Equipartition:

For a monatomic gas \( \langle E \rangle = \frac{3}{2} kT \)

Total internal energy:

\[ U = N k \langle E \rangle = \frac{3}{2} N k T \]

For a molecule:

\[ U = \frac{3}{2} R T \]

The heat capacity is:

\[ C_v = \left. \frac{\partial U}{\partial T} \right|_V = \frac{3}{2} R \]

Constant volume \( \Rightarrow \) no work \( \Rightarrow \) all 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 \( E \).

For ideal gas:

\[ K = \frac{1}{2} m V^2 = \frac{1}{2} m (x_x^2 + y_y^2 + z_z^2) \]

3 independent quadratic terms \( \Rightarrow \) 3 \( \frac{1}{2} kT \)
\[ C_{\text{vis}} = -\frac{m v^2}{2\hbar^2} - \frac{I(u_1^2 + u_2^2)}{2\hbar^2} + C_{\text{rot}} e^{-\frac{I(u_1^2 + u_2^2)}{2\hbar^2}} e \]

\[ \text{determinant} \int f \, du_1 \, du_2 = 1 \]

\[ C_{\text{rot}} = \sqrt{\frac{I}{2\hbar^2}} \]

\[ \langle E_{\text{rot}} \rangle = C_{\text{rot}} \int du_1 \int du_2 \frac{1}{2} I (u_1^2 + u_2^2) e^{-\frac{I(u_1^2 + u_2^2)}{2\hbar^2}} \]

\[ \langle E \rangle_{\text{total}} = C \int du \frac{I u^2}{2} e^{-\frac{I u^2}{2\hbar^2}} \]

\[ = \frac{1}{2} \hbar \Omega \]

\[ \langle E_{\text{rot}} \rangle = 2 \langle E \rangle_{\text{total}} \]
How about a diatomic molecule?

\[ E_{\text{rot}} = \frac{1}{2} \left( I \omega_1^2 + I \omega_2^2 \right) \]

2 dof \[ \Rightarrow \langle E_{\text{rot}} \rangle = 2 \left( \frac{1}{2} \hbar \omega \right) \]

So,

\[ \langle E_T \rangle = \langle E_{\text{kin}} \rangle + \langle E_{\text{rot}} \rangle \]

\[ = \frac{1}{2} m \left( u_x^2 + u_y^2 + u_z^2 \right) + \frac{1}{2} I \left( \omega_1^2 + \omega_2^2 \right) \]

\[ \langle E_T \rangle = 5 \left( \frac{1}{2} \hbar \omega \right) \]

How about oscillating diatomic molecules?

\[ E_{\text{osc}} = \frac{p^2}{2m} + \frac{1}{2} \hbar x^2 \]

2 more dof

\[ \langle E_{\text{osc}} \rangle = 2 \left( \frac{1}{2} \hbar \omega \right) \]

So,

\[ \langle E_T \rangle_{\text{total}} = (3 + 2 + 2) \left( \frac{1}{2} \hbar \omega \right) = \frac{7}{2} \hbar \omega \]
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/ \( \frac{1}{2} \hbar \dot{T} = kT \) \( v \times 3 \text{ dimensions} \)

\[ U = N \frac{3}{2} kT = 3kT N_A = 3RT \]

\[ \sum n = 3R \]  \[ \text{Law of Dulong and Petit} \]

Crystalline substances.

\[ T \]

\[ \frac{3R}{C_v} \]

Vice dictated by the need to supply enough energy to satisfy Tweedie's work of energy to each lattice site = 0.145 kJ.

Notice that the lattice contributes 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. => 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

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

and the degeneracy is \( g_n = n^2 \)

**Ground state:**

\[ E_1 = -13.6 \text{ eV} \]
\[ E_2 = -3.40 \text{ eV} \]
\[ E_3 = -1.51 \text{ eV} \]

Want \( \frac{n_2}{n_1} \) and \( \frac{n_3}{n_1} \)

\[
\frac{n_2}{n_1} = \frac{g_2}{g_1} \frac{e^{\frac{E_2}{kT}}}{e^{\frac{E_1}{kT}}} = \frac{g_2}{g_1} e^{\frac{(E_1 - E_2)}{kT}}
\]

\[
= 4 \left( \frac{4}{1} e \right) ^{\frac{-10.2}{(8.617 \times 10^{-5} \text{ eV K})(300 \text{ K})}} = 4 e^{-3.95}
\]

\( \Rightarrow \) Atomic hydrogen is overwhelmingly in the ground state
Example 2

STP \rightarrow 1 \text{ mole } H_2 \text{ gas occupies } 22.4 \times 10^{-3} \text{ m}^3

and contains \( 6.023 \times 10^{23} \) molecules.

\[ m_{H_2} = 3.34 \times 10^{-27} \text{ kg} \]

\[ \frac{N}{V} \left( \frac{h}{3 m k T} \right)^3 = \left( \frac{6.023 \times 10^{23}}{22.4 \times 10^{-3} \text{ m}^3} \right) \left( \frac{6.626 \times 10^{-34} \text{ J s}}{3 \times 3.34 \times 10^{-27} \text{ kg}} \right)^3 (300) \]

\[ = 3.37 \times 10^{-5} \text{ which is } \ll 1 \]

so we can use MB statistics for H_2 gas at STP.
6 particles of \( E \) states of energy

\[
\begin{array}{cccccc}
8 & \_ & \_ & \_ & \_ & \\
7 & \_ & \_ & \_ & \_ & \\
6 & \_ & \_ & \_ & \_ & \\
5 & \_ & \_ & \_ & \_ & \\
4 & \_ & \_ & \_ & \_ & \\
3 & \_ & \_ & \_ & \_ & \\
2 & \_ & \_ & \_ & \_ & \\
1 & \_ & \_ & \_ & \_ & \\
0 & \_ & \_ & \_ & \_ & \\
\end{array}
\]

\[E_r = 8 \quad \& \quad N = 6\]

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

(5000000001) macrostate
coloring them is a classical idea.
We can calculate them for each macrostate.

For the \((5000000001)\) macrostate, once you raise one to the \(E=8\) level— you could recalculate the remaining 5 in the \(E=0\) state— don't want to double-count particular energy states, so divide them out

\[
\text{# microstates in } \frac{6!}{5!} = 6
\]

**Fundamental Assumption of Statistical Mechanics**—

ALL MICROSTATES ARE EQUALLY LIKELY.
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$N_{MB} (\text{B}) = 2.3 \times 10^{-5}, 14.79 \times 10^{-4}, 23.16 \times 10^{-3}, 0.02, 0.005 \frac{\text{g}}{\text{cm}^2} \xi d_{MB} = 12.87$
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

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

$P_2(E=0) = 4 \left( \frac{90}{1287} \right) = 0.093$

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

$\mu(E_i)$

$E$

an exponential...
Let $p_j$ be the probability to be in the j-th MAC

$n_j(E_i) \rightarrow *$ in MAC with $E_i$

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

$$= g_i f(E_i) \text{ which is what Boltzmann found:}$$

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

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

$g_i$ = the “degeneracy” or “statistical weight” of i-th state.
If the energy levels are close together...

\[ g_i \rightarrow g(E) \, dE \]

\[ F_{MB} \rightarrow A \, e^{-E/kt} = F_{MB}(E) \]

\[ g(E) \text{ is density of states, per unit volume per energy interval } dE. \]

\[ n(E) = \int_{0}^{E} n(E) \, dE = g(E) \int_{0}^{E} e^{-E/kt} \, dE \]

\[ \sum n(E) = N \rightarrow \frac{N}{V} = \int_{0}^{\infty} n(E) \, dE = \int_{0}^{\infty} g(E) \int_{0}^{E} e^{-E/kt} \, dE \]

\[ = \int_{0}^{\infty} g(E) A \, e^{-E/kt} \, dE \]

For the gas example...

\[ n(E) \, dE = \frac{2\pi \frac{1}{2} E^3/2}{(\pi k T)^{3/2}} \, e^{-E/kt} \, dE \]

\[ g_{MB} = E^{3/2} \]

\[ = \frac{2 \sqrt{\pi} E^{3/2}}{m^{3/2}} \]
So, the probability of obtaining an energy $E$ in a classical system is

$$P(E) = \frac{n(E)}{n} = \frac{g(E) e^{-\frac{E}{kT}}}{\sum_i g(E_i) e^{-\frac{E_i}{kT}}}$$
Example 1
Find the populations of the first and second excited states for atomic hydrogen in a stellar atmosphere of $T = 300K$. Calculate relative to the ground state. Ignore spin.

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