macrostate of a system?

Consider a closed (or isolated) system
- System does not interact with surroundings, cannot exchange energy, particles, etc.
- Total energy U, number of particles N are fixed (particles in system can exchange energy with each other, but total energy is constant)
- Macrostate of system defined by U, N so $\Omega = \Omega(U,N)$

How does the multiplicity depend on U and N?
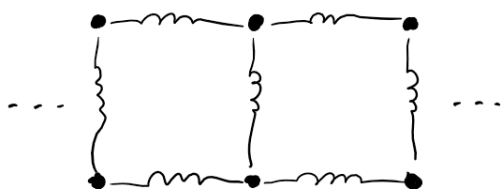
Ex 1: Einstein model of a solid

Imagine a solid of N atoms as a collection of N identical independent quantum harmonic oscillators

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Review of 1-D harmonic oscillator from undergraduate quantum mechanics:

The Hamiltonian for each oscillator i has kinetic energy and harmonic potential energy terms

$$H\psi(x_i,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2}\psi(x_i,t) + \frac{1}{2}m\omega^2 x_i^2 \psi(x_i,t) = \varepsilon_i \psi(x_i,t)$$

This equation has energy eigenvalues

$$\varepsilon_i = \hbar\omega\left(s_i + \frac{1}{2}\right), \text{ with } s_i = 0,1,2\cdots$$

So the energy of each oscillator is quantized. The $\frac{1}{2}\hbar\omega$ term is called the zero-point energy.

For N independent, identical oscillators the total energy U is

$$U = \sum_{i=1}^{N}\varepsilon_i = \hbar\omega\left(n + \frac{N}{2}\right), \text{ with } n \equiv \sum_{i=1}^{N} s_i$$

The zero-point energy is an offset. Does not affect statistics so let's ignore it.

To get the multiplicity Ω, we want to count number of microstates (i.e. the set of integers $\{s_i\}$) that give the same macrostate (i.e. total energy U for N oscillators).

How many ways can we have $s_1 + s_2 + \cdots s_N = n$?
Here is a graphical way of solving this problem (from Schroeder):

$$• \;|\; • \; • \; • \;|\;|\; • \; • \; • \; • \;|\; • \;|\; • \; • \; • \quad \text{...} \quad |\; • \; •$$

| | s_1 | s_2 | s_3 | s_4 | s_5 | s_6 | | s_N | = n |

Dots • = quanta   Lines | = partitions between oscillators

(example above corresponds to microstate $\{s_i\} = \{1,3,0,4,1,3,\cdots2\}$)
Just like a binary system! Each position can be a • or a |

Question 1: What is the multiplicity Ω?

We have n quanta (•), $N-1$ partitions (|), and a total of $n + N - 1$ positions or slots for them.

There are $\dbinom{n+N-1}{n} = \dfrac{n+N-1!}{n!(N-1)!}$ possible ways to arrange n dots in $n + N - 1$ slots, so

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

KEY CONCEPT: the Stirling approximation

For all systems we treat in class, $N \gg 1$ (e.g. $N \sim 10^{20}$)

The <u>Stirling approximation</u> is very useful for estimating $\ln N!$ when $N \gg 1$

$$\ln N! = \ln N + \ln(N-1) + \cdots \ln2 + \ln1 = \sum_{x=1}^{N} \ln x$$

$$\approx \int_1^N dx \ln x = x\ln x - x \Big|_1^N \approx N\ln N - N$$

ignoring any 1's compared to N.
This approximation is correct to order $\ln N$ (e.g. $N = 100$, $\ln N! = 363.7$ but $N\ln N - N = 360.5$).
(For more rigorous derivation, see K & K Appendix A).

If the Einstein solid is large $N \gg 1$ ($\sim 10^{20}$), and unless nearly all the s_i are zero $n \gg 1$ too, so

$$\ln\Omega(n,N) \approx \ln(n+N)! - \ln N! - \ln n!$$
$$\approx (n+N)\ln(n+N) - (\cancel{n} + \cancel{N}) - N\ln N + \cancel{N} - n\ln n + \cancel{n}$$
$$\approx (n+N)\ln(n+N) - N\ln N - n\ln n$$

where we've ignored the 1's.

Also, if on average the oscillators have $s_i \gg 1$ (i.e. they are in a high energy level), then $n \gg N$ (This is called the "high temperature limit"):

$$\ln(n+N) = \ln\left[n\left(1+\frac{N}{n}\right)\right] = \ln n + \ln\left(1+\frac{N}{n}\right)$$
$$\approx \ln n + \frac{N}{n}, \qquad \text{using } \ln(1+x) \approx x \text{ when } x \ll 1$$

So,

$$\ln\Omega(n,N) \approx (\cancel{n} + N)\ln n + (n+N)\frac{N}{n} - N\ln N - \cancel{n\ln n}$$
$$\approx N\ln\frac{n}{N} + N\left(1+\frac{N}{n}\right) \approx N\ln\frac{n}{N} + N$$

In terms of the energy

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

Valid in limit that $U \gg N\hbar\omega$. If $N \sim 10^{20}$, U^N is a very rapidly increasing function of energy! (You will explore "low-temperature limit" in problem set)

Result makes sense: the larger the total energy, the more ways there are of distributing that energy among the N oscillators

For many systems, $\Omega \sim U^f$ with $f \propto N$ (e.g. Einstein solid today, ideal gas in Lect. 4). However, there are other systems that do not behave this way

KEY CONCEPT: <u>Entropy</u> is defined as $\sigma \equiv \ln\Omega$
Why define entropy as a natural log?

Take two independent systems A and B with multiplicities Ω_A and Ω_B, the total multiplicity of both systems together is $\Omega_{A+B} = \Omega_A \Omega_B$, so $\sigma_{A+B} = \sigma_A + \sigma_B$.

Entropies are additive, multiplicities are multiplicative

Entropy is an example of an <u>extensive</u> quantity, which scales linearly with the system size (i.e. if the system size doubles, the entropy doubles). <u>Intensive</u> quantities are independent of system size.
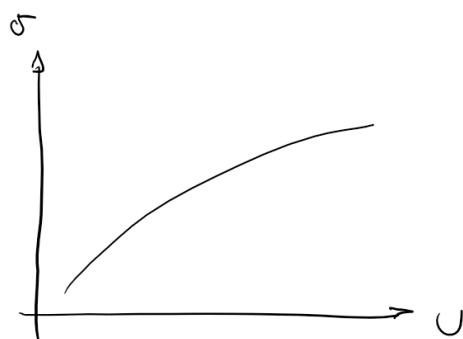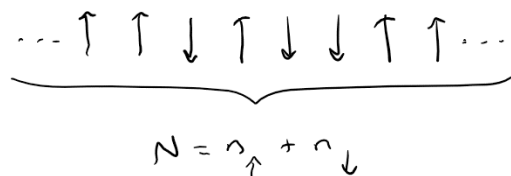

Entropy: $\sigma(U,N) = N\ln\dfrac{eU}{N\hbar\omega}$

(Note: if system doubles $N \to 2N$ and $U \to 2U$, $\sigma \to 2\sigma$)

(Note: we need to be careful to use this expression only in limit that $U \gg N\hbar\omega$. It is NOT correct to say that $\sigma(U \to 0) \sim N\ln U \to -\infty$. In fact, it must be that $\sigma(U \to 0) \to 0$, since $U = 0$ corresponds to all $\{s_i\} = 0$ and there can only be one way to configure the system this way: $\Omega(U \to 0) = 1$, and $\sigma(U \to 0) = \ln\Omega = 0$.)

Ex 2: <u>Paramagnet</u>

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

Model a paramagnetic system as a collection of N independent spins.

Assuming spin ½ particles $n_\uparrow$ are "up", $n_\downarrow = N - n_\uparrow$ are "down"


Review of spin and magnetic moment:

Spins have a magnetic dipole moment $\vec{\mu} = g\dfrac{q}{2m}\vec{s}$ where q and m are the particle charge and mass, and g is the "gyromagnetic ratio"

In the presence of a magnetic field B pointing along z, the dipole moments have energy $\varepsilon = -\vec{\mu} \cdot \vec{B} = -\mu_z B$

The *z*-component of the dipole moment is quantized according to: $\mu_z = g\dfrac{q\hbar}{2m}m_s$, with

$m_s = -s, -s+1, \cdots, s-1, s$

For spin $s = \frac{1}{2}$ particles, each spin can be up or down
$m_s = +\frac{1}{2}$ "up", $-\frac{1}{2}$ "down", so there are two energy levels
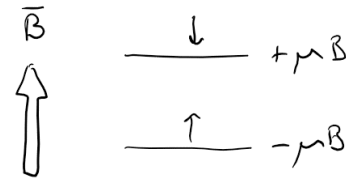
Ex: for electrons spin is $\frac{1}{2}$ and $g \approx 2$; $\mu_B \equiv \dfrac{e\hbar}{2m_e}$ is called the "Bohr magneton"

Electron spins can be in one of two states in a *B* field:
"aligned" $\varepsilon = -\mu B$ or "anti-aligned" $\varepsilon = +\mu B$, with $\mu \approx \mu_B$.

For a system with *N* spins, the total energy *U* in a *B* field is:

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

Question 2: What is the multiplicity of a spin-1/2 paramagnet?

This is just a binary system! So,

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

In terms of *U* this is

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

which is symmetric in *U*

Calculate the entropy assuming system is large $N \gg 1$ ($\sim 10^{20}$) and $n_\uparrow \gg 1$, using the Stirling approximation:

$$\ln\Omega(n_\uparrow, N) \approx \ln N! - \ln(N - n_\uparrow)! - \ln n_\uparrow!$$
$$\approx N\ln N - N - (N - n_\uparrow)\ln(N - n_\uparrow) + (N - n_\uparrow) - n_\uparrow \ln n_\uparrow + n_\uparrow$$
$$\approx N\ln N - (N - n_\uparrow)\ln(N - n_\uparrow) - n_\uparrow \ln n_\uparrow$$

So

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

What does $\sigma(U,N)$ look like?

In contrast to the Einstein solid, where there is no upper bound to the total energy U, in the paramagnet there is a lower and upper bound to U:

$U_{min} = -\mu BN$ when $n_\uparrow = N$, i.e. all spins are aligned to the B field

$U_{max} = +\mu BN$ when $n_\downarrow = N$, i.e. all spins are anti-aligned to the B field

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Question 3: Sketch the entropy of the paramagnet $\sigma(U)$ vs. U by a) determining $\sigma(U)$ at U_{min} and U_{max}, and b) determining if $\sigma(U)$ has a maximum, and if so where.

a) At $U = U_{min}$, all spins are aligned to the B field. There is only one way to configure the spins in this way, so $\Omega = 1$ and $\sigma(U_{min}) = 0$.

At $U = U_{max}$, all spins are anti-aligned to the B field. Again, there is only one way to configure the spins in this way, so $\Omega = 1$ and $\sigma(U_{max}) = 0$.
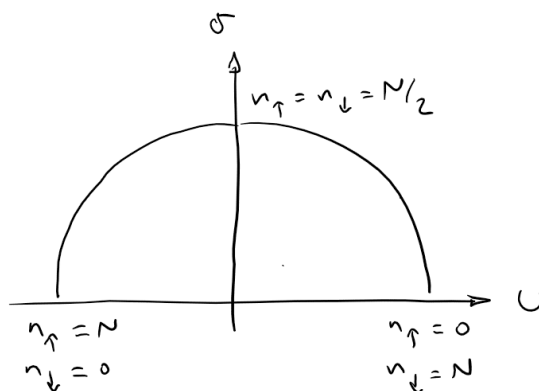
(Can easily check using the binomial coefficient:

$$\Omega(n_\uparrow,N) = \frac{N!}{n_\uparrow! n_\downarrow!}, \text{ so } \Omega(N,N) = \frac{N!}{N!0!} = 1 \text{ and } \Omega(0,N) = \frac{N!}{0!N!} = 1$$

Note: by definition 0! = 1)

b) From Lect. 1, we expect that the state with the highest multiplicity should be one with equal number of spins aligned and anti-aligned, i.e.
$n_\uparrow = n_\downarrow$ and $U = 0$

So, $\sigma(U)$ is peaked at $U = 0$:

What is the value of the maximum entropy $\sigma(U=0)$?

$$\sigma(U=0,N) = N\ln N - N\ln\left(\frac{N}{2}\right) = N\ln 2$$

Makes sense: when the total energy $U = 0$, each spin direction is equally likely so $\Omega = 2^N$ and $\sigma = N\ln 2$ for N independent spins.

So, the entropy depends on total energy U differently depending on the system.

- In the Einstein solid (and many other systems), entropy increases as U increases as $\sigma \sim N\ln U$
- In the paramagnet, entropy peaks and decreases back to zero; slope becomes negative
- In the Einstein solid the entropy vs. energy curve is everywhere concave-down. In some systems (e.g. stars, black holes), the curve is actually concave-up
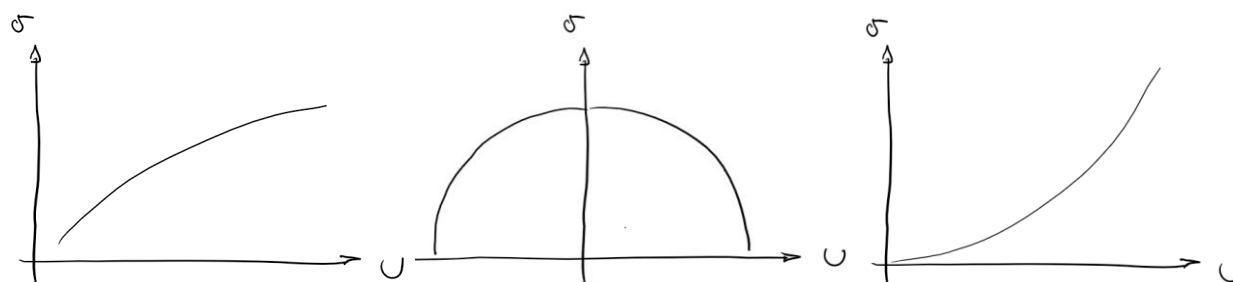
In all systems $\sigma(U) \to 0$ (or a very small number) as U approaches its minimum value, i.e. as the system goes to its ground state. This is called the 3rd law of thermodynamics.

Next lecture, we will see that the absolute temperature is related to the inverse of the slope of the σ vs. U curve. Systems like the Einstein solid grow hotter as U increases, systems like black holes grow colder as U increases, and systems like the paramagnet have a negative temperature!