

A brief history

Ideal gas laws:

1662 - Robert Boyle, at const T , $P_1 V_1 = P_2 V_2$

1787 - Jacques Charles, at const P , $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

1809 - Joseph Louis Gay-Lussac, at const V , $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

1811 - Amedeo Avogadro, at const T and P , $\frac{V_1}{N_1} = \frac{V_2}{N_2}$

1824 - Carnot

1834 - Emile Clapeyron, Ideal Gas Law, $PV = Nk_B T$
(also developed idea of entropy 1865)

Kinetic theory of ideal gas

50 BCE - Lucretius - from philosophical principle,

1738 - Daniel Bernoulli - showed pressure is related to impact of particles hitting a wall, and that heat is related to kinetic energy of particles

But his work was largely ignored

1856 - August Kronig

1857 - Rudolf Clausius

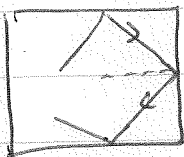
1859 - Maxwell

1905 - Einstein - Brownian motion

1906 - Marian Smolachowski

Kinetic Theory of ideal gas

pressure = average force per unit area



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

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

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

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

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

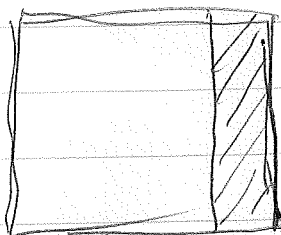
$$= \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle$$

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

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

$$PV = N k_B T$$

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



← l →
particles that hit wall in time t
are

$$\frac{1}{2} \left(\frac{N}{V} \right) A l$$

where $l = v_{\perp} t$

$$\frac{\text{rate}}{\text{area}} = \frac{\#}{A t} = \frac{1}{2} \frac{N A v_{\perp} t}{V A t}$$

$$= \frac{1}{2} \frac{N}{V} v_{\perp}$$

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 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 normalizable

$C' > 0$ prob ≥ 0

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

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

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

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!)

(1902 Gibbs)

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

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

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

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 ~~passing through~~ ~~via~~ ~~no~~ ~~external~~ ~~time~~ ~~region~~. 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:

$$\langle f \rangle = \frac{1}{2} \int_{t_0}^{t_0 + \tau} dt f[q_i(t), p_i(t)]$$

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: ^{for a system in equilibrium} during any time interval τ , 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.

The ergodic hypothesis cannot in general be proven. But the existence of thermodynamics, as an empirically consistent theory, suggests why it may be true.

(1) Liouville's Theorem (see later)

(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, V, N . 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, ad vice versa. One could imagine, therefore, that systems in these two disjoint regions of phase space might have different properties, ~~and~~ i.e. 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.