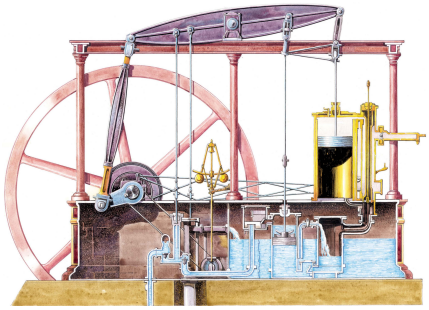
Lecture 15: Intro to thermodynamics

The reach of thermodynamics

Thermodynamics can be approached as **the science of heat and heat engines**, or as **the science of macroscopic systems in equilibrium**.[2]

How does energy flow, and what can that flow accomplish?



What kind of subject is thermodynamics?

熱學這一門科學起源於人類對於熱與冷現象的本質的追求。由於在有史以前人類已經發明了火，我們可以想像到，追求熱與冷現象的本質的企圖可能是人類最初對自然界法則的追求之一。

> The attempt to understand the nature of heat and cold may have been one of humanity's earliest quests for the laws of nature. — Wang Zhuxi, *Thermodynamics* (1955)[2]







Ideal systems and universal principles

Ideal systems that do not exist offer the deepest insights into physical reality.[2]

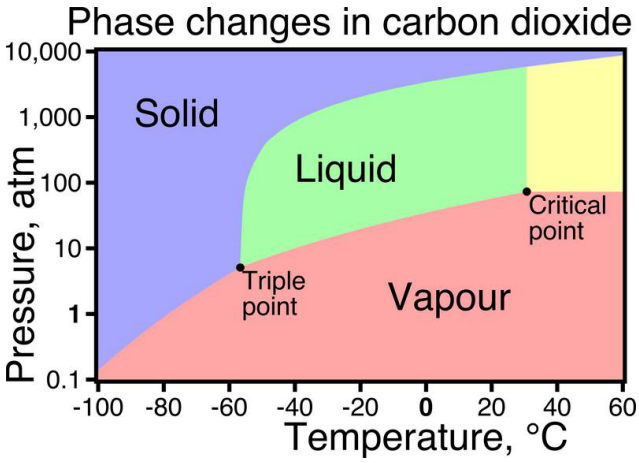
> Thermodynamics is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown. — Albert Einstein[2]

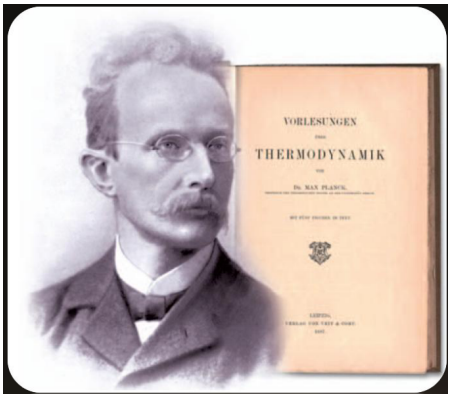
Learning thermodynamics

> The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier one must pass over well-travelled roads; of these one of the safest and surest is the **broad highway of thermodynamics**. — Gilbert N. Lewis (1923)[2]

After learning thermodynamics

The same framework describes phase changes in matter and thermal equilibrium of radiation.





What spectrum does light have in thermal equilibrium?

In 1900, Planck introduced finite energy elements in his statistical treatment of radiation; the full paper followed in 1901. **A question about thermal equilibrium helped initiate quantum theory.**[3]

15.1 The study of matter

More is different! — P. W. Anderson

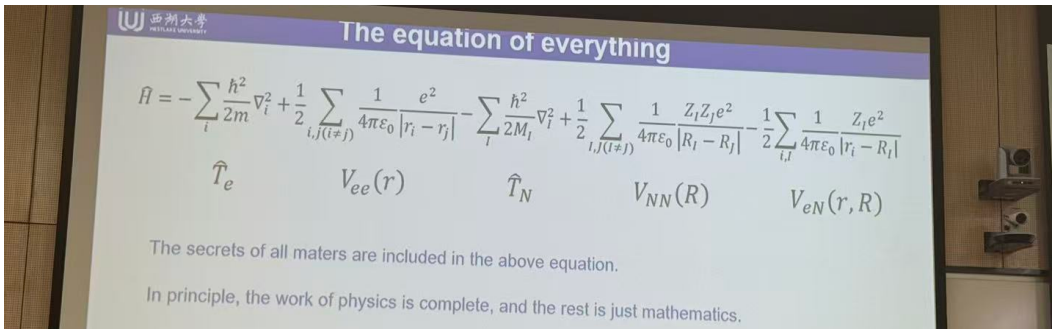


Fig. 1: The gap between microscopic laws and macroscopic properties.

The analysis of matter from a physical perspective is complex, given that it is made of numerous atoms interacting electrically and mechanically. In mechanics, we started with precise laws such as Newton's laws. Matter is too intricate to be understood directly from these laws alone.

The study of matter requires understanding the probabilistic behavior of many atoms and its macroscopic consequences. Thermodynamics developed from empirical laws; classical and quantum statistical mechanics connect these laws to the motion of atoms.[1]

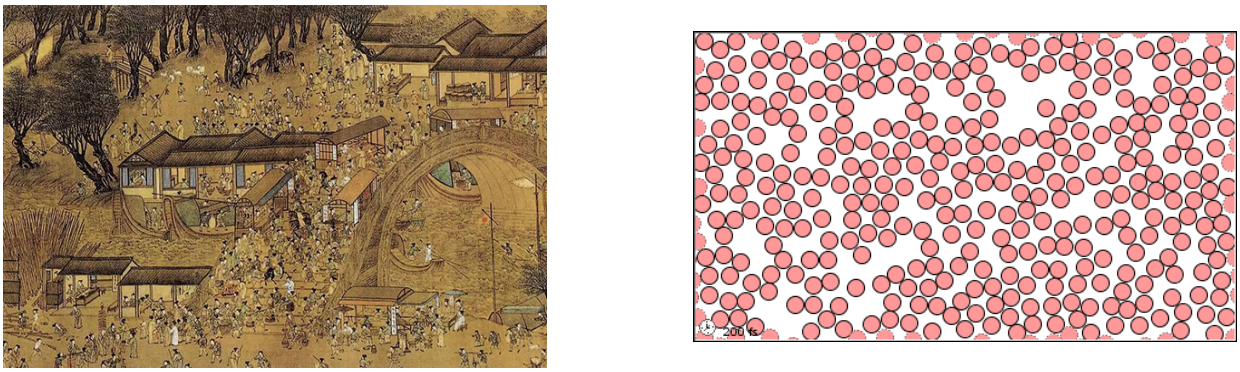


Fig. 2: Matter viewed on macroscopic and molecular scales.

15.2 Physics is the art of approximation

The world is too complex to be described exactly: we need **approximations**（近似）.

Real-world analysis of matter starts with physical intuition and appropriate approximations, rather than direct mathematical solutions from fundamental equations. The discussion begins with gases and their properties, such as pressure, volume and temperature. Many of the rules are empirical at first.

We will understand: why do equal volumes of gas at the same temperature and pressure have the same number of molecules? Why does a gas heat up as it is compressed, or expand as it is heated?



15.3 Gas pressure

Gas molecules in constant motion exert a force on surfaces, such as an eardrum. This is perceived as pressure:

$$P = \frac{F}{A}.$$

Consider a box of volume V, containing N atoms of mass m. Its number density is

$$n = \frac{N}{V}.$$

The atoms move with various velocities and collide with the piston. We take the piston to be a perfect reflector, so a collision with the stationary piston is elastic.

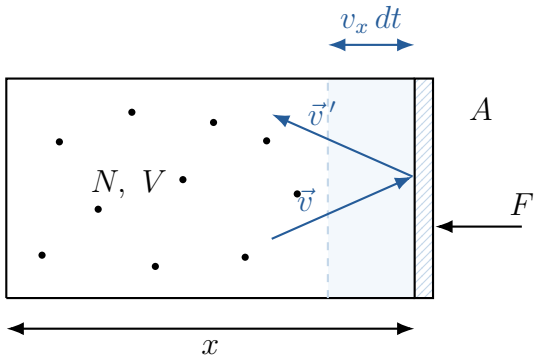


Fig. 3: Molecular impacts on a piston of area A. The force F balances the impacts. For a given incoming normal velocity v_x, atoms within a distance $v_x\,dt$ can reach the piston during dt.

15.3.1 Momentum transferred by one atom

Take $+x$ toward the piston. The normal momentum of an incoming atom is mv_x; after reflection it is $-mv_x$. The momentum delivered to the piston is therefore

$$\Delta p_x = mv_x - (-mv_x) = 2mv_x.$$

15.3.2 How many atoms hit the piston?

First consider a velocity group with normal speed $|v_x|$ and number density n_g. In an equilibrium gas, half of this group moves toward the piston, and half moves away.

For the incoming atoms, $v_x > 0$. The small volume containing the atoms that can reach the piston in time dt is

$$dV_{\text{hit}} = v_x A\, dt.$$

The number of impacts from this group is

$$dN_{\text{hit}} = \frac{n_g}{2}\, v_x A\, dt.$$

Multiplying the momentum per impact by the number of impacts gives

$$dp_{x,\text{piston}} = (2mv_x)\left(\frac{n_g}{2}\, v_x A\, dt\right),$$

$$F_g = \frac{dp_{x,\text{piston}}}{dt} = n_g m A v_x^2.$$

The factor of 2 from reflection cancels the factor of 1/2 from the fraction of atoms moving toward the piston.

The different velocity groups contribute additively. With $n = \sum_g n_g$ and the average taken over all atoms,

$$F = mA \sum_g n_g v_{x,g}^2 = nmA \left\langle v_x^2 \right\rangle,$$

$$P = nm \left\langle v_x^2 \right\rangle.$$

15.3.3 Pressure and internal energy

There is no preferred direction in the equilibrium gas, so

$$\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{1}{3} \left\langle v^2 \right\rangle.$$

Hence

$$P = \frac{1}{3} nm \left\langle v^2 \right\rangle$$

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

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

For a monatomic ideal gas, we disregard excitation or motion inside the atoms and the interaction energy between them. The total internal energy is then

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

Thus

$$\boxed{PV = \frac{2}{3} U.}$$

15.4 Kinetic energy: two gases separated by a piston

In container (1) the atoms have mass m_1, velocities $\vec{v}_1$ and number density n_1. The corresponding quantities in container (2) are m_2, $\vec{v}_2$ and n_2. What are the conditions for equilibrium?

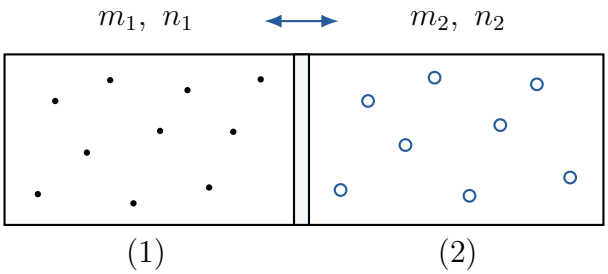


Fig. 4: Two monatomic gases separated by a movable piston. The piston can fluctuate and exchange energy with both gases.

At mechanical equilibrium, the pressures are equal. From the pressure formula,

$$P_1 = P_2,$$

$$n_1 \left\langle \frac{1}{2} m_1 v_1^2 \right\rangle = n_2 \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle .$$

The piston wiggles because the impacts of individual atoms are irregular. It transfers energy between the two gases. Over time, they approach thermal equilibrium: the piston picks up energy from each gas at the same average rate as it returns energy to it.

To find the condition on the molecular kinetic energies, consider the simpler case of two gases mixed in the same box.

15.5 Kinetic energy: two gases mixed

Two molecules of different masses collide. Their center-of-mass velocity and relative velocity are

$$\vec{V}_{\mathrm{CM}} = \frac{m_1 \vec{v}_1 + m_2 \vec{v}_2}{m_1 + m_2}, \qquad \vec{w} = \vec{v}_1 - \vec{v}_2.$$

In the center-of-mass frame, momentum and energy conservation imply that an elastic collision changes the direction of the relative velocity, while preserving its magnitude:

$$|\vec{w}\,'| = |\vec{w}|.$$

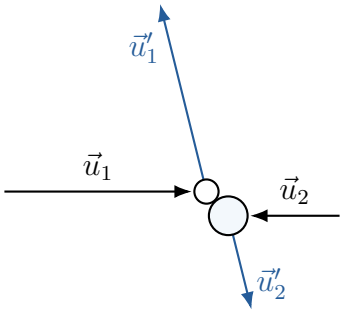


Fig. 5: An elastic collision between unequal molecules in the center-of-mass frame. Black arrows show incoming velocities; blue arrows show outgoing velocities. Here $\vec{u}_i = \vec{v}_i - \vec{V}_{\mathrm{CM}}$, with $m_1\vec{u}_1 + m_2\vec{u}_2 = 0$. The relative velocity is $\vec{w} = \vec{u}_1 - \vec{u}_2 = \vec{v}_1 - \vec{v}_2$.

At equilibrium, collisions randomize the direction of $\vec{w}$ relative to $\vec{V}_{\mathrm{CM}}$. Using this randomization in the elementary collision argument,[1]

$$\left\langle \vec{V}_{\mathrm{CM}} \cdot \vec{w} \right\rangle = 0.$$

Expand the scalar product:

$$\begin{aligned} \vec{V}_{\mathrm{CM}} \cdot \vec{w} &= \frac{(m_1\vec{v}_1 + m_2\vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2)}{m_1 + m_2} \\ &= \frac{m_1 v_1^2 - m_2 v_2^2 + (m_2 - m_1)\vec{v}_1 \cdot \vec{v}_2}{m_1 + m_2}. \end{aligned}$$

The two molecular velocities have uncorrelated directions and zero mean in the equilibrium gas, so

$$\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0.$$

Taking the average of the expanded expression then gives

$$0 = \frac{m_1 \langle v_1^2 \rangle - m_2 \langle v_2^2 \rangle}{m_1 + m_2},$$

and therefore

$$\boxed{\left\langle \frac{1}{2} m_1 v_1^2 \right\rangle = \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle}.$$

The two gases have the same average molecular kinetic energy at equilibrium.

References

[1] R. P. Feynman et al., *The Feynman Lectures on Physics*, Vol. I, Ch. 39 (including the collision-argument note) and Ch. 44.

[2] Z. Cao, *Thermodynamique: legend of a simple principle*, 31 December 2023. Original figures and translated passages: supplied slides, pp. 12–15, 264, 295 and 308.

[3] M. Planck, *Annalen der Physik* **4**, 553–563 (1901). Original paper.