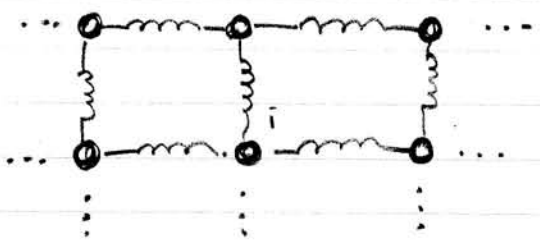
Lecture 2

Einstein model of a solid:



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

$$H = \frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 x_i^2 \qquad E_i = \hbar\omega\left(s_i + \frac{1}{2}\right) \qquad s_i = 0, 1, 2 \cdots$$

Each oscillator's energy is quantized

For N oscillators:

$$U_{tot} = \sum_{i=1}^{N} E_i = \frac{1}{2} N\hbar\omega + n\hbar\omega \qquad \text{where } n \equiv \sum_{i=1}^{N} s_i$$

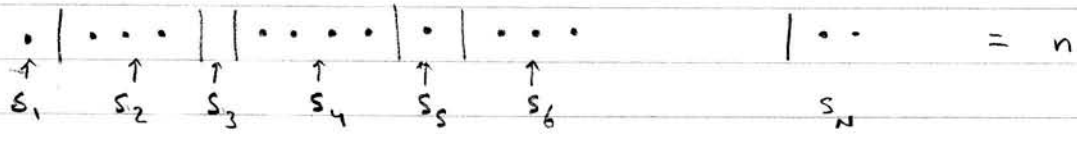
↑ zero-point energy is an offset. Does not affect statistics so let's ignore it

$$U = n\hbar\omega$$

Want multiplicity $\Omega(N, U) = \Omega(n)$

How many ways can we have $s_1 + s_2 + s_3 \cdots s_N = n$?

Represent graphically:



We have n quanta (dots), N-1 partitions (lines) and a total of $n+N-1$ positions for both

Just like binary system! Each position can be a • or |

∴ There are $\binom{n+N-1}{n} = \frac{(n+N-1)!}{n!\,(N-1)!}$ possible arrangements with n dots (= quanta)

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

Now consider $N \gg 1$ and $n \gg 1$ $(U \gg \hbar\omega)$
How do we treat $N!$ for large N

Stirling approximation: $\ln N! \approx N \ln N - N$ for $N \gg 1$

$$\begin{aligned}\ln \Omega(n) &= \ln(n+N)! - \ln N! - \ln n! \qquad \text{(ignore 1's)}\\ &\approx (n+N)\ln(n+N) - (n+N)\\ &\quad - N\ln N + N\\ &\quad - n\ln n + n\\ &\approx (n+N)\ln(n+N) - N\ln N - n\ln n\end{aligned}$$

"High temperature limit"
If most of the oscillators have $s_i \gg 1$, $n \gg N$

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

$$\approx \ln n + \frac{N}{n} \qquad \ln(1+x) \approx x$$

$$\therefore \ln \Omega(n) = (n+N)\ln n + (n+N)\frac{N}{n} - N\ln N - n\ln n$$

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

$$\Omega(n) = e^N \left(\frac{n}{N}\right)^N$$

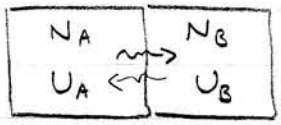
$$\Omega(N, U) = e^N \left(\frac{U}{N\hbar\omega}\right)^N \qquad U = n\hbar\omega = \text{total energy}$$

Multiplicity depends on N, U as U^N
Very large number if $N \sim 10^{20}$!

Note: this system is an isolated system. Does not interact with surroundings, exchange energy $\therefore$ U = constant

What happens when we bring 2 Einstein solids into thermal contact? Can exchange energy (not particles)

isolated
N_A, N_B fixed
U_A, U_B fixed



in contact
N_A, N_B fixed
$U = U_A + U_B$ fixed

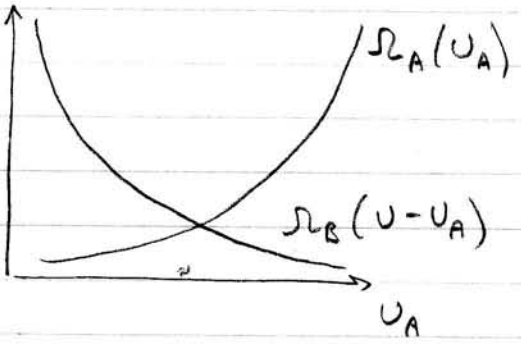
U_A, U_B can vary

$$\Omega_{tot} = \Omega_A(U_A)\,\Omega_B(U_B)$$

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

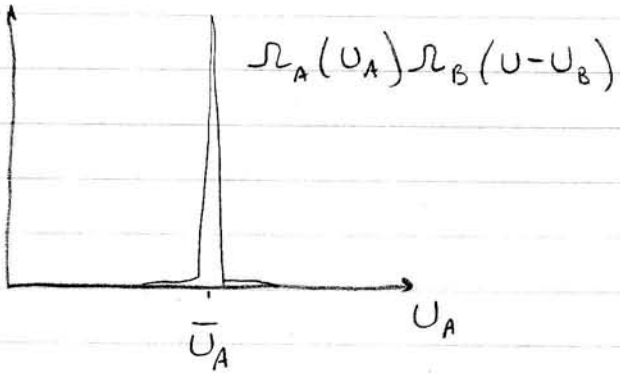
What does $\Omega_A(U_A)\,\Omega_B(U - U_A)$ look like?

$$\Omega(U) \sim U^N$$



Both functions are extremely rapid functions of U_A

$\therefore$ Product $\Omega_A \Omega_B$ is very sharply peaked



Multiplicity is maximized at one energy
$U_A = \bar{U}_A$, $U_B = U - \bar{U}_A$

This is the most likely macrostate of the system
Any other state is extremely unlikely

$$\therefore \quad \Omega_{tot}(U) = \sum_{U_A} \Omega_A(U_A)\,\Omega_B(U-U_A)$$

$$\approx \Omega_A(\bar{U}_A)\,\Omega_B(U-\bar{U}_A)$$

How sharp is multiplicity function?

For simplicity, consider 2 Einstein solids with same # of oscillators N

$$\Omega = \Omega_A \Omega_B = \left(\frac{e\,n_A}{N}\right)^N \left(\frac{e\,n_B}{N}\right)^N \qquad n_A + n_B = n \ \text{(fixed } U\text{)}$$

$$= \left(\frac{e}{N}\right)^{2N} n_A^{\,N} (n - n_A)^N$$

By symmetry this is peaked at $\bar{n}_A = \frac{n}{2}$

Look at deviations from peak x

$$n_A = \bar{n}_A + x = \frac{n}{2} + x \qquad n_B = n - \bar{n}_A - x = \frac{n}{2} - x$$

$$\Omega = \left(\frac{e}{2}\right)^{2N} \left(\frac{n}{2} + x\right)^N \left(\frac{n}{2} - x\right)^N = \left(\frac{e}{2}\right)^{2N} \left(\left(\frac{n}{2}\right)^2 - x^2\right)^N$$

Again $N, n \gg 1$ so consider $\ln \Omega$

$$\ln \Omega = 2N \ln\left(\frac{e}{2}\right) + N \ln\left(\left(\frac{n}{2}\right)^2 - x^2\right)$$

$$= 2N \ln\left(\frac{e}{2}\right) + N \ln\left[\left(\frac{n}{2}\right)^2 \left(1 - \left(\frac{2x}{n}\right)^2\right)\right]$$

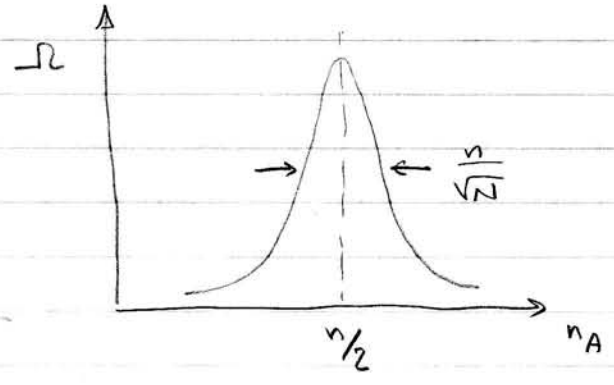
$$= 2N \ln\left(\frac{e}{2}\right) + N \ln\left(\frac{n}{2}\right)^2 + N \ln\left[1 - \left(\frac{2x}{n}\right)^2\right]$$

$$\approx 2N \ln\left(\frac{e}{2}\right) + N \ln\left(\frac{n}{2}\right)^2 - N\left(\frac{2x}{n}\right)^2 \qquad \frac{2x}{n} \ll 1$$

$$\Omega = \underbrace{\left(\frac{e}{2}\right)^{2N} e^{N \ln\left(\frac{n}{2}\right)^2}}_{\text{Constant}} \underbrace{e^{-N\left(\frac{2x}{n}\right)^2}}_{\text{Gaussian}}$$

peak at $x = 0$

width of $\frac{n}{\sqrt{2N}}$



If $N \sim 10^{20}$ width is 10^{-10} of total range of the graph

Extremely sharp

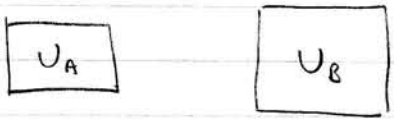
System will be in macrostate that maximizes multiplicity Ω

$$\Omega_{tot} = \Omega_A(\bar{U}_A)\,\Omega_B(U-\bar{U}_A)$$

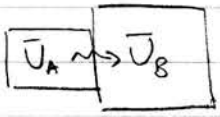
$\Rightarrow$ <u>maximizes entropy</u> $\sigma = \ln \Omega$

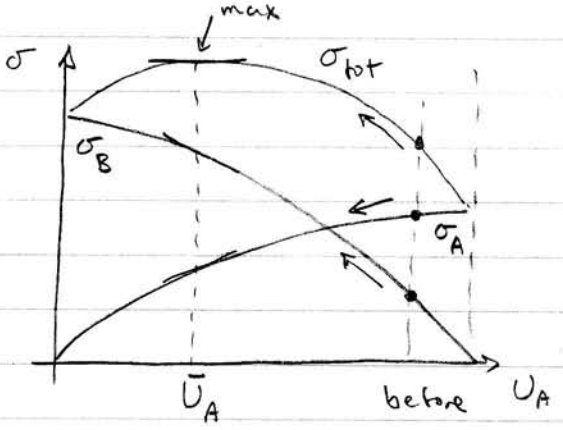
$$\sigma_{tot} = \sigma_A(\bar{U}_A) + \sigma_B(U-\bar{U}_A)$$

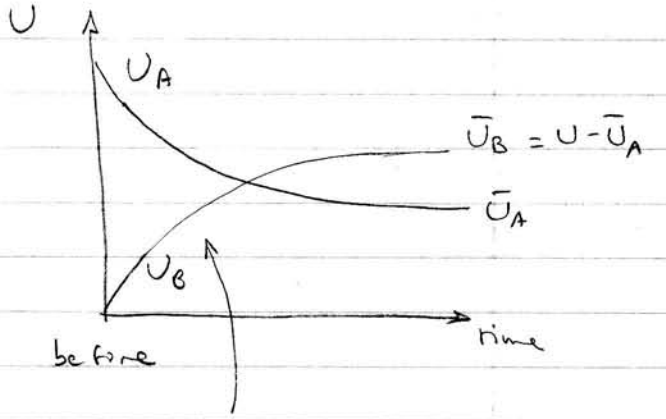
Before



After







Energy is transfered $A \to B$

σ_{tot} is maximized

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

$$= \frac{\partial \sigma_A}{\partial U_A} + \frac{\partial \sigma_B}{\partial U_B}\underbrace{\frac{\partial U_B}{\partial U_A}}_{-1} \quad \Rightarrow \quad \frac{\partial \sigma_A}{\partial U_A} = \frac{\partial \sigma_B}{\partial U_B}$$

This condition is called <u>thermal equilibrium</u>

Formal definition of fundamental temperature τ

$$\frac{1}{\tau} \equiv \left.\frac{\partial \sigma}{\partial U}\right|_N$$

↑ fixed N

Before contact $\tau_A \neq \tau_B$. Energy is transfered (in the form of heat – see future lecture). Thermal equilibrium is reached $\tau_A = \tau_B$. Hotter object loses heat

Note: τ has units of energy since σ is unitless

Absolute temperature T in Kelvin
Conversion factor is Boltzmann's constant

$$k_B = 1.381 \times 10^{-23}\ J/K$$

$$\therefore \quad \frac{1}{T} = k_B \left.\frac{\partial \sigma}{\partial U}\right|_N = \left.\frac{\partial S}{\partial U}\right|_N$$

Define conventional entropy $S \equiv k_B \ln \Omega$

Also, note that individual entropies σ_A, σ_B can decrease but total entropy σ_{tot} is always increased to its maximum

(In this example σ_A, U_A, T_A decrease, σ_B, U_B, T_B increase)

Look back at multiplicity of Einstein solid

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

$$S = k_B \ln \Omega = N k_B \ln\left(\frac{e\,U}{N\hbar\omega}\right)$$

$$= N k_B \left(1 + \ln \frac{U}{\hbar\omega} - \ln N\right)$$

$$\therefore \frac{1}{T} = \frac{\partial S}{\partial U}\bigg|_N = N k_B \frac{1}{U}$$

$$U = N k_B T$$

This result will be re-derived later using the equipartition theorem

Laws of thermodynamics

0th - If $T_A = T_B$ and $T_B = T_C$, then $T_A = T_C$

1st - Conservation of energy

2nd - Most likely macrostate will be where multiplicity (entropy) is maximum
or Multiplicity (entropy) tends to increase: $\Delta S \geq 0$

3rd - As $T \to 0$ $S(T) \to$ const.
or approach ground state multiplicity $\Omega(0)$ which is 1 or a small number