Kinetic Theory of Ideal Gas

Pressure = average force per unit area

\[ P = \langle \frac{\Delta (mv_f)}{\text{area}} \cdot \text{rate} \rangle \text{ average over all molecules and time} \]

\[ \Delta (mv_f) = 2mv_1 \text{ elastic collision} \]

\[ \frac{1}{2} \frac{N}{V} v_1 = \text{rate/area} \]

\[ \frac{1}{2} \text{ towards wall} \quad \frac{N}{V} = \text{uniform density} \]

\[ P = 2m \left( \frac{1}{2} \frac{N}{V} \right) \langle v_1^2 \rangle \]

For isotropic gas \( \langle v_1^2 \rangle = \frac{1}{3} \langle v^2 \rangle \)

\[ P = \frac{1}{3} m \left( \frac{N}{V} \right) \langle v^2 \rangle \]

\[ = \frac{2}{3} \frac{N}{V} \langle \frac{1}{2} mv^2 \rangle \]

\[ = \frac{2}{3} \frac{N}{V} \langle E_{\text{kinetic}} \rangle \]

\[ PV = N \frac{2}{3} \langle E_{\text{kinetic}} \rangle \]

\[ pV = Nk_B T \quad \Rightarrow \quad \langle E_{\text{kinetic}} \rangle = \frac{3}{2} k_B T \]
Maxwell velocity distribution (1860)

\[ p(\vec{v}) = \text{prob. density mole in gas has velocity } \vec{v} \]

\[ \int d^3v \ p(\vec{v}) = 1 \]

1) Assume

\[ \vec{v} = (v_x, v_y, v_z) \]

\[ v_x, v_y, v_z \text{ statistically independent} \]

2) Azimuthal

Assume \( p(v^2) \) is function only of \( v^2 \)

\[ p(v^2) = p_x(v_x) p_y(v_y) p_z(v_z) = f(v^2) = f(v_x^2 + v_y^2 + v_z^2) \]

Solution: \( p_x(v_x) = C v_x^n \) a power

So that \( C v_x^2 v_y^2 v_z^2 = C \)

Can always write in the form

\[ p_x(v_x) = C e^{-A v_x^2} \]

\[ A < 0 \text{ prob. normalized} \]

\[ C > 0 \text{ prob. > 0} \]

\[ p(\vec{v}) = C e^{-A v^2} \]

Gaussian distribution: Define \( A = -\frac{1}{2 \sigma^2} \) then

\[ p_x(v_x) = \frac{1}{(2\pi)^{1/2} \sigma} e^{-\frac{v_x^2}{2 \sigma^2}} \]
Standard deviation $\sigma$

$$\sigma^2 = \langle \nu^2 \rangle - \langle \nu \rangle^2 \quad \langle \nu \rangle = 0 \text{ by symmetry}$$

$$\sigma^2 = \frac{1}{3} \langle \nu^2 \rangle = \frac{2}{3m} \langle \frac{1}{2} mu^2 \rangle = \frac{2}{3m} \langle \varepsilon_{kin} \rangle$$

$$= \frac{2}{3m} \frac{3}{2} k_B T = \frac{k_B T}{m}$$

$$p_{\nu} (\nu) = \frac{1}{(2\pi)^{1/2} \sqrt{k_B T/m}} e^{-\nu^2/2k_B T/m}$$

$$p (\vec{u}) = p_x (\nu_x) p_y (\nu_y) p_z (\nu_z)$$

$$p (\vec{u}) = \frac{1}{(2\pi k_B T/m)^{3/2}} e^{-m\nu^2/2k_B T}$$

What is in the exponent is $G (\vec{u})$ where $G (\vec{u}) = \frac{m\nu^2}{k_B T}$ the kinetic energy of the molecule (the Boltzmann factor $e$)
Statistical Ensembles

Ergodic hypothesis

Consider a system of $N$ particles, each with three degrees of freedom, $x, y, z$. The system is described in Hamiltonian classical mechanics, by $3N$ canonical variables

$$g_{1,2,\ldots,2N}, p_{1,2,\ldots,2N}$$

Hamilton's equations

$$\dot{g}_i = -\frac{\partial H}{\partial p_i} \quad \gamma = 1, \ldots, 2N$$

$$\dot{p}_i = \frac{\partial H}{\partial g_i}$$

give the trajectory of the system $\{g_i(t), p_i(t)\}$ in "phase space" - a $3N$ dimensional space whose coordinates are the $g_i$ and $p_i$.

In general, energy will be conserved as the system moves, leaving phase space without external time dependence. The condition $H\{g_i, p_i\} = E$ defines a $3N-1$ dimensional surface in phase space on which the system's trajectory is confined.

If one wanted to compute the average value of some quantity, averaged over an interval of time $T$, it is measured...
\[ \langle f \rangle = \frac{1}{2} \int_{t_0}^{t_0 + \tau} dt \int_{-\infty}^{\infty} f \cdot \{ q_i(t), p_i(t) \} \]

In general, for large \( \tau \), we expect the trajectory to be some horribly complicated curve on the constant energy surface, that we have no way of computing directly.

To compute \( \langle f \rangle \) we therefore need to make an assumption. The ergodic hypothesis says: during any time interval \( T \) sufficiently long, the location of the system in phase space \( \{ q_i(t), p_i(t) \} \) is equally likely to be anywhere on the surface of constant energy \( E \).

Therefore \( \langle f \rangle = \int dq_i dp_i f \{ q_i, p_i \} \rho (q_i, p_i) \)

where \( \rho (q_i, p_i) = C \delta (H(q_i, p_i) - E) \)

where \( C \) is a normalizing factor such that \( \int dq dp \rho (q, p) = 1 \);

\( \rho \) is called the density matrix.

With the above form, \( \rho \) is called the microcanonical ensemble.
The ergodic hypothesis cannot in general be proven. But the existence of thermodynamic, as an empirically consistent theory, suggests why it may be true.

1. Liouville's theorem (see text)

2. By thermodynamics we assume that the macroscopic properties of a system are completely described by a set of a few macroscopic variables, such as total energy $E$, momentum $p$. If the ergodic hypothesis were not true, there would be parts of phase space with the same value of $E$, that never "saw" each other — i.e., a trajectory in one part would not enter the other, and vice versa. One could imagine, therefore, that systems in these two disjoint regions of phase space might have different properties. However, this would have different time averages of some particular property $F[q,p]$. One, therefore, might expect them to represent thermodynamically distinguishable states. But this would contradict the assumption that $E$ alone is the important thermodynamic variable.

Alternatively, if ergodicity fails, there might be some other important macroscopic variable (for example, magnetization) which one overlooked. The disjoint regions of the constant energy surface could correspond to different values of this new macroscopic variable.
In other words, in the absence of any further information, we assume that all microscopic states \( \{ q_i, p_i \} \), consistent with a given set of macroscopic thermodynamic variables \( E, N, V \), are equally likely.

In the ensemble theory, one abandons any effort to compute thermodynamic properties from the explicitly time-dependent trajectory of the system in phase space. Rather, one describes the thermodynamic state as represented by a particular ensemble, given by the density matrix \( \rho(q, p_i) \).

The ensemble average \( \langle S \rangle = \int dq dp f(q, p) \rho(q, p) \) is the value one would find not for a single isolated system moving on its trajectory, but for a collection but for the average of a collection of systems distributed in phase space according to the density \( f \). The ergodic hypothesis asserts that these two types of averages are equal.

\( \rho(q, p_i) \) can be viewed as the probability density that the system will be found in phase space at \( q, p \).

Equilibrium is described by a density matrix that does not vary in time.