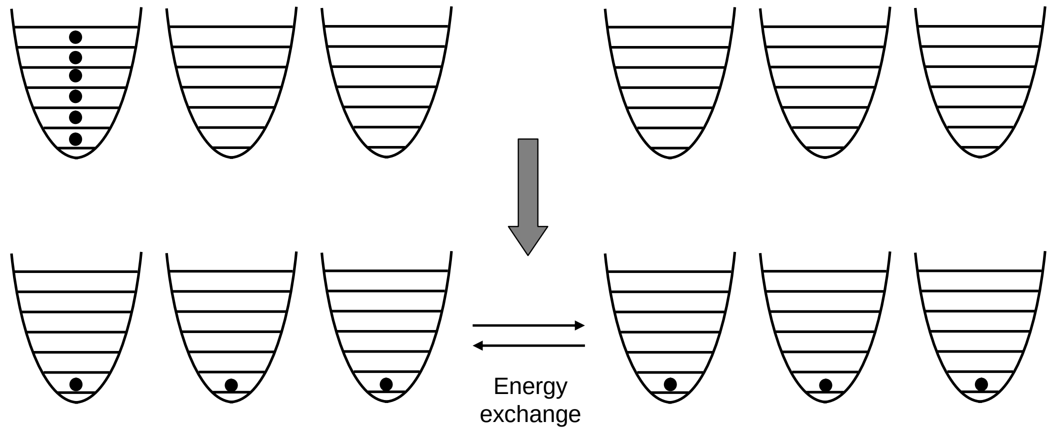
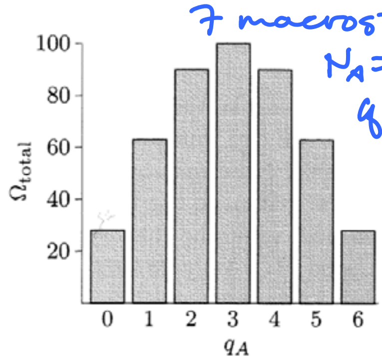
Review of Multiplicity

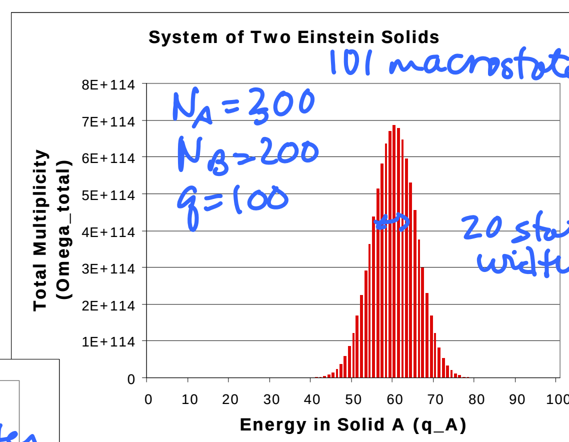


- At equilibrium, a system will be found in the macrostate with the greatest multiplicity
- Multiplicity of a very large system is a sharp Gaussian distribution

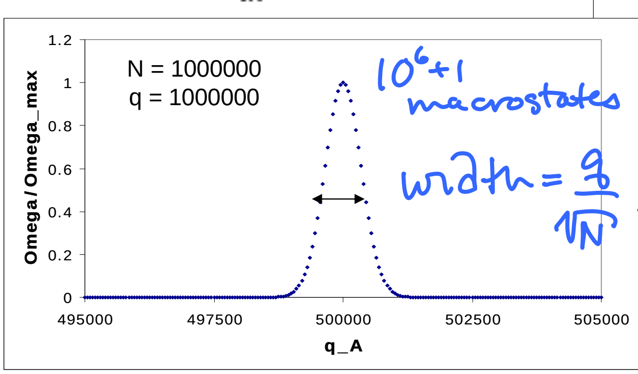
Multiplicities of Two Einstein Solids

7 macrostates
$N_A = N_B = 3$
$q = 6$





101 macrostates
$N_A = 300$
$N_B = 200$
$q = 100$
20 state width



10^6+1 macrostates

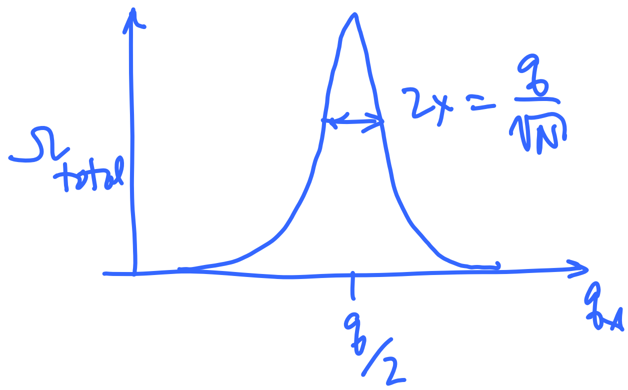
width $= \frac{q}{\sqrt{N}} \approx 1000$

→ as system gets very large
– thermodynamic limit!

Gaussian Distribution

$$\Omega = \Omega_{max} e^{-N(2x/q)^2}$$

$x = 0 \rightarrow$ peak function at $q/2$ $\downarrow$ Ω_{max}



width when Ω is $\frac{1}{e}$ of Ω_{max}

$$1 = N(2x/q)^2$$

$$x = \frac{q}{2\sqrt{N}}$$

Second Law of Thermodynamics

In general, we have seen that

- Any large system in equilibrium will be found in the macrostate with the greatest multiplicity
  - Aside from fluctuations that are normally too small to measure
- This is a more general statement of the second law of thermodynamics
  - Multiplicity tends to increase
- Since multiplicities tend to be very large numbers, it is easier to work with the natural logarithms of these…

Entropy

- Second law of thermodynamics
  - Entropy tends to increase

S

- Define entropy of system as $S \equiv k \ln \Omega$ ← unit of J/K
- For a large Einstein solid with $q >> N >> 1$,

$\Omega = \left(\frac{eq}{N}\right)^N$ ← from last class

$S = k \ln \left(\frac{eq}{N}\right)^N = Nk\left[\ln\left(\frac{q}{N}\right)+1\right]$

example $N = 10^{22}$ oscillators ; $q = 10^{24}$ units of energy

$S = Nk\left[\ln\left(\frac{10^{24}}{10^{22}}\right)+1\right] = Nk(5.6)$

$= 5.6 \times 10^{22}\, k$

$= 0.77$ J/K

Entropy

- Entropy increases when
  - Total number of possible arrangements increases

- Entropy is often thought of as synonymous with disorder

- For a composite system, entropy is sum of entropies of parts

$$S_{total} = k \ln \Omega_{total}$$

$\Omega_{total} = \Omega_A \Omega_B$

$= k \ln (\Omega_A \Omega_B)$

$= k \ln \Omega_A + k \ln \Omega_B$

$= S_A + S_B$

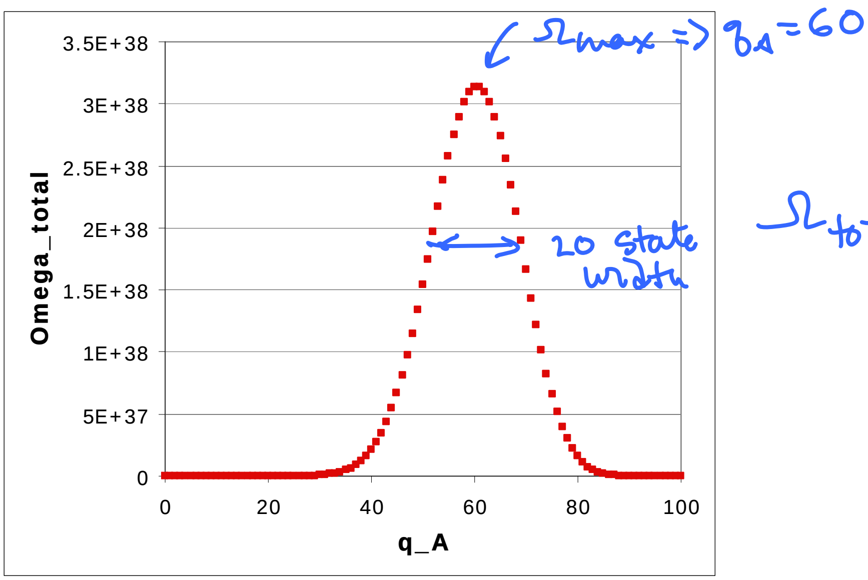
More on Entropy

- Spontaneous processes occur because there is a net increase in entropy
- But what about human intervention?
  - For example, sorting a deck of shuffled cards
  - This requires work by the person doing the sorting and this comes from chemical reactions in their body
  - Resulting increase in entropy is much greater than the decrease in entropy provided by ordering the cards
  - For 52 playing cards, multiplicity is 52!

Entropy and Thermal Equilibrium

Consider two weakly-coupled Einstein solids (A and B)

- $N_A = 30$; $N_B = 20$; $q = q_A + q_B$ $= 100$



$\Omega_{total} = \Omega_A \Omega_B$

Entropy and Thermal Equilibrium

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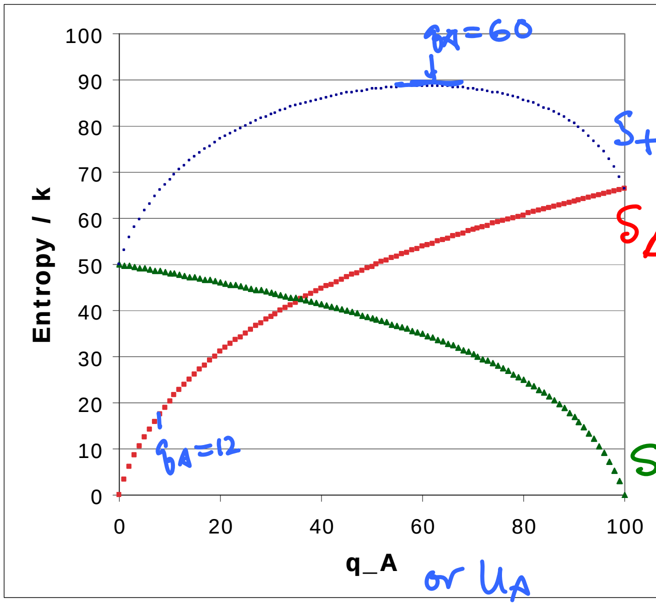


$U = q\varepsilon = qhf$ ← freq.

$\frac{\partial S_{total}}{\partial q_A} = 0$ at eq.

or $\frac{\partial S_{total}}{\partial U_A} = 0$

$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$

since $S_{total} = S_A + S_B$

$dU_A = -dU_B$

$\therefore \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$ at eq.

need $\frac{1}{T}$ relation

think in terms of "steepness" of $\frac{\partial S}{\partial U}$

relate to gain of energy and to T

→ when slopes the same → no exchange of energy → thermal eq T the same.

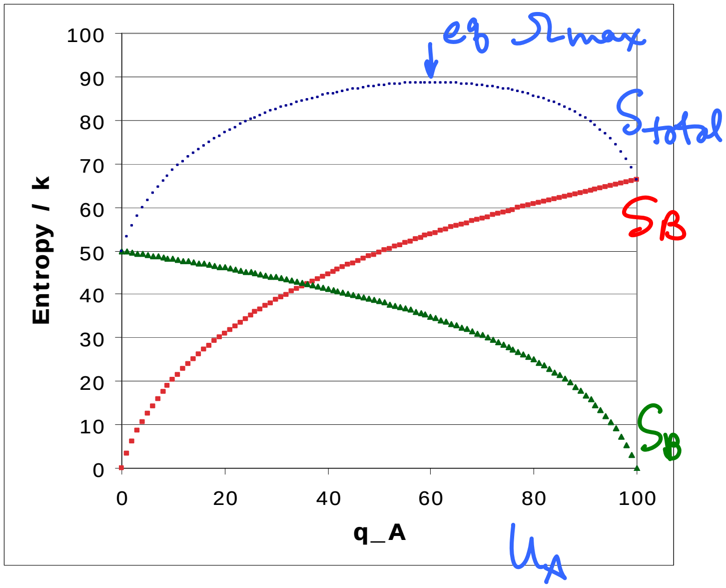
$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$$

Temperature

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

Slope $\rightarrow \frac{1}{T}$

Units: $k = 1.38 \times 10^{-23}$ J/K



Temperature

- Example, an Einstein solid

$U = q \cdot \varepsilon = q \cdot hf$ ← freq.

large solid $q \gg N$

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

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

$$S = Nk\ln U - Nk\ln(\varepsilon N) + Nk$$

from previous $T = \left(\frac{\partial S}{\partial U}\right)^{-1}$

$$T = \left(\frac{Nk}{U}\right)^{-1}$$

$\hookrightarrow U = NkT$

equipartition

$$U = N \cdot f \cdot \frac{1}{2}kT$$

for solid $f = 2$

! remember N is oscillators in this definition not atoms!

How to Measure Entropy

- For case of constant volume, no work

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

for Einstein solid $\quad q \gg N$

$$C_V = \frac{\partial}{\partial T}(NkT)$$
$$= Nk$$

use $\quad \frac{1}{T} = \frac{dS}{dU} \quad \rightarrow \quad dS = \frac{dU}{T} = \frac{Q}{T}$ ← heat added

could write as

$$dS = C_V \frac{dT}{T}$$

changes in entropy

$$\Delta S = S_f - S_i$$
$$= \int_{T_i}^{T_f} \frac{C_V}{T}\, dT$$

example $\quad$ heating 200g H_2O

$20°C \rightarrow 100°C \quad$ calc ΔS

$$\Delta S = C_V \int_{293}^{373} \frac{1}{T}\, dT$$

heat cap. of 200g of H_2O →

$$= (840\ J/K)\left[\ln\left(\frac{373}{293}\right)\right]$$

$$\simeq 200\ J/K$$

↳ $1.5 \times 10^{25}\ k$