

Lect 1 : Kinetic theory of gases.

- More is different
- pressure, $\frac{ad}{b}$ iatic process
- thermo-equilibrium — temperature.

§ More is different.

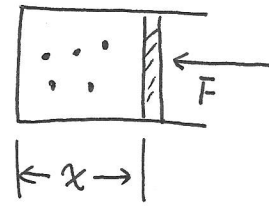
How do a great many atoms form matter? Even at the classic level, we are not able to solve 10^{23} differential equation and plug in initial conditions. Even though we were able to do this, it's impossible to extract useful information from the massive data. We need the understanding of the underlying principles of matter. And we need to change the methodology.

We will use probability description, or, statistical method, to build up connections between microscopic behavior with the macroscopic observables, such as pressure, temperature, and volume, etc. Essentially, the physics should be quantum mechanical, but we will begin with classic statistical mechanics, and gradually develop thermal dynamics.

We will understand why equal volume of gases at the same temperature and ^{the} same pressure hold the same number of molecules. Why the gas is heated when it's compressed, and when it's heated, it expands. Why work can be converted to heat completely, but heat cannot be converted to work completely, etc.

2: Pressure

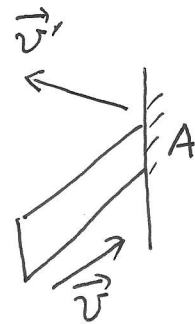
The piston receives the collisions from gas atoms. Each collision transfers a certain amount of momentum. To hold the piston still,



we need a force $F = PA$, where A is the cross section area.

$$dw = -F dx = -PA dx = -pdV$$

The piston is assumed to be a perfect reflector, i.e., the piston does not absorb energy, otherwise, it will be heated up. The equilibrium is assumed to be reached.



Consider a gas atom with velocity \vec{v} colliding with the piston, and is reflected. Within time dt , the volume that the gas atoms can stay

$$dV = \vec{v} dt \cdot \vec{A} = v_x A dt.$$

Assume there are $n(\vec{v})$ atoms with this velocity. Then the momentum transferred to the piston is $2m v_x \cdot n(\vec{v}) v_x A dt$.

We sum over all velocity, \Rightarrow

$$dF = \sum_{\vec{v}} 2m v_x^2 n(\vec{v}) A \cdot \frac{1}{2} \leftarrow$$

$\frac{1}{2}$ comes from that only half of the atoms move towards the wall.

$$= nm \sum v_x^2 n(\vec{v}) / \sum n(\vec{v}) \cdot A$$

$$= nm \langle v_x^2 \rangle A \Rightarrow P = F/A = \frac{2n}{3} \left\langle \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \right\rangle = \frac{2n}{3} \left\langle \frac{mv^2}{2} \right\rangle$$

For monoatom gases without interatomic interaction, the energy is just the kinetic one. This is called the internal energy U . Then we arrive at

$$P = \frac{2}{3} n U, \text{ or } PV = \frac{2}{3} U, \leftarrow n = N/V.$$

↓
equation of state

3: Adiabatic process.

Suppose that we push the piston, ~~and~~ Then we do the work, which will heat up the gas. Assume the energy is not leaking outside, how much pressure is needed as ~~pressing~~ squeezing the volume down?

For later convenience, we define a parameter γ , that the equation of state is expressed as $PV = (\gamma - 1)U$. Here $\gamma = 1 + \frac{2}{3} = \frac{5}{3}$.

In homework, you will need to prove that γ is the ratio between the heat capacity^{ies}, or, the specific heats, at fixed pressure and at fixed volume, i.e. $\gamma = C_p / C_v$ relate to physical observable.

In the adiabatic process, all the work is converted to the internal energy, i.e.

$$dU = dW = -pdV.$$

Then $PV = (\gamma - 1)U \Rightarrow pdV + Vdp = (\gamma - 1)dU = -(\gamma - 1)pdV$

$$\gamma p dv + v dp = 0 \Rightarrow \gamma \frac{dv}{V} + \frac{dp}{p} = 0$$

$$d \ln(PV^\gamma) = 0 \Rightarrow \boxed{PV^\gamma = C \text{ (a constant)}}$$

For a monoatomic gas, $p \propto V^{-\frac{5}{3}}$ during an adiabatic compress.

★ Equation of states for radiation — photon gas

we still have $p = n \langle p_x v_x \rangle = \frac{n}{3} \langle \vec{p} \cdot \vec{v} \rangle$ ($v=c$ actually)

\downarrow
 momentum

but for photons, ~~momentum~~, photon ~~dispersion~~ dispersion $E = pc$

$$\langle \vec{p} \cdot \vec{v} \rangle = pc = E \Rightarrow \boxed{pV = \frac{2}{3} U} \rightarrow \gamma = \frac{4}{3}$$

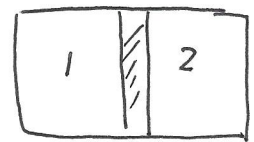
If under compression adiabatically $\Rightarrow pV^{\frac{4}{3}} = C$

This result is used in the radiation pressure ~~in~~ a star.
inside

⑤ Temperature

So far we have not define temperature yet, since T is a macroscopic quantity which is difficult to connect to microscopic quantities. Nevertheless, we assume temperature is such a quantity that when two objects are in equilibrium, their temperatures need to be the same.

Consider a box with a piston in the middle. The first condition of equilibrium should be of mechanical, i.e. $P_1 = P_2$, $\Rightarrow n_1 \langle \frac{m_1 v_1^2}{2} \rangle = n_2 \langle \frac{m_2 v_2^2}{2} \rangle$.



But in addition to this mechanical condition, if we let time evolves long enough, new condition — thermal equilibrium will appear.

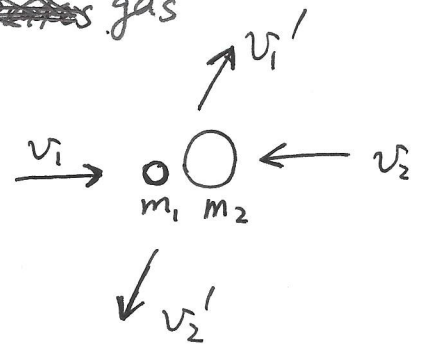
This is because the piston itself jiggles. Say, if the side 1 has a small n , such that $n_1 < n_2$, but $\langle \frac{m_1 v_1^2}{2} \rangle > \langle \frac{m_2 v_2^2}{2} \rangle$ to maintain $P_1 = P_2$, then the gas atoms collide from the LHS more strongly. Then the LHS of the piston jiggles more strongly, which propagate to the RHS, and then pass the energy to the RHS. This is essentially what happens during the heat conduction.

Let's consider a simple problem: Consider a box of two gases with atom masses m_1 and m_2 , and velocities v_1 and v_2 . They mixing collide with each other, and what's the condition for equilibrium?

Consider a collision between two un-equal ~~masses~~ gas

The center of mass (CM) velocity.

$$\vec{v}_{cm} = (m_1 \vec{v}_1 + m_2 \vec{v}_2) / (m_1 + m_2).$$



The relative velocity $\vec{w} = \vec{v}_1 - \vec{v}_2$, and

after collision, it changes to \vec{w}' . $|\vec{w}'| = |\vec{w}|$, but their

directions are changed. When equilibrium is reached, we assume

that all directions of \vec{w} are equally distributed, since the

collisions will randomize it. In other words, \vec{w} has no correlation

with \vec{v}_{cm} , i.e. $\langle \vec{w} \cdot \vec{v}_{cm} \rangle = 0$.

$$\begin{aligned}
 \text{Then } \vec{w} \cdot \vec{v}_{cm} &= (\vec{v}_1 - \vec{v}_2) \cdot (m_1 \vec{v}_1 + m_2 \vec{v}_2) / (m_1 + m_2) \\
 &= [(m_1 v_1^2 - m_2 v_2^2) + (m_2 - m_1) (\vec{v}_1 \cdot \vec{v}_2)] / (m_1 + m_2).
 \end{aligned}$$

Since 1 and 2 are two independent particles, $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = \langle \vec{v}_1 \rangle \cdot \langle \vec{v}_2 \rangle = 0$

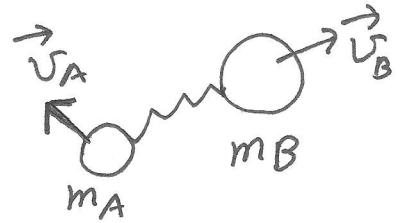
$$\Rightarrow \langle \vec{w} \cdot \vec{v}_{cm} \rangle = 0 \Rightarrow \boxed{\langle \frac{1}{2} m_1 v_1^2 \rangle = \langle \frac{1}{2} m_2 v_2^2 \rangle}$$

Hence, the average of kinetic energy should be the same

when thermal equilibrium is reached!

⊗ A diatomic gas

The gas molecule is composed of 2 types of atoms. Imagine there exists a spring between two atoms. In principle, due to the spring, \vec{v}_A and \vec{v}_B could exist certain correlations. Let us examine by decomposing them into center of mass $\vec{v}_M = (m_A \vec{v}_A + m_B \vec{v}_B) / (m_A + m_B)$, $\vec{w} = \vec{v}_A - \vec{v}_B$. Since the center of mass can collide with other molecules, randomly, and \vec{w} can also be kicked by other molecules, both are random. Hence $\langle \vec{v}_M \cdot \vec{w} \rangle = 0$.



Then
$$\langle \vec{v}_A \cdot \vec{v}_B \rangle = \left\langle \left(\vec{v}_M + \frac{m_B}{m_A + m_B} \vec{w} \right) \cdot \left(\vec{v}_M - \frac{m_A}{m_A + m_B} \vec{w} \right) \right\rangle$$

$$= \langle v_M^2 \rangle - \frac{m_A m_B}{(m_A + m_B)^2} \langle w^2 \rangle$$

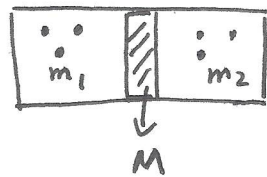
We consider the situation that \vec{v}_A and \vec{v}_B are randomized even though they are connected by a spring. Hence the spring cannot be a rigid rod, otherwise the projections of \vec{v}_A and \vec{v}_B along the rod direction should be the same, then $\langle \vec{v}_A \cdot \vec{v}_B \rangle \neq 0$. We consider that the vibration mode is sufficiently excited, such that \vec{v}_A and \vec{v}_B become independent, i.e. $\langle \vec{v}_A \cdot \vec{v}_B \rangle = 0$.

then
$$\langle v_M^2 \rangle (m_A + m_B) = \frac{m_A m_B}{m_A + m_B} \langle w^2 \rangle, \text{ i.e.}$$

$$M \langle v_M^2 \rangle = \mu \langle w^2 \rangle$$

← internal motion and CM motion become equilibrium.

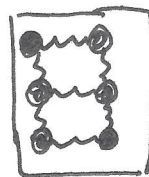
If the piston is a rigid body, i.e. it only has one degree of freedom moving along the wall of box without friction. Then if we repeat the above reasoning,



we have $\langle m_1 v_x^2 \rangle = \langle M u_x^2 \rangle = \langle m_2 v_x^2 \rangle$.

Since $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$, we conclude that $\langle m_1 v^2 \rangle = \langle m_2 v^2 \rangle$ across the piston.

Actually, a better viewpoint of the piston will be a bunch of atoms locked by elastic springs. Actually this is indeed the modeling of a solid! When the collisions by the molecules from the left and right hand sides sufficiently randomized the motion, we conclude that every degree of its energy average is equal!



(provided that the energy is expressed in terms of a quadratic form of the motion of that degree of freedom!

Actually, we can use this average energy to define temperature per degree of freedom.

$$\langle \mathcal{E} \rangle = \frac{1}{2} k_B T$$

where $k_B = \frac{R}{N_A} = \frac{8.3}{6.02 \times 10^{23}} \text{ J/K}$
 $= 1.38 \times 10^{-23} \text{ J/K}$

Boltzmann Constant.

⑩ How to count degrees of freedom?



For a molecule with r -atoms, each atom has 3-degrees of freedom. In total, $3r$ degrees of freedom.

Six of them correspond to an overall motion, ~~at~~ (3-translation + 3-rotation).

and $3r - 6$ vibration modes depending on intra-molecular interaction.

The vibration modes not only depend on momentum but also energy of on coordinates

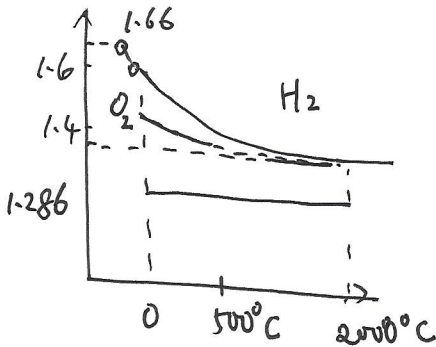
Hence, each molecule has $6 + (3r - 6) \times 2 = 6r - 6$ degrees of freedom.
 r -atom for $r \geq 3$.

$r=1$ # degrees of freedom 3

$r=2$ 7.

But quantum mechanically, the story is very different. The vibrational degrees of freedom are very difficult to excite. Often only translation and rotational degrees of freedom, i.e. rigid body motion are relevant!

variation of γ



classical theory $u = \frac{1}{2}(5+2) k_B T = \frac{7}{2} k_B T$

$$\frac{u}{\frac{1}{2} k_B T} = \frac{2}{\gamma-1} = 7 \Rightarrow \gamma = 1 \frac{2}{7} = 1.286$$

But: $\gamma = 1.6$ at low temperature for H_2

$$\Rightarrow \frac{u}{\frac{1}{2} k_B T} = \frac{2}{\gamma-1} = \frac{2}{0.66} \approx 3 \quad (\text{only translation degree of freedom}).$$

as increasing temperature $\gamma = 1.4$

$$\Rightarrow \frac{u}{\frac{1}{2} k_B T} \approx 5.$$

This means at different temperature regions, there're different numbers of degrees of freedom. More and more degrees of freedom are excited as increasing T . This means discrete energy levels.

$$\frac{P_{\text{excited}}}{P_0} = \frac{e^{-E_1/k_B T}}{e^{-E_0/k_B T}} = e^{-(E_1-E_0)/k_B T}$$

Hence, when $k_B T \ll E_1 - E_0$ (gap), like the vibration mode, that degree of freedom is frozen! No contribution to specific heat.

— failure of classic physics!