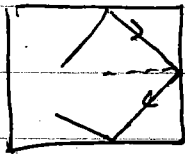


Kinetic Theory of ideal gas



$$\text{pressure } P = \left\langle \frac{\Delta(mv_{\perp}) \cdot \text{rate}}{\text{area}} \right\rangle$$

average over
all molecules
and time

$$\Delta(mv_{\perp}) = 2m v_{\perp} \quad \text{elastic collision}$$

$$\frac{1}{2} \frac{N}{V} v_{\perp} = \text{rate/area}$$

↑

$\frac{1}{2}$ towards wall

$\frac{N}{V}$ = uniform density

$$P = 2m \left(\frac{1}{2} \frac{N}{V} \right) \langle v_{\perp}^2 \rangle$$

$$\text{for isotropic gas } \langle v_{\perp}^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

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

$$= \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle$$

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

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

$$PV = N k_B T$$

$$\Rightarrow \langle E_{\text{kinetic}} \rangle = \frac{3}{2} k_B T$$

Maxwell velocity distribution (1860)

$p(\vec{v})$ = prob density molec in gas has velocity \vec{v}

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

a) assume

$$p(\vec{v}) = p_x(v_x) p_y(v_y) p_z(v_z)$$

v_x, v_y, v_z statistically independent

b) isotropic

assume $p(\vec{v})$ is function of only of v^2

$$p(\vec{v}) = p_x(v_x) p_y(v_y) p_z(v_z) = f(v^2) = f(v_x^2 + v_y^2 + v_z^2)$$

solution is $p_\mu(v_\mu) \propto C v_\mu^2$ a power

$$\text{so that } C v_x^2 C v_y^2 C v_z^2 = C v^2$$

can always write in the form

$$p_\mu(v_\mu) = C' e^{A v_\mu^2}$$

$A < 0$ prob normalized

$C' > 0$ prob ≥ 0

$$p(\vec{v}) = C' e^{A v^2}$$

Gaussian distribution define $A = -\frac{1}{2\sigma^2}$ then

$$p_\mu(v_\mu) = \frac{1}{(\sqrt{2\pi})^{1/2} \sigma} e^{-\frac{1}{2} \frac{v_\mu^2}{\sigma^2}}$$

standard deviation σ

$$\begin{aligned}\sigma^2 &= \langle v_\mu^2 \rangle - \langle v_\mu \rangle^2 && \langle v_\mu \rangle = 0 \text{ by symmetry} \\ &= \langle v_\mu^2 \rangle = \frac{1}{3} \langle v^2 \rangle = \frac{2}{3m} \langle \frac{1}{2} m v^2 \rangle = \frac{2}{3m} \langle E_{kin} \rangle \\ &= \frac{2}{3m} \frac{3}{2} k_B T = \frac{k_B T}{m}\end{aligned}$$

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

$$p(\vec{v}) = p_x(v_x) p_y(v_y) p_z(v_z)$$

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

What is in the exponent is

$\frac{E(\vec{v})}{k_B T}$ where $E(\vec{v}) = \frac{m v^2}{2}$
the kinetic energy of
the molecule

(the Boltzmann factor!)

Statistical Ensembles

How do we make connection between thermodynamics and mechanics?

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 $6N$ canonical variables

$$q_1, q_2, \dots, q_{3N}, p_1, \dots, p_{3N}$$

Hamilton's eqns
$$\begin{aligned} \dot{p}_i &= -\frac{\partial H}{\partial q_i} \\ \dot{q}_i &= \frac{\partial H}{\partial p_i} \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} i=1, \dots, 3N$$

give the trajectory of the system $\{q_i(t), p_i(t)\}$ in "phase space" - a $6N$ dimensional space whose coordinates are the q_i and p_i .

In general, ^{total} energy will be conserved as the system moves ~~assuming there are no external time~~ ~~regions~~. The condition $H[q_i, p_i] = E$ defines a $6N-1$ dimensional surface in phase space on which the system's trajectory is confined.

If one wanted to compute the ^{measured} ~~average~~ value of some quantity, averaged over an interval of time τ , it is:

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} dt f[q_i(t), p_i(t)]$$

In general, for large N , 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 τ , ~~this~~ 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 .

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

$$\text{where } \rho(q_i, p_i) = C \delta(H[q_i, p_i] - E)$$

where C is a normalizing factor such that $\int dq_i dp_i \rho[q_i, p_i] = 1$

ρ is called the density matrix.

with the above form, ρ is called the microcanonical ensemble.

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 $f(q_i, p_i)$

The ensemble average $\langle f \rangle = \int dq_i dp_i f(q_i, p_i) f(q_i, p_i)$ 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 these two types of averages are equal.

$f(q_i, p_i)$ can be viewed as the probability density that the system will be found in phase space at $\{q_i, p_i\}$.

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