

Ch 3: The micro-macro connection

Ch 1 was "normal" thermo

Macroscopic views of heat flow, pressure, energy, etc.

temp

Ch 2 took a microscopic look to explain why systems evolve the way they do

Big idea: Every macrostate has some # of microstates associated w/ it (multiplicity)

A system will evolve until it reaches its maximum multiplicity

$$\text{Entropy } S = k \ln \Omega$$

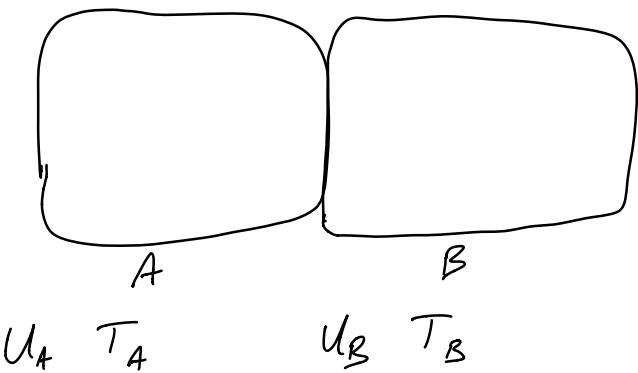
$$\Delta S_{\text{universe}} \geq 0$$

We now wish to connect our microscopic interpretation to our macroscopic observables

- The key is entropy

A macroscopic observable which is directly related to the microscopic multiplicity

Consider 2 blocks which are in contact with one another



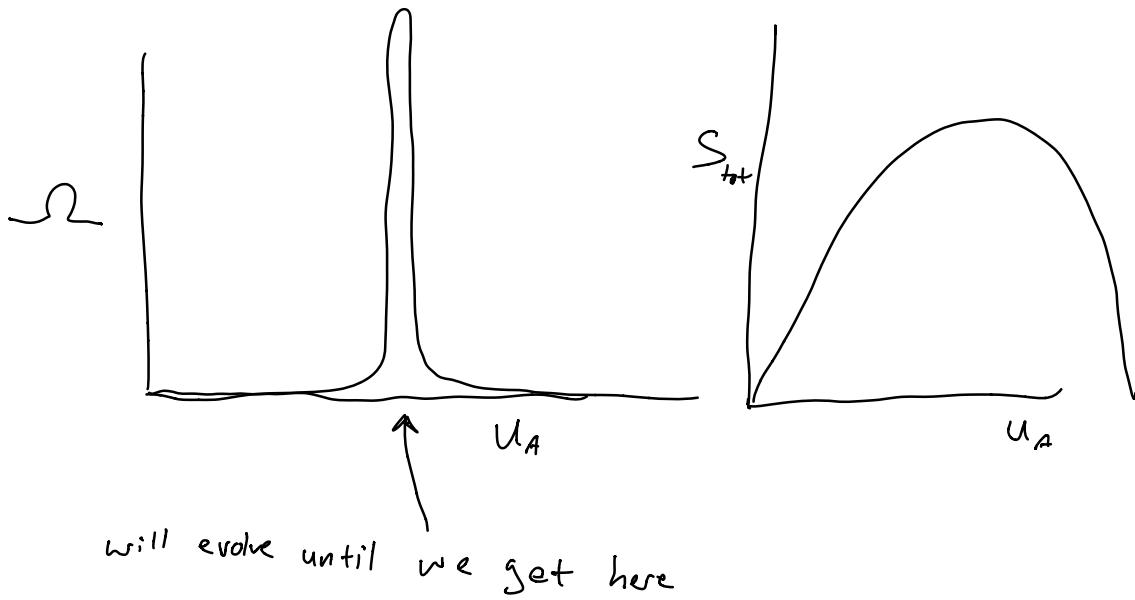
Energy will flow from hot to cold until both blocks are at the same temperature

Thermal equilibrium: No significant movement of energy between blocks

$$\overline{T}_A = \overline{T}_B$$

What is true of the entropy at thermal equilibrium?

- \overline{I}^+ is maximized



$$A + \text{equilibrium} \quad \frac{\partial S_{\text{tot}}}{\partial U_A} = 0$$

$$S_{\text{tot}} = S_A + S_B$$

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

$$U_A = U_{\text{tot}} - U_B$$

$$\partial U_A = 0 - \partial U_B$$

$$\frac{\partial S_B}{\partial U_A} = - \frac{\partial S_B}{\partial U_B} \Rightarrow \quad \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

At equilibrium:

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

AND

$$T_A = T_B$$

There is a relationship between

$$\frac{\partial S}{\partial U} + T$$

Look at ideal gas

mono-atomic

$$S = NK \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m}{3Nk^2} \right)^{3/2} U^{3/2} \right) + \frac{5}{2} \right]$$

$$= NK \ln(CU^{3/2}) + \frac{5}{2} NK$$

$$S = NK \ln C + \frac{3}{2} NK \ln U + \frac{5}{2} NK$$

$$\frac{\partial S}{\partial U} = \frac{3}{2} NK \frac{1}{U}$$

$$U = \frac{3}{2} NkT$$

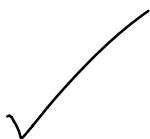
$$\frac{\partial S}{\partial U} = \frac{\frac{3}{2} NK}{\frac{3}{2} NkT} = \frac{1}{T}$$

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

$$[S] = [k_B] = \frac{\text{Energy}}{\text{Temp}}$$

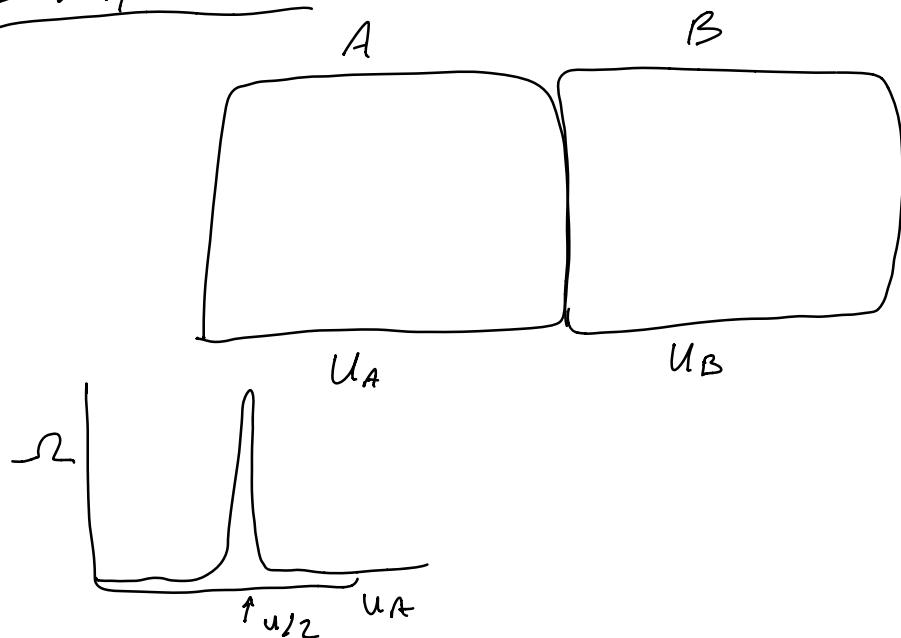
$$[U] = \text{Energy}$$

$$\left[\frac{S}{U} \right] = \frac{1}{\text{Temp}}$$



-This is a "proof by example" but it really is general & holds for all systems

Interpretation



$$\text{Initially: } U_A = 0.25 U$$

$$U_B = 0.75 U$$

$$\text{Later: } U_A = 0.5 U$$

$$U_B = 0.5 U$$

The energy input to A raised its entropy
(σ is greater for higher energy)

How much does the entropy increase? Depends on
the temperature of A

$$\Delta S_A = \frac{\Delta U_A}{T}$$

$$\frac{\Delta S_A}{\Delta U_A} = \frac{1}{T_A}$$

For the same ΔU , ΔS is less at higher temps

(of course, increasing U will also increase T)

So in reality we must consider +infinitesimal
change in energy dU)

As energy increases, so does the number of possible configurations of the system

of microstates gained per unit energy depends on temperature

Adding 50 J to a gas at $T = 0^\circ\text{C}$ will open up

many more configs than

Adding 50 J to a gas
at $T = 300^\circ\text{C}$

This is how we define temperature

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

Ex: Temperature of an Einstein Solid

N oscillators, ϵ energy units

$$\epsilon \gg N, \quad \Omega = \left(\frac{e^\epsilon}{N} \right)^N$$

$$S = K \ln \Omega = K N \ln \left(\frac{e^\epsilon}{N} \right) \\ = NK \left(\ln \frac{\epsilon}{N} + \ln e \right)$$

$$S(\epsilon) = NK \left(\ln \frac{\epsilon}{N} + 1 \right)$$

$$U = \hbar \omega \epsilon$$

$$\epsilon = \frac{U}{\hbar \omega}$$

$$S(U) = NK \left[\ln \left(\frac{U}{N \hbar \omega} \right) + 1 \right]$$

$$S(U) = NK \ln U - NK \ln(N \hbar \omega) + NK$$

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

$$\frac{1}{T} = \frac{\partial}{\partial U} (NK \ln U) = \frac{NK}{U}$$

$$T = \frac{U}{NK} \Rightarrow U = NK T$$

This matches with equipartition

$$U = \frac{1}{2} f N k T$$

N is the # of oscillators

For each oscillator, $f=2$ $(E = \frac{1}{2} \times x^2 + \frac{1}{2} m v^2)$



$$U = N k T$$

This gives us a route to calculate, rather than measure, heat capacity

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

Einstein Solid

$$U = N k T , C_v = N k$$

Find $\Omega(u, v, N)$ QMN , combinatorics



$$S = k \ln \Omega$$



$$\frac{1}{T} = \frac{\partial S}{\partial u}$$



$$u(\tau, v, N)$$



$$C_v = \frac{\partial U}{\partial T}$$

Easier Said than done!

Consider:

If some tiny amount of heat is input into a system,
while no work is done on it

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} \rightarrow \frac{dS}{dU}$$

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

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

$$dS = \frac{dU}{T}$$

$$dU = Q + \cancel{w} = Q$$

$$dS = \frac{Q}{T}$$

The original defn of
entropy
(Rudolf Clausius, 1865)

"How will the entropy of a system change if I
add some heat to it?"

Ex: Heat 200 g of water from 20°C to 100°C
 How much does the entropy increase?

$$\Delta S = \frac{Q}{T}$$

We know $Q = C_v \Delta T$, but what is T ?

We have to find dS for each little step

$$\Delta S = \frac{C_v(T_1 - T_0)}{T_0} + \frac{C_v(T_2 - T_1)}{T_1} + \frac{C_v(T_3 - T_2)}{T_2} + \dots$$

$$Q = C_v dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v dT}{T}$$

C_v can depend on temperature!

For water in this range, it does not

$$C_v = (4.2 \frac{\text{J}}{\text{gK}}) (200 \text{ g}) = 840 \frac{\text{J}}{\text{K}}$$

$$\Delta S = C_v \int_{T_i}^{T_f} \frac{dT}{T} = C_v \ln\left(\frac{T_f}{T_i}\right) = (840) \ln\left(\frac{373}{293}\right)$$

$$\Delta S \approx 203 \frac{\text{J}}{\text{K}}$$

What does this mean?

$$\Delta S \approx 200 = k \ln \frac{S_f}{S_i} - k \ln 1$$

$$200 = k \ln \left(\frac{S_f}{S_i} \right)$$

$$\frac{S_f}{S_i} = e^{\frac{200}{k}} \approx e^{(10^{25})}$$

Total Entropy

$$S - S(0) = \int_0^{T_f} \frac{C_v}{T} dT$$

In theory, $S(0)$ should be 0

At absolute zero, there is no motion

so only one microstate

$$S = k \ln (1) = 0$$

In practice, $S(0)$ is usually a bit greater than 0
 $S(0)$ is a well-defined constant

$\int_0^{T_f} \frac{C_v}{T} dT$ does not diverge
at $T=0$ because

as $T \rightarrow 0$

$C_v \rightarrow 0$

such that $\frac{C_v}{T}$ is finite

$S(0)$ is constant + minimum

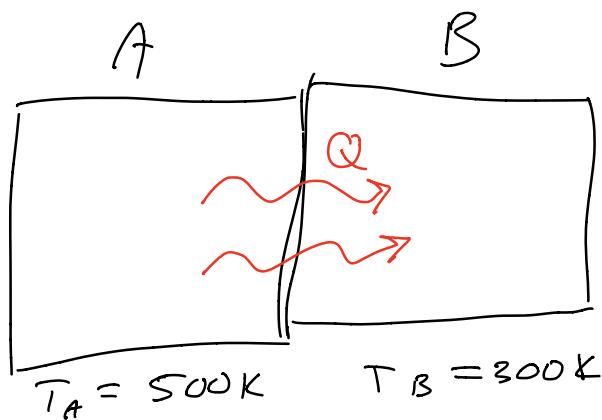
\exists^{def} Law of Thermodynamics

Historical View of entropy

$$dS = \frac{Q}{T}$$

Heat "carries" entropy

Temperature difference determines how much

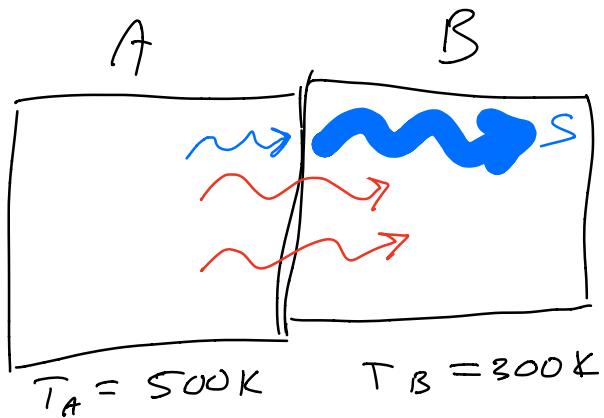


Over some time interval, 1500 J flows from $A \rightarrow B$.
 $A + B$ are very large (C_v is big) so this
doesn't change their temperatures

$$\Delta S_A = \frac{\Delta U_A}{T_A} = \frac{-1500\text{ J}}{500\text{ K}} = -3 \text{ J/K}$$

$$\Delta S_B = \frac{\Delta U_B}{T_B} = \frac{1500\text{ J}}{300\text{ K}} = 5 \text{ J/K}$$

I imagine entropy, much like energy, "flows" from A to B



$$v_i A_i = v_f A_f , \quad A_f < A_i \Rightarrow v_f > v_i$$

$$\Delta S_A T_A = \Delta S_B T_B$$

\uparrow \nearrow
 heat leaving heat entering B
 A

$T_B < T_A$
 $\Delta S_B > \Delta S_A$

Except this isn't true

Entropy does not "flow" like energy
does

A lost some microstates

B gained more than A lost