

Equipartition -

review. - for monatomic gas $\langle E \rangle = \frac{3}{2} kT$

total internal energy
for a mole $U = N_A \langle E \rangle = \frac{3}{2} N_A kT$

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

The heat capacity is $C_V = \left. \frac{\partial U}{\partial T} \right|_V = \frac{3}{2} R$

constant volume \Rightarrow no work $\Rightarrow \Delta U$ all heat related.

Equipartition Theorem: In equilibrium a mean energy of $\frac{1}{2} kT$ per molecule is associated with every degree of freedom.

degree of freedom? \rightarrow each quadratic term in the expression for E of the molecule.

For ideal gas

$$K = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

3 independent quadratic terms $\Rightarrow 3 \left(\frac{1}{2} kT \right)$

Can now —

$$f = C_{\text{rot}} e^{-mv^2/2kT} e^{-I(\omega_1^2 + \omega_2^2)/2kT}$$

demand $\int f d\omega_1 d\omega_2 = 1$

$$C_{\text{rot}} = \sqrt{\frac{I}{2\pi kT}}$$

$$\langle E_{\text{rot}} \rangle = C_{\text{rot}} \int d\omega_1 \int d\omega_2 \frac{1}{2} I (\omega_1^2 + \omega_2^2) e^{-I(\omega_1^2 + \omega_2^2)/2kT}$$

$$\langle E \rangle_{\text{each}} = C \int_{-\infty}^{\infty} d\omega \frac{I\omega^2}{2} e^{-I\omega^2/2kT}$$

$$= \frac{1}{2} kT$$

$$\langle E_{\text{rot}} \rangle = 2 \langle E \rangle_{\text{each}}$$

How about a diatomic molecule?



2 independent rotations.

$$E_{\text{rot}} = \frac{1}{2} (I\omega_1^2 + I\omega_2^2)$$

2 dof $\Rightarrow \langle E_{\text{rot}} \rangle = 2 \left(\frac{1}{2} kT \right)$

So, $\langle E_T \rangle = \langle E_{\text{kin}} \rangle + \langle E_{\text{rot}} \rangle$

$$= \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) + \frac{1}{2} I (\omega_1^2 + \omega_2^2)$$

$$\langle E_T \rangle = 5 \left(\frac{1}{2} kT \right)$$

How about oscillating diatomic molecules?

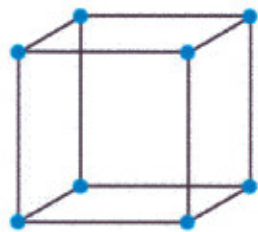


$$E_{\text{vib}} = \frac{p^2}{2\mu} + \frac{1}{2} kx^2$$

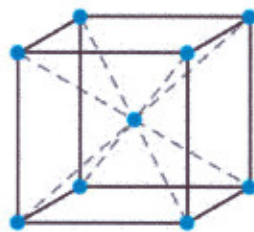
2 more dof.

$$\langle E_{\text{vib}} \rangle = 2 \left(\frac{1}{2} kT \right)$$

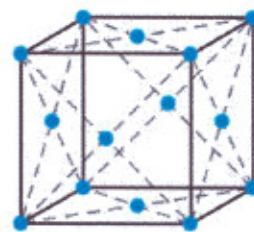
So $\langle E_T \rangle_{\text{diat.}} = (3 + 2 + 2) \left(\frac{1}{2} kT \right) = \frac{7}{2} kT$



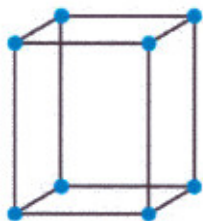
Simple cubic



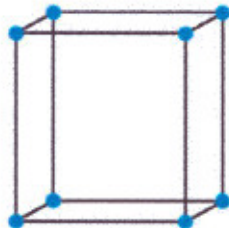
Body-centered cubic



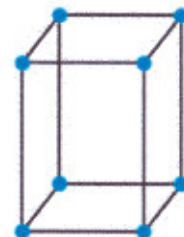
Face-centered cubic



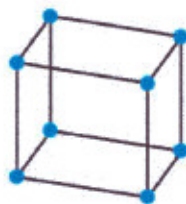
Tetragonal



Orthorhombic



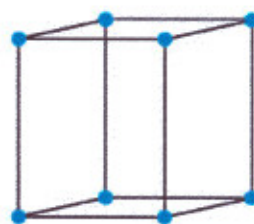
Monoclinic



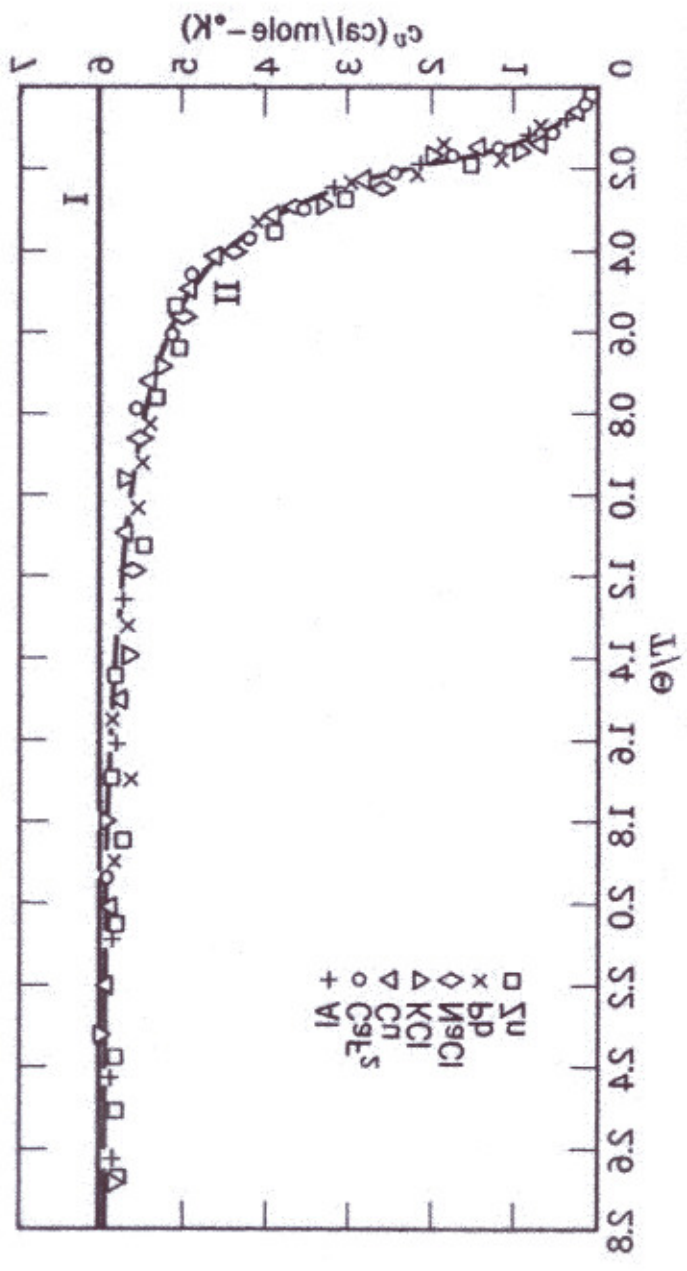
Triclinic



Trigonal



Trigonal and hexagonal



Cu:



face-centered cubic lattice

molecules/atoms are constrained: no rotation, no translation

But, they vibrate, each atom w/ $2 \frac{1}{2} kT = kT$ if $\langle E_{vib} \rangle$
x 3 dimensions.

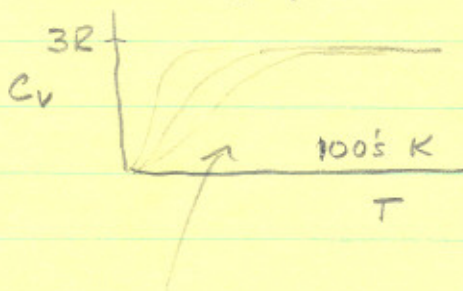
$$\text{w/le } U_{Cu} = N \cdot 3 \cdot 2 \cdot \frac{1}{2} kT = 3kTN_A = 3RT$$

no

$$C_V = 3R$$

Law of Dulong and Petit.

Crystalline substances.



rise dictated by the need to supply enough energy to satisfy the kT 's worth of energy to each lattice site \rightarrow OH SHO.

\rightarrow notice that the lattice contributions solve the problem... what about the electrons?

Classical Distributions have the following properties

1. Particles are identical in terms of physical properties, but distinguishable in terms of position. \rightarrow energies identical
2. The equilibrium distribution is the most probable way subject to constraints on # particles and total E .
3. There is no limit on the fraction of the total number of particles in a given energy state.

example

Atomic hydrogen's energy levels are

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

and the degeneracy is $g_n = n^2$

ground state:	$E_1 = -13.6 \text{ eV}$	$g_1 = 1$
	$E_2 = -3.40 \text{ eV}$	$g_2 = 4$
	$E_3 = -1.51 \text{ eV}$	$g_3 = 9$

want $\frac{n_2}{n_1}$ and $\frac{n_3}{n_1}$

$$\begin{aligned}\frac{n_2}{n_1} &= \frac{g_2 A e^{-E_2/kT}}{g_1 A e^{-E_1/kT}} = \frac{g_2}{g_1} e^{(E_1 - E_2)/kT} \\ &= \frac{4}{1} e^{-10.2 / (8.617 \times 10^{-5} \text{ eV K})(300 \text{ K})} = 4 e^{-395}\end{aligned}$$

\Rightarrow atomic hydrogen is overwhelmingly in the ground state

Example 2

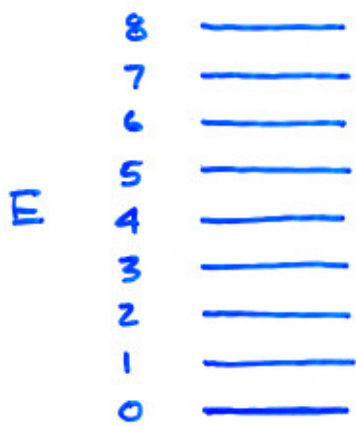
STP \rightarrow 1 mole H_2 gas occupies $22.4 \times 10^{-3} m^3$
and contains 6.023×10^{23} molecules.

$$m_{H_2} = 3.34 \times 10^{-27} \text{ kg.}$$

$$\left(\frac{N}{V}\right) \frac{h^3}{(3mkT)^{3/2}} = \left(\frac{6.023 \times 10^{23}}{22.4 \times 10^{-3} m^3}\right) \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^3}{(3)(3.34 \times 10^{-27} \text{ kg})(1.4 \times 10^{-23})(300)}$$
$$= 3.37 \times 10^{-5} \quad \text{which is } \ll 1$$

So can use MB statistics for H_2 gas at STP

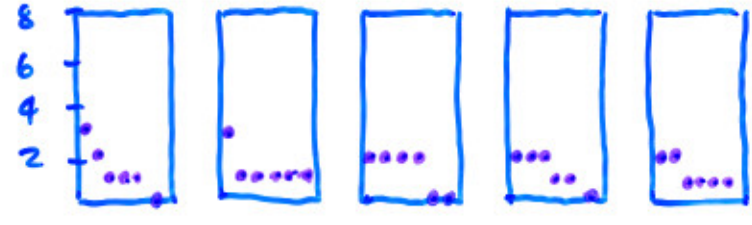
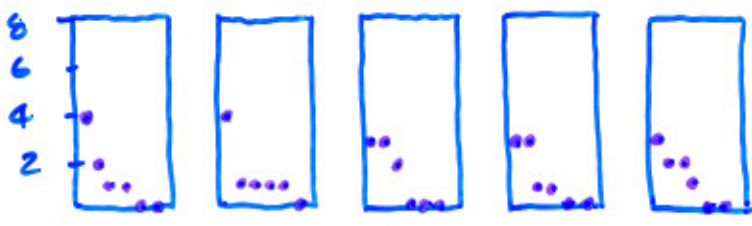
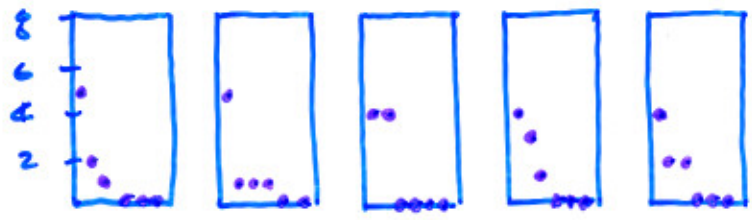
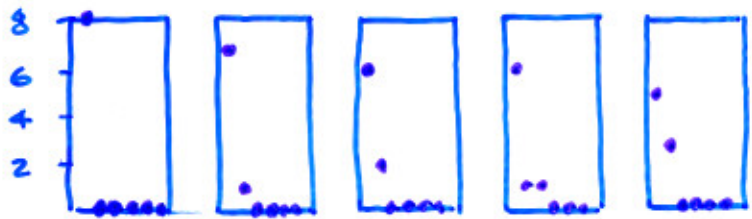
6 particles & 8 states of energy



.....
↙ to be distributed so that

$$E_T = 8 \quad \& \quad N = 6$$

There are 20 ways to do this.



EACH OF THESE
ARE
"MACROSTATES"

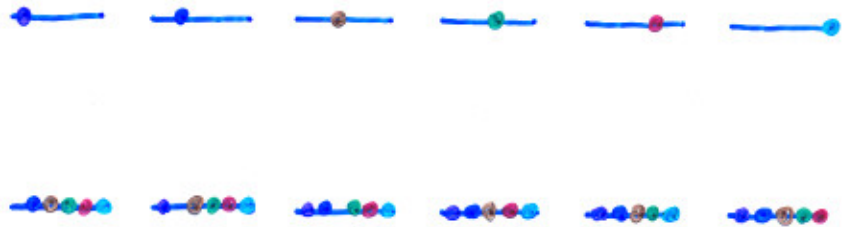
WITHIN EACH MACROSTATE

If you can label each particle

there are a number of MICROSTATES



can be realized as



- 6 different microstates correspond to the

(5 0 0 0 0 0 0 0 1) macrostate

coloring them is a classical idea.

We can calculate them for each macrostate.

For the (50000001) macrostate, once you raise one to the $E = \epsilon$ level... you could rearrange the remaining 5 in the $E = 0$ state - don't want to double-count particular energy states, so divide them out

$$\# \text{ microstates in } (50000001) = \frac{6!}{5!} = 6$$

Fundamental Assumption of Statistical Mechanics -

ALL MICROSTATES ARE EQUALLY LIKELY.

Mac.

MB. (E)

1	5	0	0	0	0	0	0	0	1	6
2	4	1	0	0	0	0	0	1	0	30
3	4	0	1	0	0	0	1	0	0	30
4	4	0	0	1	0	1	0	0	0	30
5	4	0	0	0	2	0	0	0	0	15
6	3	2	0	0	0	0	1	0	0	60
7	3	0	2	0	1	0	0	0	0	60
8	3	0	1	2	0	0	0	0	0	60
9	3	1	1	0	0	1	0	0	0	120
10	3	1	0	1	1	0	0	0	0	120
11	2	0	4	0	0	0	0	0	0	15
12	2	2	0	2	0	0	0	0	0	90
13	2	1	2	1	0	0	0	0	0	180
14	2	2	1	0	1	0	0	0	0	60
15	2	3	0	0	0	1	0	0	0	30
16	1	4	0	0	1	0	0	0	0	120
17	1	3	1	1	0	0	0	0	0	60
18	1	2	3	0	0	0	0	0	0	60
19	0	4	2	0	0	0	0	0	0	15
20	0	5	0	1	0	0	0	0	0	6

2, 31, 1, 57, 14, 59, 33, 16, 07, 02, 005

1287

$n_{MB}(E)$

The fundamental problem: the likelihood to be in a particular energy state. ... out of 1287, how many are in each E_i ?

Take $E=0$. - how many microstates contribute to $E=0$?

all but MAC_{19} and MAC_{20} .

Take MAC_1 .

The likelihood to be in MAC_1 is $\frac{6}{1287}$

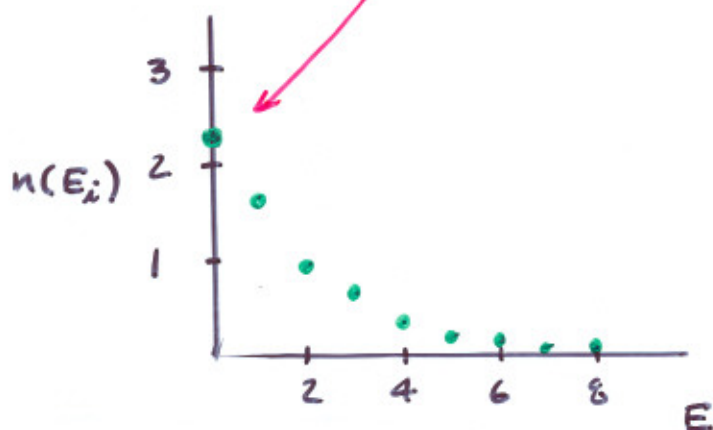
The number of $E=0$ states in MAC_1 is 5

$$P_1(E=0) = 5 \left(\frac{6}{1287} \right) = 0.023$$

$$P_2(E=0) = 4 \left(\frac{30}{1287} \right) = 0.093$$

⋮

TOTAL = 2.31 will be found to have $E=0$.



an exponential...

Let $p_j \rightarrow$ probability to be in j^{th} MAC

$n_j(E_i) \rightarrow$ # in MAC_j with E_i

$$n(E_i) = \sum_{\substack{\text{MAC} \\ j}} n_j(E_i) p_j$$

$= g_i f(E_i)$ which is what Boltzmann found:

$$n(E_i) = g_i F_{\text{MB}}$$

$$F_{\text{MB}} = A e^{-E_i/kT}$$

$g_i =$ the "degeneracy" or

"statistical weight"

of i^{th} state

If the energy levels are close together...

$$g_i \rightarrow g(E) dE$$

$$F_{MB} \rightarrow A e^{-E/kT} = F_{MB}(E)$$

$g(E)$ is density of states.
per unit volume per
energy interval dE .

$$n(E_i) = g_i F_{MB} \rightarrow n(E) dE = g(E) F_{MB}(E) dE$$

$$\begin{aligned} \sum n(E_i) = N &\rightarrow \frac{N}{V} = \int_0^{\infty} n(E) dE = \int_0^{\infty} g(E) F_{MB}(E) dE \\ &= \int_0^{\infty} g(E) A e^{-E/kT} dE \end{aligned}$$

For the gas example

$$n(E) dE = 2\pi \frac{1}{(\pi h T)^{3/2}} E^{1/2} e^{-E/kT} dE$$

$$\begin{aligned} g(E)_{MB} &\sim E^{1/2} \\ &= \frac{2\sqrt{2}}{m^{3/2}} E^{1/2} \end{aligned}$$

So, the probability of obtaining an energy E in a classical system is

$$P(E_i) = \frac{n(E_i)}{n} = \frac{g(E_i) e^{-E_i/kT}}{\sum_i g(E_i) e^{-E_i/kT}}$$

Example 1 Find the populations of the first and second excited states for atomic hydrogen in a stellar atmosphere of $T = 300\text{K}$. Calculate relative to the ground state. Ignore spin.

Example 2 Are M.B. statistics valid for hydrogen gas at STP?