Lecture 16: Temperature and the first law

Based on *The Feynman Lectures on Physics*, Vol. I, Chs. 39, 40 and 44.[1–3]

16.1 Thermal equilibrium and temperature

We use temperature to describe everyday conditions and to control experiments. But what is temperature exactly?

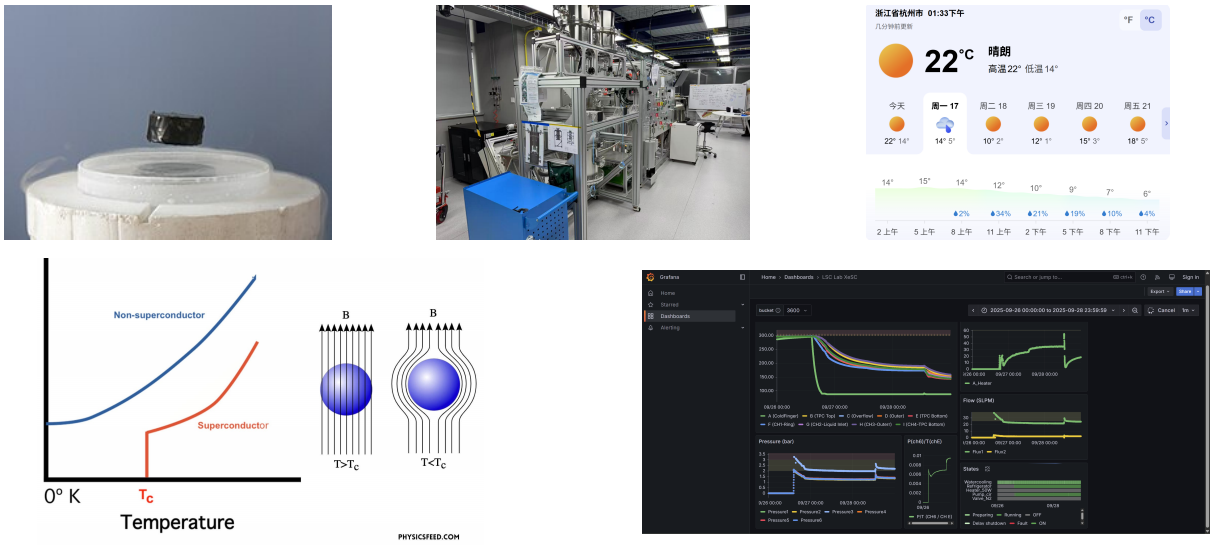


Fig. 1: Temperature in everyday life and experiments: magnetic levitation, laboratory apparatus, weather, superconductivity and experimental monitoring.

Bodies in thermal equilibrium have the same temperature. If A and B are each in thermal equilibrium with the same thermometer, they are in thermal equilibrium with each other.



Fig. 2: The same thermometer can be used to compare the temperatures of two bodies.

Melting and boiling pure water at atmospheric pressure provide reference points. The Kelvin scale is the natural temperature scale in physics. The Celsius temperature t and absolute temperature T are related by

$$\frac{T}{\mathrm{K}} = \frac{t}{^\circ\mathrm{C}} + 273.15.$$

16.2 Temperature and molecular motion

At equilibrium, two gases have the same mean translational kinetic energy. On average, heavier molecules move more slowly:

$$\left\langle \frac{1}{2} m_1 v_1^2 \right\rangle = \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle = \frac{3}{2} k_\mathrm{B} T.$$

Temperature is a property of all matter. Gases, liquids and solids can be compared by bringing them into thermal equilibrium. For a classical gas, the mean molecular kinetic energy is directly proportional to the absolute temperature.[1]

16.2.1 The Boltzmann constant

The constant linking the temperature scale to the molecular energy scale is the **Boltzmann constant**, k_B:

$$k_\mathrm{B} = 1.380649 \times 10^{-23}\ \mathrm{J\,K^{-1}}.$$

Its units are J/K: multiplying a temperature by k_B gives an energy scale. The value above is exact in the SI.[4]

An Austrian physicist, Ludwig Eduard Boltzmann developed the statistical approach to thermodynamics, showing how the collective behavior of atoms gives rise to macroscopic physical laws.

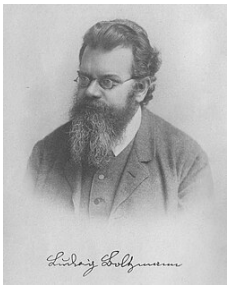


Fig. 3: Ludwig Eduard Boltzmann (1844–1906).

16.2.2 Degrees of freedom

A **degree of freedom**（自由度）is an independent coordinate needed to describe the motion. Translation in three dimensions has three degrees of freedom: x, y and z.

In classical thermal equilibrium, the average contribution of **each independent quadratic energy term** is $k_\mathrm{B}T/2$. For molecular translation,

$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \left\langle \frac{1}{2} m v_y^2 \right\rangle = \left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{1}{2} k_\mathrm{B} T.$$

Adding the three components gives

$$\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \times \frac{1}{2} k_\mathrm{B} T = \frac{3}{2} k_\mathrm{B} T.$$

16.3 The ideal gas law

Recall the pressure calculation from the previous lecture and substitute the mean molecular kinetic energy:

$$\begin{aligned} PV &= \frac{2}{3}N\left\langle \frac{1}{2}mv^2 \right\rangle \\ &= \frac{2}{3}N\left(\frac{3}{2}k_{\mathrm{B}}T\right) \\ &= Nk_{\mathrm{B}}T. \end{aligned}$$

The ideal gas law relates the pressure P, volume V, number of molecules N and absolute temperature T.

> So equal volumes of different gases, at the same pressure and temperature, have the same number of molecules, **because of Newton's laws. That is an amazing conclusion!**[1]

Chemists count particles in moles. One mole contains Avogadro's number of particles. We use N for the number of molecules and ν for the amount of substance in moles:

$$N_{\mathrm{A}} = 6.02214076 \times 10^{23}\ \mathrm{mol}^{-1}, \qquad N = \nu N_{\mathrm{A}}.$$

Defining the molar gas constant $R = N_{\mathrm{A}}k_{\mathrm{B}}$ gives

$$\boxed{PV = \nu RT}, \qquad R \simeq 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}.$$

Some textbooks use N for the number of moles and write $PV = NRT$. Here N counts molecules and ν counts moles.[4]

16.4 Diatomic gas

16.4.1 Separating the motion

Two atoms are joined by a chemical bond. Separate their motion into center-of-mass translation and relative motion.

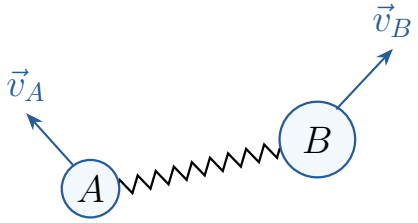


Fig. 4: A classical diatomic molecule. The bond can stretch, and both atoms contribute to the molecular motion.

Define the total mass, reduced mass, center-of-mass velocity and relative velocity:

$$M = m_A + m_B, \qquad \mu = \frac{m_A m_B}{M},$$

$$\vec{V} = \frac{m_A\vec{v}_A + m_B\vec{v}_B}{M}, \quad \vec{w} = \vec{v}_A - \vec{v}_B.$$

The individual velocities are

$$\vec{v}_A = \vec{V} + \frac{m_B}{M}\vec{w}, \qquad \vec{v}_B = \vec{V} - \frac{m_A}{M}\vec{w}.$$

Substituting these velocities into the kinetic energy, the cross terms cancel:

$$m_A\frac{m_B}{M} - m_B\frac{m_A}{M} = 0.$$

The coefficient of w^2 is

$$m_A\left(\frac{m_B}{M}\right)^2 + m_B\left(\frac{m_A}{M}\right)^2 = \frac{m_A m_B}{M} = \mu.$$

Therefore

$$\begin{aligned} K &= \frac{1}{2}m_A v_A^2 + \frac{1}{2}m_B v_B^2 \\ &= \boxed{\frac{1}{2}MV^2 + \frac{1}{2}\mu w^2}. \end{aligned}$$

The kinetic energy separates exactly into center-of-mass and internal motion, for any mass ratio.

16.4.2 Kinetic energy at temperature T

In classical equilibrium, each independent quadratic kinetic-energy term contributes $k_{\mathrm{B}}T/2$. The three center-of-mass terms give

$$\langle K_{\mathrm{CM}}\rangle = \sum_{j=x,y,z}\left\langle \frac{1}{2}MV_j^2 \right\rangle = \frac{3}{2}k_{\mathrm{B}}T.$$

The total kinetic energy of the two atoms has six quadratic terms:

$$\langle K\rangle = \frac{3}{2}k_{\mathrm{B}}T + \frac{3}{2}k_{\mathrm{B}}T = 3k_{\mathrm{B}}T.$$

Hence

$$\boxed{\langle K_{\mathrm{internal}}\rangle = \langle K\rangle - \langle K_{\mathrm{CM}}\rangle = \frac{3}{2}k_{\mathrm{B}}T.}$$

Internal motion includes rotation and vibration. The total internal energy also includes the potential energy stored in the bond.[1,2]

16.5 Heat, work and the first law

16.5.1 Temperature, heat and internal energy

Temperature T characterizes thermal equilibrium. **Internal energy** U is the energy associated with microscopic motion and interactions. **Heat** Q is energy transferred because of a temperature difference.

For melting ice at fixed pressure, heat enters and U increases while T stays nearly constant, as long as ice and water coexist.[8]



Fig. 5: Heat supplied to an ice–water mixture can change the amount of liquid while the temperature remains nearly constant.

16.5.2 Work on a gas

Let the piston move by dx, with the positive direction outward. Work W is positive when done on the gas.

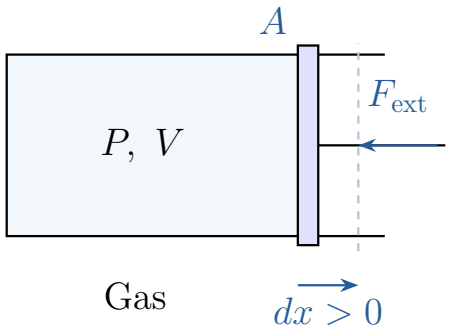


Fig. 6: Work on the gas: the external force points inward, while a positive displacement dx increases the volume.

For piston area A,

$$dV = A\,dx,$$

$$\delta W = -F_{\text{ext}}\,dx$$

$$= -P_{\text{ext}}\,dV.$$

Expansion has $dV > 0$ and $W < 0$; compression has $dV < 0$ and $W > 0$. For a quasistatic process with negligible friction, $P_{\text{ext}} \simeq P$, so

$$\boxed{\delta W = -P\,dV.}$$

16.5.3 The first law of thermodynamics

For a closed, stationary system at fixed height, energy transferred as heat or work changes its internal energy.[3]

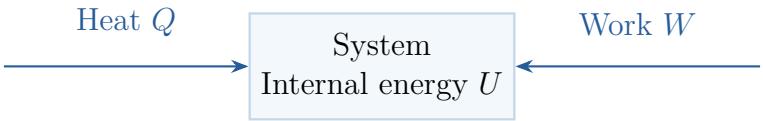


Fig. 7: Heat and work transfer energy to the system. Both arrows indicate the positive sign convention.

$$\boxed{\Delta U = Q + W}, \qquad dU = \delta Q + \delta W.$$

The signs are

$Q > 0$: heat enters, $Q < 0$: heat leaves,

$W > 0$: work is done on the system, $W < 0$: work is done by the system.

For quasistatic pressure–volume work,

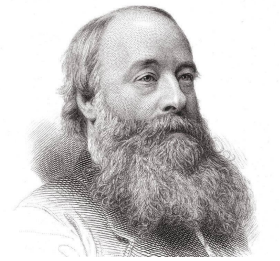
$$\boxed{dU = \delta Q - P\,dV.}$$

16.5.4 Conservation of energy and Joule's experiment

In the 1840s, work by Mayer, Joule and Helmholtz helped establish energy conservation and the connection between heat and mechanical work. In 1842, Mayer argued for a quantitative relation between heat and work; Joule measured the mechanical equivalent of heat in a series of experiments; in 1847, Helmholtz formulated energy conservation as a general physical principle.[5–7]



Julius Robert von Mayer



James Prescott Joule



Hermann von Helmholtz

Fig. 8: Three contributors to the development of energy conservation.

In Joule's experiment, falling weights pull ropes over pulleys and turn a shaft. Paddles rotate between four sets of stationary vanes to stir the water. The liquid is sealed in a copper vessel. Heat losses are measured and corrected for, so the temperature rise measures the energy supplied. After the bulk motion dies away, the water is warmer.[6]

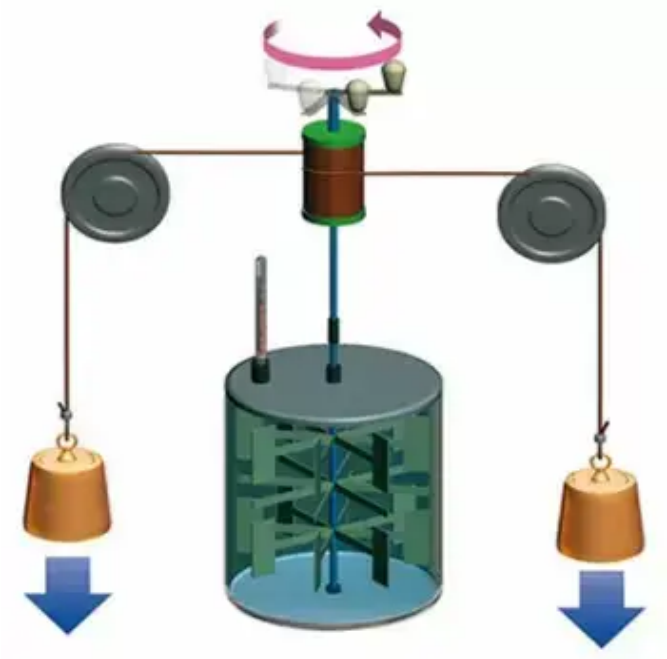


Fig. 9: Mechanical work is supplied to the liquid through a rotating shaft. The falling weights are outside the liquid–calorimeter system.

Mechanical work can produce the same change in internal energy as heating. The experiments can be repeated by changing the way work is supplied and by changing the liquid and its properties. Water and mercury give a consistent mechanical equivalent of heat when their different heat capacities are taken into account.

For the approximately adiabatic energy balance,

$$Q \simeq 0, \qquad \Delta U = W, \qquad \Delta T \simeq \frac{W}{C_{\text{system}}}.$$

Here C_{system} is the heat capacity of the liquid and calorimeter. Equal work can give different temperature rises.

16.6 Heat capacities and internal energy

16.6.1 Heat capacities

How much heat is needed to raise the temperature? The answer depends on the constraint. Define the heat capacities at fixed volume and fixed pressure:

$$C_V \equiv \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V,$$

$$C_P \equiv \left(\frac{\delta Q}{dT}\right)_P.$$

At fixed volume, no pressure–volume work is done, so the supplied heat changes the internal energy. For an ideal gas, U depends only on T, and

$$dU = C_V\, dT.$$

Here C_V and C_P refer to the chosen amount of gas; their units are J/K.

16.6.2 Why is C_P larger than C_V?

At fixed pressure, some of the supplied heat also provides the work of expansion. For a fixed amount of ideal gas, $P\,dV = Nk_{\mathrm{B}}\,dT$. The first law gives

$$\delta Q = dU + P\,dV,$$

$$C_P\,dT = C_V\,dT + Nk_{\mathrm{B}}\,dT.$$

Therefore

$$\boxed{C_P - C_V = Nk_{\mathrm{B}} = \nu R.}$$

For a monatomic ideal gas, the internal energy is the molecular translational kinetic energy:

$$U = \frac{3}{2}Nk_{\mathrm{B}}T = \frac{3}{2}PV.$$

Consequently,

$$C_V = \frac{3}{2}Nk_{\mathrm{B}}, \qquad C_P = \frac{5}{2}Nk_{\mathrm{B}}.$$

16.6.3 The heat-capacity ratio

Define

$$\gamma \equiv \frac{C_P}{C_V}.$$

For a fixed amount of ideal gas with constant heat capacities,

$$\gamma = 1 + \frac{Nk_{\mathrm{B}}}{C_V},$$

$$C_V = \frac{Nk_{\mathrm{B}}}{\gamma - 1},$$

$$U = C_V T = \frac{Nk_{\mathrm{B}}T}{\gamma - 1} = \frac{PV}{\gamma - 1}.$$

The zero of U is chosen so that $U = C_V T$. Thus

$$\boxed{PV = (\gamma - 1)U.}$$

We use this relation with constant γ in the adiabatic calculation.

16.6.4 Heat capacities reveal molecular energy

Measuring the heat-capacity ratio tells us how much internal energy a gas stores at a given temperature. A monatomic ideal gas stores energy in its three translational motions:

$$U = \frac{3}{2}Nk_{\mathrm{B}}T \quad \Longrightarrow \quad \gamma = \frac{5/2}{3/2} = \frac{5}{3} \simeq 1.667.$$

Helium, argon and krypton approach this value in the ideal-gas regime, supporting the molecular picture. The measured ratios are close to the monatomic prediction:[2]

Gas	**Temperature** (°C)	γ
He	−180	1.660
Kr	19	1.68
Ar	15	1.668

16.7 Isothermal expansion

Expansion and compression require specifying how the gas changes. For an **isothermal**（等温）process, the temperature remains constant:

$$T = \text{const.} \quad \Longrightarrow \quad PV = Nk_{\mathrm{B}}T = \text{const.}$$

The gas expands slowly against a piston and does work on it. Without incoming heat, the gas would cool. Heat flows in from the surroundings to keep the temperature constant.

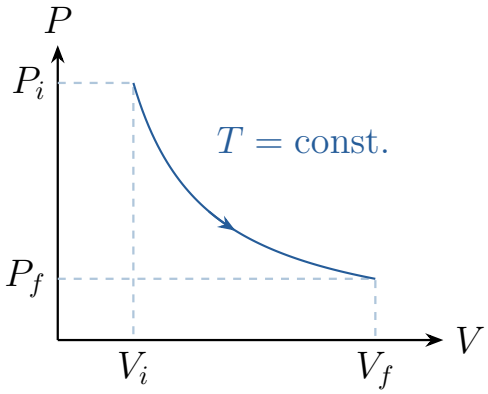


Fig. 10: Isothermal expansion from (P_i, V_i) to (P_f, V_f). An isotherm is a hyperbola on the P–V diagram.

For an ideal gas, U depends only on T. Therefore

$$\Delta U = 0.$$

The work done on the gas is

$$\begin{aligned} W &= -\int_{V_i}^{V_f} P\,dV \\ &= -Nk_{\mathrm{B}}T \int_{V_i}^{V_f} \frac{dV}{V} \\ &= -Nk_{\mathrm{B}}T \ln\left(\frac{V_f}{V_i}\right). \end{aligned}$$

Using the first law,

$$\boxed{Q = -W = Nk_{\mathrm{B}}T \ln\left(\frac{V_f}{V_i}\right).}$$

During expansion, $V_f > V_i$: the gas does work, $W < 0$, and heat enters, $Q > 0$.

16.8 Adiabatic compression

Adiabatic（绝热）means that no heat is transferred across the boundary:

$$Q = 0, \qquad \Delta U = W.$$

Work done on the gas increases its internal energy and temperature.

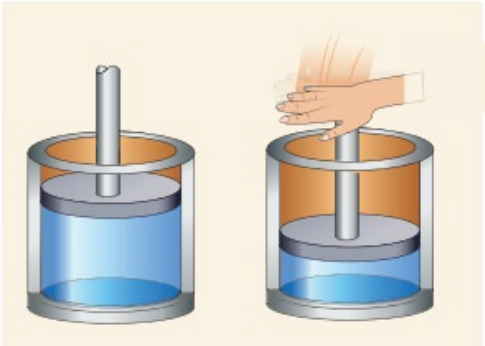


Fig. 11: Compression supplies work to the gas and can increase its temperature.

A sufficiently rapid compression leaves little time for heat exchange. The gas can behave approximately adiabatically even when the cylinder has no thermal insulation. For the following calculation, use a **quasistatic adiabatic process with constant** γ.

16.8.1 The differential relation

Use the first law and $U = PV/(\gamma - 1)$:

$$\begin{aligned} P\,dV &= -dU \\ &= -\frac{P\,dV + V\,dP}{\gamma - 1}. \end{aligned}$$

Rearranging gives

$$\gamma P\,dV + V\,dP = 0,$$

$$\frac{dP}{P} + \gamma\frac{dV}{V} = 0.$$

16.8.2 Integration and energy balance

Integrate between the initial and final equilibrium conditions:

$$\ln\left(\frac{P_f}{P_i}\right) + \gamma \ln\left(\frac{V_f}{V_i}\right) = 0.$$

Hence

$$\boxed{P_f V_f^{\gamma} = P_i V_i^{\gamma}}, \qquad PV^{\gamma} = \text{const.}$$

Using $PV = Nk_{\mathrm{B}}T$ also gives

$$\boxed{T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}}, \qquad TV^{\gamma-1} = \text{const.}$$

The work done on the gas becomes its increase in internal energy:

$$W = \Delta U = \frac{N k_{\mathrm{B}}(T_f - T_i)}{\gamma - 1} = \frac{P_f V_f - P_i V_i}{\gamma - 1}.$$

For compression, $V_f < V_i$, so $T_f > T_i$ and $W > 0$.

16.9 Isothermal and adiabatic expansion

Starting from the same initial pressure and volume,

$$\text{Isothermal:} \qquad P = P_i \frac{V_i}{V},$$

$$\text{Adiabatic:} \qquad P = P_i \left(\frac{V_i}{V}\right)^{\gamma}.$$

In isothermal expansion, heat enters and the temperature stays constant. In adiabatic expansion, the gas cools as it does work, so its pressure falls more steeply. For monatomic gases, $\gamma \simeq 5/3$ agrees with experiment under these conditions.

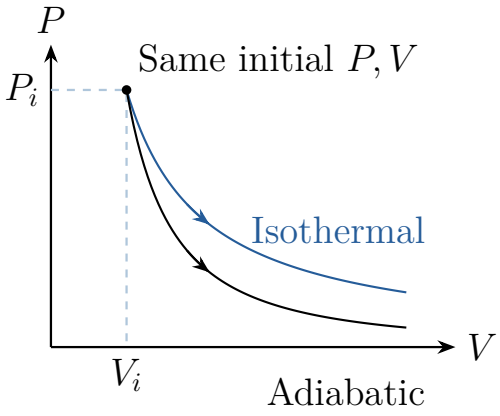


Fig. 12: Isothermal and quasistatic adiabatic expansion from the same initial condition. The adiabatic curve shown has $\gamma = 5/3$.

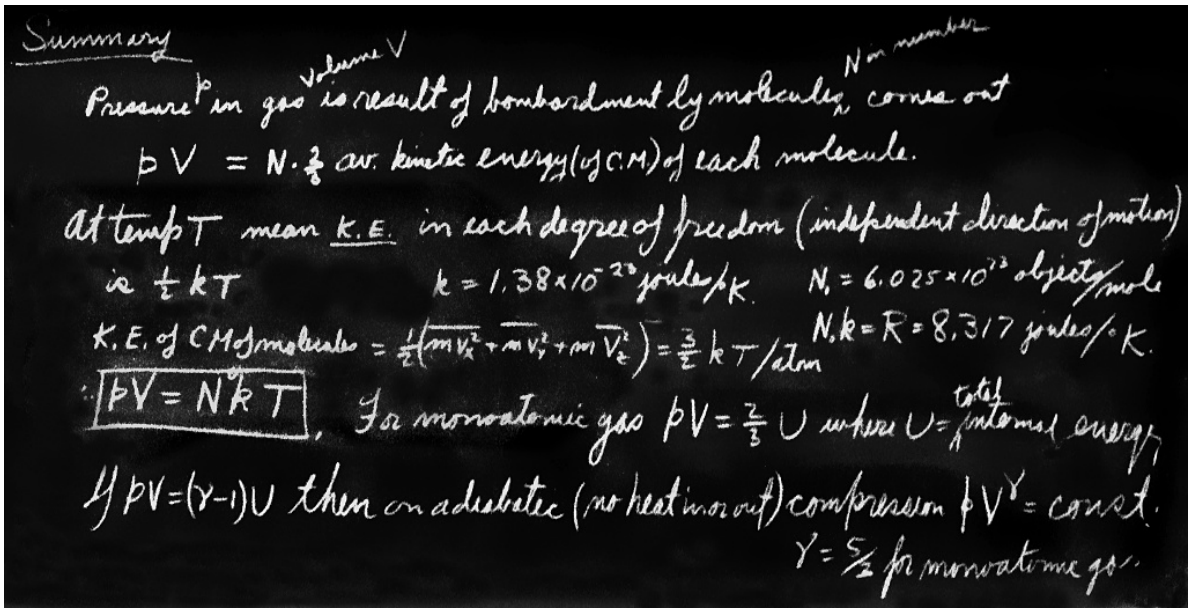


Fig. 13: Feynman's Chapter 39 blackboard summary. The original notation N_{mol} denotes the number of moles; this lecture uses ν.[1]

The virial theorem

For a system of particles, define the scalar quantity

$$G = \sum_i \vec{p}_i \cdot \vec{r}_i, \qquad \vec{p}_i = m_i \vec{v}_i.$$

Differentiating term by term gives

$$\begin{aligned} \frac{dG}{dt} &= \sum_i \vec{p}_i \cdot \dot{\vec{r}}_i + \sum_i \dot{\vec{p}}_i \cdot \vec{r}_i \\ &= \sum_i m_i v_i^2 + \sum_i \vec{F}_i \cdot \vec{r}_i \\ &= 2K + \sum_i \vec{F}_i \cdot \vec{r}_i. \end{aligned}$$

Here K is the total kinetic energy.[2]

Time averaging the virial relation

For bounded motion, the endpoint term divided by the averaging time tends to zero:

$$\frac{1}{\tau}\int_0^\tau \frac{dG}{dt}\,dt = \frac{G(\tau)-G(0)}{\tau} \longrightarrow 0.$$

The overbar denotes a long-time average. Averaging the preceding identity gives

$$0 = 2\overline{K} + \overline{\sum_i \vec{F}_i \cdot \vec{r}_i},$$

$$\overline{K} = -\frac{1}{2}\overline{\sum_i \vec{F}_i \cdot \vec{r}_i}.$$

Central forces and power-law potentials

For a particle in a central potential $U_{\text{pot}}(r)$,

$$\vec{F} = -\vec{\nabla}U_{\text{pot}},$$

$$\overline{K} = \frac{1}{2}\overline{\vec{r}\cdot\vec{\nabla}U_{\text{pot}}} = \frac{1}{2}r\overline{\frac{dU_{\text{pot}}}{dr}}.$$

For a power-law potential,

$$U_{\text{pot}} = \kappa r^{n+1}, \qquad F_r = -\kappa(n+1)r^n,$$

$$r\frac{dU_{\text{pot}}}{dr} = (n+1)U_{\text{pot}},$$

$$\overline{K} = \frac{n+1}{2}\overline{U_{\text{pot}}}.$$

Two applications of the virial theorem

Harmonic oscillator.

$$U_{\text{pot}} = \frac{1}{2}\kappa x^2 \quad\Longrightarrow\quad \overline{K} = \overline{U_{\text{pot}}} = \frac{E}{2}.$$

The mean kinetic and potential energies are each half of the total energy.

Inverse-square attraction.

$$U_{\text{pot}} = -\frac{a}{r} \quad\Longrightarrow\quad \overline{K} = -\frac{1}{2}\overline{U_{\text{pot}}}.$$

This applies to planetary motion and to the Coulomb orbit in the Bohr model.

References

[1] R. P. Feynman et al., *The Feynman Lectures on Physics*, Vol. I, Ch. 39: The kinetic theory of gases.

[2] R. P. Feynman et al., Vol. I, Ch. 40: The principles of statistical mechanics.

[3] R. P. Feynman et al., Vol. I, Ch. 44: The laws of thermodynamics.

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[5] J. R. Mayer, *Bemerkungen über die Kräfte der unbelebten Natur* (1842). Original paper.

[6] J. P. Joule, *On the mechanical equivalent of heat*, *Philosophical Transactions of the Royal Society of London* **140**, 61–82 (1850). Original paper.

[7] H. von Helmholtz, *Über die Erhaltung der Kraft* (1847). Original publication.

[8] Z. Cao, supplied thermodynamics lecture slides, discussion of heat, temperature and internal energy.