Ideal gas of monoatomic particles

- only translational motion, no rotational or vibrational degrees of freedom

motion of the center of mass.

At low densities, high temperatures, or particles with large mass, classical statistics applies: \( Q(N,V,T) = q(v,T)^N/N! \rightarrow \text{interactions} \)

where \( q(v,T) \) is single-particle partition function.

Note: this itself may be summed over quantum states or classical states.

For monoatomic particles: \( q(v,T) = q_{\text{trans}}, q_{\text{rot}}, q_{\text{vib}} \).

These degrees of freedom are independent of each other.

\( q_{\text{trans}}, \text{ translational partition function:} \)

Particle in a box of side \( L \).

Allowed energies are given as:

\[ \varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{8mL^2} (nx^2 + ny^2 + nz^2) \]

\[ n_x, n_y, n_z = 1, 2, \ldots \]

\[ q_{\text{trans}} = \frac{\infty}{n_x, n_y, n_z = 1} e^{-\beta \varepsilon_{n_x, n_y, n_z}} \]

\[ q_{\text{trans}} = \left( \frac{\infty}{n_x = 1} e^{-\beta \varepsilon_{n_x, n_y, n_z}} \right) \left( \frac{\infty}{n_y = 1} e^{-\beta \varepsilon_{n_x, n_y, n_z}} \right) \left( \frac{\infty}{n_z = 1} e^{-\beta \varepsilon_{n_x, n_y, n_z}} \right) \]

\[ q_{\text{trans}} = \left( \sum_{n_x = 1}^{\infty} \exp \left( -\beta n_x^2 \frac{\hbar^2}{8mL^2} \right) \right)^3 \]

Three degrees of freedom are independent.

The three directions are identical.
\[ q_{\text{trans}} (V,T) = \left( \int_0^\infty e^{-\frac{\hbar v^2}{2m}} \, dv \right)^3 \]

Thus the discrete sum is replaced by a continuous distribution of energies. At room temperatures, typical value of \(\hbar N / 2\) is \(O(10^3)\), so \(\hbar\) is so small.

Set \( x = \hbar \sqrt{8 k T M} \).

\[ q_{\text{trans}} = \left( \int_0^\infty e^{-x^2} \, dx \cdot \frac{\sqrt{8 k T M}}{\hbar} \right)^3 \]

\[ q_{\text{trans}} = \left( \frac{8 k T M}{\hbar^2} \right)^{3/2} \cdot \sqrt{\frac{\sqrt{8 k T M}}{\hbar}} \]

\[ q_{\text{trans}} = \left( \frac{8 k T M}{\hbar^2} \right)^{3/2} \sqrt{\frac{1}{2^3}} \]

\[ q_{\text{trans}} = \left( \frac{8 k T M}{\hbar^2} \right)^{3/2} \frac{1}{2^3} \]

\[ q_{\text{trans}} = \left( \frac{2 mk T \hbar}{\hbar^2} \right)^{3/2} \] \( \sqrt{\frac{\hbar^2}{2m k T \hbar}} \)

\[ q_{\text{trans}} = \frac{V}{\lambda^3} \]

When \(\lambda^3 < \sqrt{V}\), the energy levels can be assumed to have a continuous distribution, and \(q_{\text{trans}}\) is evaluated in the classical limit.

The matter wave extends much smaller than the size of the box. In the permitted energy levels, can be treated as a classical continuum.
Energy of translation for a particle is given by

$$E_{\text{trans}} = \frac{m \cdot v_{\text{avg}}}{c^2}$$

$$E_{\text{trans}} = kT \left( \frac{m \cdot v_{\text{avg}}}{c^2} \right)$$

$$E_{\text{trans}} = kT \left( \frac{3}{2} \right) = \frac{3kT}{2}$$

For each one of the degrees of freedom, $q_{\text{trans}} \approx \frac{1}{2}$

$$e_{\text{trans}} = \frac{1}{2} kT$$

Thus, average energy is $\frac{1}{2} kT$ per degree of freedom. We'll soon see that this is quite a general result (known as the theorem of equipartition of energy).

Electronic and Nuclear partition function:

$$q_{\text{elec}} = \sum \left[ \frac{1}{e^{\varepsilon_i/kT} + 1} \right]$$

Here $\varepsilon_i$ is degeneracy and $\varepsilon_i$ is energy of $i^{th}$ state.

By setting $kT$ arbitrarily to 0, we express $q_{\text{elec}}$ in terms of ground state.

Energy levels of electronic levels w.r.t. ground level.

$$q_{\text{elec}} = a_{q_1} + a_{q_2} e^{-\frac{\beta \varepsilon_{q2}}{kT}} + \ldots$$

$\Delta \varepsilon_{q_i}$ is energy level of $i^{th}$ level w.r.t. ground level.

Typical $\beta \varepsilon$ is O(few eVs) for $\varepsilon_i$ at room temperature. Thus, in most cases, only first term counts.

For some atoms (halogens), a few terms count.

(Note the degeneracies of the electronic levels do not increase exponentially as a function of energy.)
Nuclear partition function has some form of electronic partition function. However, nuclear energies are of the order of MeVs so nuclei are excited only at temperatures of $O(10^{10}$ K). So at thermal temperatures, nuclei can be assumed to be in their ground state, which is assumed to have zero energy.

Only first term counts. The nuclear partition function $q = w_n$ introduces a simple multiplicative factor to $q$ and a simple additive factor to entropy and free energies. This is usually neglected/omitted even though it is not 1.

$$q_{\text{trans}} = \left( \frac{g_{\text{elec}} N \text{trans} N \text{trans}}{V} \right)^N / N!$$

$$V = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$q_{\text{elec}} = w_1 + w_2 e^{-\beta \Delta E_{12}} + ...$$

$$\Delta E_{12} = -kT \ln g_{\text{elec}} = -kT \ln \left( \frac{g_{\text{elec}}}{N} \right)^N = -N kT \ln \left( \frac{g_{\text{elec}}}{N} \right)$$

$$= -N kT \left( \ln \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V e + \ln \left( w_1 + w_2 e^{-\beta \Delta E_{12}} \right) \right)$$

$$E = kT \frac{d \ln q}{dT} = N kT^2 \frac{3}{2} \frac{T}{2} + \frac{N kT^2 w_{12} e^{-\beta \Delta E_{12}}}{kT}$$

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

$$\phi = kT \frac{\Delta \ln q}{\Delta V} = kTN \frac{1}{V} + 0 \text{ since } q_{\text{elec}} \text{ must depend on container volume only on volume of atom.}$$
\[ \bar{p}V = NkT \quad \cdots \quad \text{ideal gas law relationship between } p, V, T. \]

Note only contribution to pressure from translational degrees of freedom. Electronic and nuclear degrees of freedom do not contribute.

This is intuitive since pressure results from bombardment of walls by atoms of the gas.

Entropy:
\[ S = \frac{3}{2} \frac{NkT}{2} + Nk \ln \left( \frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} \frac{V}{N} \]

\[ S = 3Nk + Nk \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} \frac{V}{N} \right] \]

Chemical potential:
\[ \mu = \frac{-\partial \Omega}{\partial N} = -kT \ln \left( \frac{N!}{\sqrt{2\pi N}} \right) \]
\[ = -kT \left[ \ln(Ne/N)^N - N \ln(Ne/N) \right] \]
\[ = -kT \left( \ln(e/N) + N(1/e) \right) \]
\[ = -kT \ln \left( \frac{N!}{\sqrt{2\pi N} e^N} \right) \]

For single particles, unaffected by \( N \), since no interactions in ideal gas system.
\[ \mu = -kT \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kT}{p} \right] - kT \ln q_{eqn} \]

\[ \mu = -kT \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kT}{p} \right] - kT \ln q_{eqn} + kT \ln p \]

\[ \mu = \mu_0 + kT \ln p \quad \mu = f(T, p) \]

\( \mu_0 \) is the chemical potential at a pressure of 1 atm (standard condition) for an ideal gas.

For \( v_0 \), \( \mu = \mu_0 + kT \ln (c_0) \) where \( c = \frac{N}{V} \Rightarrow \text{concentration of molecules} \).

Using partition functions to evaluate equilibrium constants:

\[ \text{Consider the reaction:} \quad v_A + v_B \rightleftharpoons v_C + v_D \]

we have determined in the past that equilibrium is described by

\[ \sum_{\text{products}} 2^j \mu_j = \sum_{\text{reactants}} 2^j \mu_j \]

i.e., \( \sum_{i} \nu_i \mu_i + \sum_{j} \nu_j \mu_j = 0 \)

As concentration increases, the chemical potential increases.

The partition function for the equilibrium mixture is given as:

\[ \Omega (\text{Na}, \text{Nb}, \text{Nc}, \text{Nd}, v_T) = \frac{v_T!}{v_A! v_B! v_C! v_D!} \]

\[ \Omega \text{ is the total number of ways to arrange the molecules.} \]

\[ \mu_A = -kT \frac{\partial \ln \Omega}{\partial N_A} \]

\[ \mu_A = -kT \ln q_{A} \frac{\partial \ln \Omega}{\partial N_A} \]

\[ \mu_0 \text{, } \mu_c \text{, } \mu_d \text{ are constant when chemical potential is evaluated.} \]

\[ \mu_A = -kT \ln q_{A} \]

\[ \frac{N_A}{N} \]

Equilibrium is given as:
\[-kT \ln \left( \frac{(q_c)^{\nu_c} (q_d)^{\nu_d}}{(N_c)^{\nu_c} (N_d)^{\nu_d}} \right) - \ln \left( \frac{(q_A)^{\nu_A} (q_B)^{\nu_B}}{(N_A)^{\nu_A} (N_B)^{\nu_B}} \right) = 0 \]

\[\Rightarrow \frac{(N_c)^{\nu_c} (N_d)^{\nu_d}}{(N_A)^{\nu_A} (N_B)^{\nu_B}} = \frac{(q_c)^{\nu_c} (q_d)^{\nu_d}}{(q_A)^{\nu_A} (q_B)^{\nu_B}}\]

\[\Rightarrow \frac{(N_c/V)^{\nu_c} (N_d/V)^{\nu_d}}{(N_A/V)^{\nu_A} (N_B/V)^{\nu_B}} = \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}}\]

Exponentially measurable. Known as an equilibrium constant \(K_c\) which has form \(f(T,V)\).

\(N/V\) represents a concentration.
\(\gamma\) represent stoichiometric coefficients.

Sometimes for gaseous reactions, equilibrium constants are expressed in terms of pressures.

\[K_p(T) = \frac{P_c^{\nu_c} P_d^{\nu_d}}{P_a^{\nu_a} P_b^{\nu_b}} = KT^{\nu_c+\nu_d-\nu_a-\nu_b} (N_c/V)^{\nu_c} (N_d/V)^{\nu_d} (N_A/V)^{\nu_A} (N_B/V)^{\nu_B}\]

\[K_p(T) = KT^{\nu_c+\nu_d-\nu_a-\nu_b} K_c(T)\]

Simply the difference in reactant & product nумesa.
"Law of equipartition of energy.

The energy of a molecule for a given degree of freedom is given as a quadratic function, e.g. of velocity \((\frac{1}{2}mv^2)\) or of displacement \((\frac{1}{2}kx^2)\) potential energy kinetic energy

So the average energy per molecule for each degree of freedom:

\[\bar{\varepsilon} = \int_{x=0}^{x} e^x e^{-\beta x^2} \, dx\]

where \(e = ax^2\) a constant velocity or displacement

\[= \int_{x=0}^{x} e^{x} e^{-\beta x^2} \, dx\]

\[= \left[ \frac{e^{x} e^{-\beta x^2}}{-2 \beta} \right]_{x=0}^{x} \]

\[= kT \int_{\frac{1}{\sqrt{\pi}}}^{\sqrt{\pi}} y^2 e^{-y^2} dy/\sqrt{\pi} \]

Substitute \(y^2 = \beta x^2\)

\[\bar{\varepsilon} = kT \int_{\frac{1}{\sqrt{\pi}}}^{\sqrt{\pi}} y^2 e^{-y^2} dy/\sqrt{\pi} \]

\[= kT \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{\pi}}/2 = kT \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{\pi}}/2 = kT \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{\pi}}/2 \]

\[= kT/2\]

So each degree of freedom (represented by a quadratic term in the Hamiltonian) contributes \(kT/2\) per molecule to the total energy.

When no forces constrain motion \(\text{purely linear} \Rightarrow \frac{kT}{2}\) contribution

E.g. each translation degree of freedom contributes \(kT\) per molecule vibration \(\text{kinetic + potential energy} \Rightarrow kT\) per molecule.
The energies can be said to be almost continuously distributed:

$$\frac{E_{n+1} - E_n}{E_n} << 1$$

$$\Rightarrow \frac{(n+1)^2 - n^2}{n^2} << 1 \Rightarrow \frac{2n+1}{n^2} << 1$$

$$\Rightarrow \frac{2n}{n^2} << 1 \Rightarrow \frac{2}{n} << 1$$

Now $$\frac{E_n}{h} = \frac{n^2 h^2}{8ML^2} \Rightarrow n = \frac{\sqrt{8mE}}{L}$$

At temperature $T$, average value of $E_n$ is $\frac{1}{2} kT$,

$$\Rightarrow \frac{\text{typical } E_n}{h} = \sqrt{\frac{8nkT}{h}}$$

$$\Rightarrow \frac{2}{h} << 1 \Rightarrow \frac{2h}{\sqrt{8nkT}} < 1$$

$$\Rightarrow \frac{h}{\sqrt{2nkT}} << 1$$

$$\Rightarrow \left(\frac{h}{\sqrt{2nkT}}\right)^3 << L^3$$

$$\Rightarrow \lambda^3 << L$$

LHS term is de-Broglie wavelength, barring for a small factor of $1/\sqrt{\pi}$

when the particle (matter wave) "rarely sees" the boundaries of the container, the energies can be treated classically, as having a continuous distribution.