

Lecture 38

Recall the entropies of the mono-atomic ("point particle") gas and "harmonic" solid :

$$\cancel{S_g} S_g(E) = \frac{3}{2} k_B N_g \log E + S_0$$

$$S_s(E) = 3 k_B N_s \log E + S_0'$$

We have suppressed how these functions depend on volume, since we are interested now in the energy dependence (in effect the volume dependence is absorbed by the constants S_0 & S_0'). When the gas and solid are in

thermal equilibrium at (38.2)
the common temperature T , then
their most probable energies are
determined by

$$\left. \frac{dS_g}{dE} \right|_{E_g} = \frac{1}{T} = \left. \frac{dS_s}{dE} \right|_{E_s}$$

$$\frac{3}{2} k_B \frac{N_g}{E_g} = \frac{1}{T} = 3 k_B \frac{N_s}{E_s}$$

$$\Rightarrow E_g = \frac{3}{2} (k_B T) N_g, \quad E_s = 3 (k_B T) N_s$$

Given a total energy E , we
can determine T from these

$$\text{and } E = E_g + E_s$$

38.3

The energy per atom in the gas ($\frac{3}{2}k_B T$) is different from the energy per atom in the solid ($3k_B T$). We interpret these results as follows:

$$k_B T = \left(\begin{array}{l} \text{microscopic scale of} \\ \text{"thermal energy"} \end{array} \right)$$

$$\frac{1}{2} k_B T = \left(\begin{array}{l} \text{energy associated with} \\ \text{each quadratic term} \\ \text{in the microscopic} \\ \text{energy (e.g. } \frac{p_x^2}{2m}, \frac{k}{2} q_y^2, \dots) \end{array} \right)$$

(38.4)

What we found for

E_g & E_s may be explained by

this:

(most probable energy
of a system in thermal
equilibrium at ~~the~~
temperature T) =

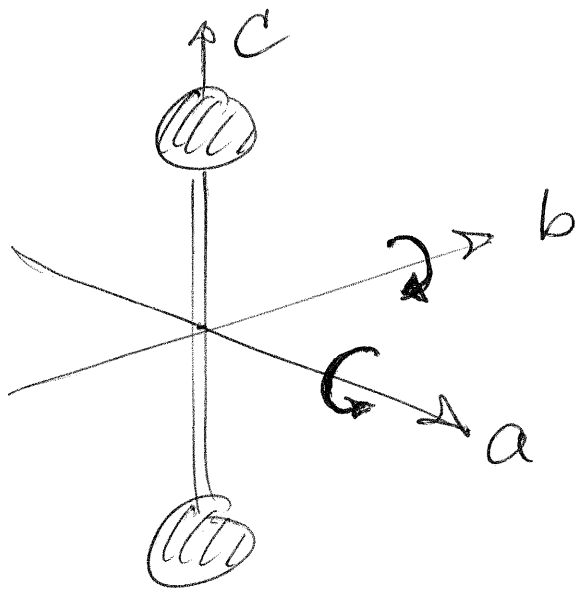
$$\frac{1}{2} k_B T \times (\text{number of quadratic energy terms in system})$$

This rule is called the "equipartition theorem". It applies only to systems whose energy is well modeled by quadratic energy terms.

One of the HW problems dealt with a gas of N diatomic molecules. In such a gas each molecule has 5 quadratic energy terms (all kinetic):

$$E_{mol.} = \frac{P_x^2 + P_y^2 + P_z^2}{2m} + \frac{L_a^2 + L_b^2}{2I}$$

$I =$ (moment of inertia ~~the~~ about either axis perpendicular to molecule axis)

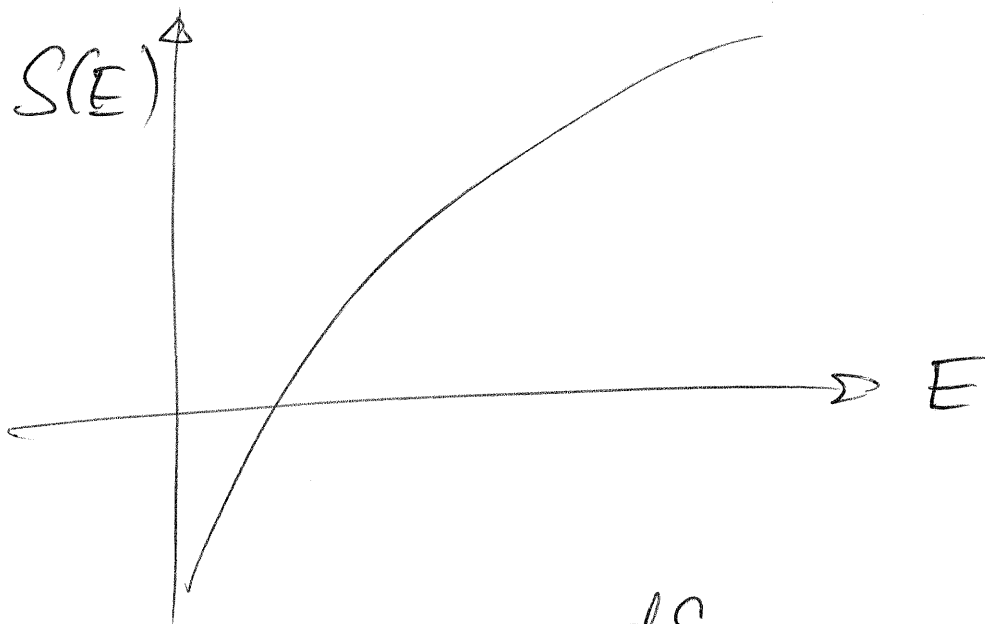


Equipartition Thm:

$$E_g = \frac{5}{2} (k_B T) N$$

In all the systems we 38.6
have looked at so far

$$S(E) = (\text{pos. num.}) k_B N \log E + (\text{const.})$$



Since $1/T = \frac{dS}{dE}$, we draw the following two conclusions from $S(E)$ functions that share the characteristics of monotonically increasing with E but with ever decreasing slope:

(38.7)

- $T > 0$
- T increases with E

This is true for almost all systems and accounts for the familiar rule "heat (energy) flows from hot (high T) to cold (low T)".

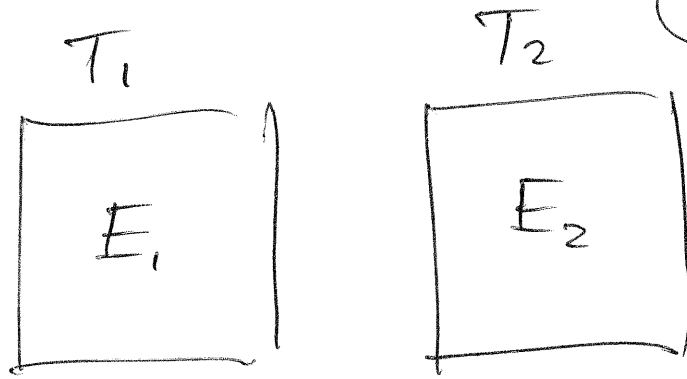
Here's the mathematical basis behind this rule:

Consider two systems, each in thermal equilibrium, but at different temperatures T_1 & T_2 .

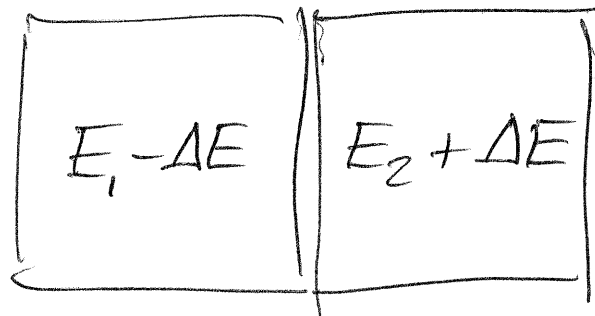
What happens when they are put in thermal contact so they can exchange energy (heat) ΔE ?

(38.8)

before:

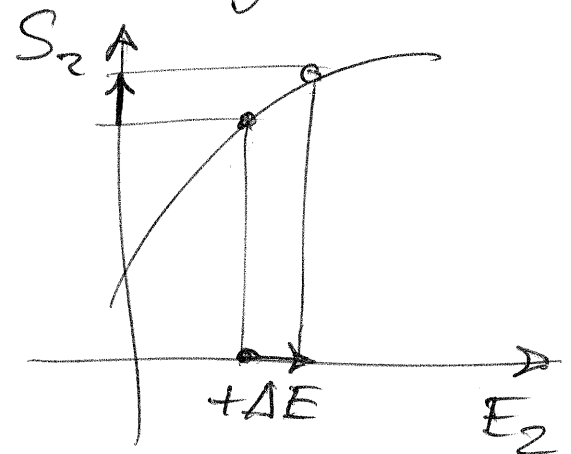
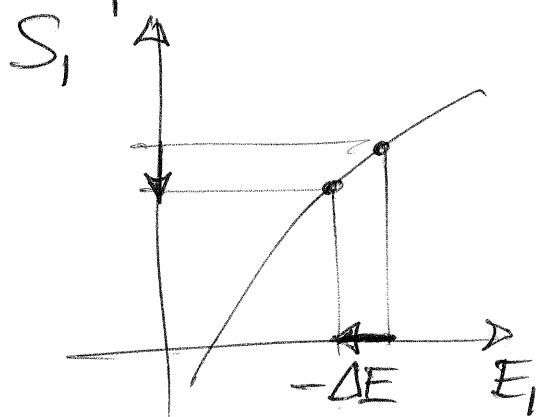


after }
thermal }
contact } :



$\Delta E =$
heat

We'll assume ΔE is sufficiently small, so the slopes of the systems' $S(E)$ curves have not changed significantly (keeping their temperatures unchanged) :



$$\Delta S_1 = \frac{-\Delta E}{T_1}, \quad \Delta S_2 = \frac{\Delta E}{T_2} \quad (38.9)$$

Since $\Omega_c = \Omega_1 \cdot \Omega_2$

is the number of microstates of the compound system,

$$S_c = S_1 + S_2$$

is the entropy ~~of~~.

$$\Delta S_c = \Delta S_1 + \Delta S_2 = \Delta E \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

As we argued several times before, changes with $\Delta S_c > 0$ are much, much, much, ..., more probable — especially when there are many atoms — than changes with

$\Delta S_c < 0$. This is (38.10)
called "The second law of
thermodynamics". So if we
regard $\Delta S_c > 0$ as essentially
guaranteed,

$$\Delta S_c > 0 \Rightarrow \Delta E \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0$$

Now, if $\Delta E > 0$, then $T_2 < T_1$;
else, if $\Delta E < 0$, then $T_1 < T_2$.

But that is just the rule that
heat flows from hot to cold!

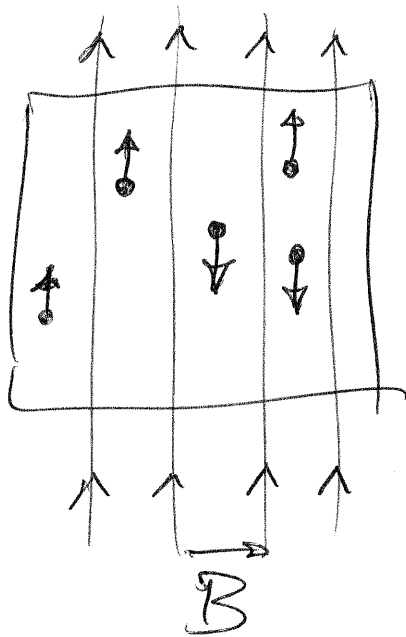
If you examine the math
carefully, you'll notice that the
argument assumed T_1 & T_2 were
positive. But there are physical

(38.11)

systems where the temperature ~~is~~ can be negative and the rule for the flow of heat is different. We'll consider an example of such a system provided by the spin magnetic moments of some particles. Our modeling makes the assumption that these magnetic moments interact only with each other (weakly) and an applied magnetic field (strongly) but no other "degrees of freedom" (particle positions, momenta, etc.). It is only in this idealization that we can model the magnetic moment physics of the system in isolation.

(38.12)

system of N
"spin- $1/2$ " magnetic moments



\uparrow : "spin-up" $\vec{\mu}$

\downarrow : "spin-down" $\vec{\mu}$

(only two states
per particle)

$$E = -\vec{\mu}_1 \cdot \vec{B} - \dots - \vec{\mu}_N \cdot \vec{B}$$

+ (no other terms that
involve $\vec{\mu}$'s)