



# General Physics I

## Lect16. Temperature and Distribution

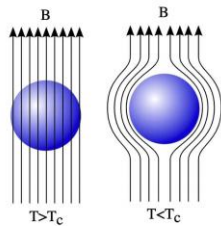
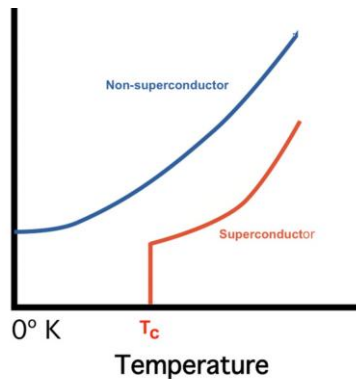
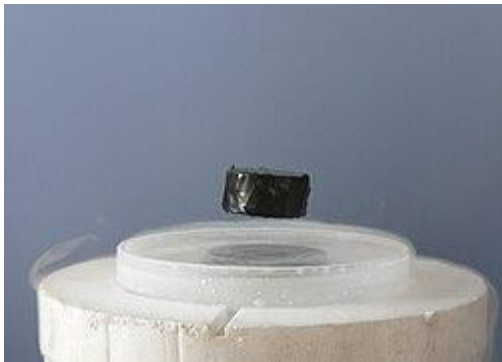
Based on Feynman Lectures Ch.39&40

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# Temperature is everywhere



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We can establish temperature scales using different reference points. Like **melting/boiling points** of pure water at atmospheric pressure. But **Kelvin** is probably the most natural one in physics.

# Temperature

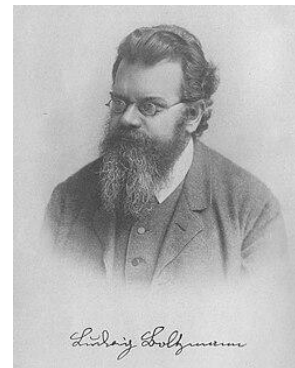
$$\langle m_1 \vec{v}_1^2 \rangle = \langle m_2 \vec{v}_2^2 \rangle$$

- For two different gases, their average kinetic energy is the **same in equilibrium**----the heavy ones will move slower than the light ones. We see that, not just for gas, this quantity seems to agree for any kind of matter.
- We use the word “**temperature**” to denote the mean molecular kinetic energy of gas, but it is rather the property of itself rather than just gas.
- There is a simple linear relation between mean kinetic energy and temperature  $T$ , for each d.o.f.

$$\frac{1}{2} k_B T$$

$k_B = 1.38 \times 10^{-23}$  joule for every Kelvin, “Boltzmann constant”

Theorem 1: the mean value of the kinetic energy is  $kT/2$  for each independent motion (d.o.f.)



**Ludwig Eduard Boltzmann**  
(1844 – 1906)

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

# The Ideal Gas Law

- Recall from the last class, we have

$$PV = \frac{2}{3} \cdot N \langle \frac{1}{2}mv^2 \rangle$$

- Let's now plug in  $\langle \frac{1}{2}mv_i^2 \rangle = \frac{1}{2}k_B T$ ,

$$PV = Nk_B T$$

- Beware, chemists count atoms in *moles*, one mole has  $N_0 = 6.02 \times 10^{23}$  objects, and they define a number  $R = N_0 k_B = 8.31 \text{ J} \cdot \text{mole}^{-1} \text{K}^{-1}$
- In chemistry/high school textbooks, while they also call it **N**, it's actually in the unit of *moles* and the ideal gas law writes

$$PV = NRT$$

- “**Equation of state**” is an equation that relates state variables. If we know the rest of the variables (e.g.,  $V$ ,  $N$ ,  $T$ ), we know the last variable (e.g.,  $P$ )

“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!”

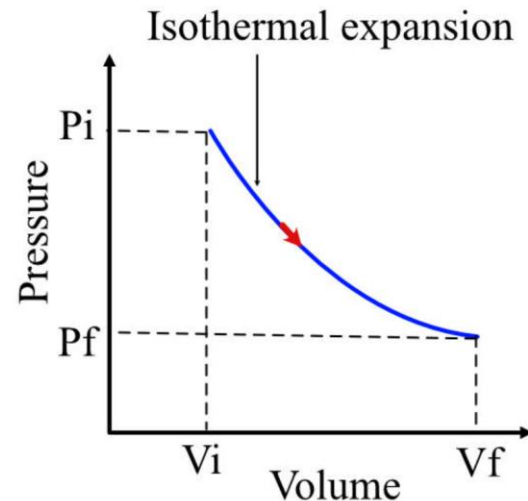
The opposite of state variable is called path-dependent variables. Like mechanical work done or heat transfer as a system moves from one state to another depends on the path taken between states (see similarity with a *conservative force potential*)

# Application: Ideal Gas Expansions

- Unlike **temperature** is a state, **expansion/compression** are processes, we need to specify how it is done, i.e., the “**path**”.
- Isothermal** (等温) means *constant temperature*.  
 $T = \text{const.} \rightarrow PV = \text{const.}$
- Consider gas expanded slowly against a piston – the gas does work on the piston, so would cool, but heat is allowed to flow in from the surroundings to keep the gas at constant temperature

$$\Delta U = 0 \quad \Rightarrow \quad dQ = dU - \delta W = p dV = \frac{RT}{V} dV$$

$$\Rightarrow \quad \Delta Q = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{RT}{V} dV = RT \ln \left( \frac{V_f}{V_i} \right)$$



**Isothermal processes** are hyperbola on a **P–V** diagram.

# Diatomic Gas

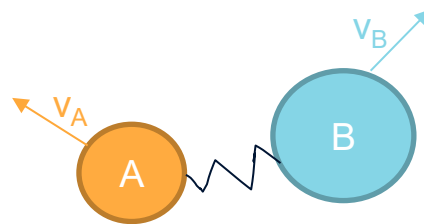
- What happens if there are **forces** present? Assume the gas molecule is composed of *two* different atoms, A and B, held by a force (chemical bond, spring). The center of mass velocity:

$$\vec{v}_{CM} = (m_A \vec{v}_A + m_B \vec{v}_B) / (m_A + m_B) = (m_A \vec{v}_A + m_B \vec{v}_B) / M$$

$$\vec{v}_{CM}^2 = [m_A^2 \vec{v}_A^2 + m_B^2 \vec{v}_B^2 + (2m_A m_B)(\vec{v}_A \cdot \vec{v}_B)] / M^2$$

$$\langle \frac{1}{2} M \vec{v}_{CM}^2 \rangle = (m_A \frac{3}{2} kT + m_B \frac{3}{2} kT + m_A m_B \langle \vec{v}_A \cdot \vec{v}_B \rangle) / M$$

$$= \frac{3}{2} kT + m_A m_B \langle \vec{v}_A \cdot \vec{v}_B \rangle / M$$

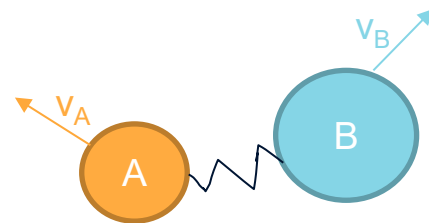


We will prove that  $\langle \vec{v}_A \cdot \vec{v}_B \rangle$  is indeed zero in the next slide..

## Diatomic Gas (Cont'd)

- To prove that  $\langle \vec{v}_A \cdot \vec{v}_B \rangle$  is zero, we do the same trick again  $\langle \mathbf{w} \cdot \mathbf{v}_{CM} \rangle = 0$

$$\begin{aligned} \mathbf{w} \cdot \mathbf{v}_{CM} &= \frac{(\mathbf{v}_A - \mathbf{v}_B) \cdot (m_A \mathbf{v}_A + m_B \mathbf{v}_B)}{M} \\ &= \frac{m_A v_A^2 + (m_B - m_A)(\mathbf{v}_A \cdot \mathbf{v}_B) - m_B v_B^2}{M} \end{aligned}$$



- Now that both A and B are in the equilibrium,  $\langle m_A v_A^2 \rangle = \langle m_B v_B^2 \rangle$   
 $(m_B - m_A) \langle \mathbf{v}_A \cdot \mathbf{v}_B \rangle = 0$
- If the masses of A and B are different, we have  $\langle \mathbf{v}_A \cdot \mathbf{v}_B \rangle = 0$ ,  
 and the entire molecule can be regarded as a single molecule of mass M, s.t.

$$\left\langle \frac{1}{2} M v_{CM}^2 \right\rangle = \frac{3}{2} kT \xrightarrow[\text{3kT/2} + \text{3kT/2}]{\text{Total K.E. 3kT}} \frac{\frac{1}{2} m_A v_A^2 + \frac{1}{2} m_B v_B^2}{\text{3kT/2} + \text{3kT/2}}$$

The average kinetic energy of the **internal** motions of the diatomic molecule is also **3kT/2!**

# Statistical Mechanics - laws of mechanics for thermal equilibrium

- How are the molecules distributed in space (i.e., with a *force field*)?
- See right, we know that molecules at all heights should have the same temperature if we neglect the convection (wind), so what changed?
- Recall  $P=nkT$ , we can write the pressure difference of  $h$  and  $h+dh$ ,  $dP=kTdn$ , which is equal to the weight of a small volume of air:  $-mgn dh = kTdn$
- So,

$$\frac{dn}{dh} = -\frac{mg}{kT} n \Rightarrow n = n_0 e^{-mgh/kT}$$

We find that the density goes down *exponentially* with height.

- For molecules of *different masses*, the exponential is different--heavier decrease with altitude faster.

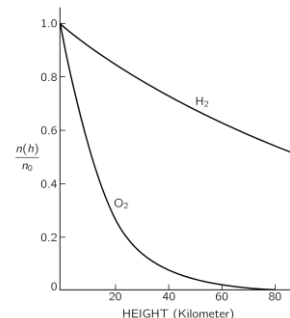
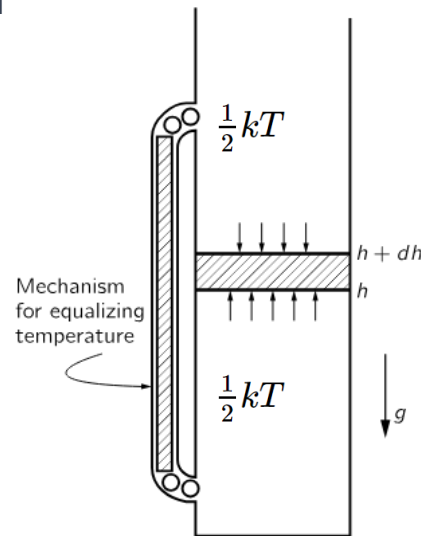


Fig. 40-2. The normalized density as a function of height in the earth's gravitational field for oxygen and for hydrogen, at constant temperature.

O2 decrease by **50%** over 10km!



# The Boltzmann's law

- Note such exponential relation can be applied to *any potential*. To generalize, assume the gas is subject to a force  $F$  in the  $x$ -direction, balanced by the pressure change s.t.  $F n dx = dP = kT dn$ , again we find

$$F = kT \frac{d}{dx} (\ln n)$$

- Notice that  $-Fdx$  is the work to take a molecule from  $x$  to  $x+dx$ , i.e., the change in potential energy (P.E.), s.t.  $d(\ln n) = -d(\text{P.E.})/kT$ .
- General spatial distribution (density) of molecule in terms of potential energy (P.E.):

$$n = (\text{constant}) e^{-\text{P.E.}/kT}$$

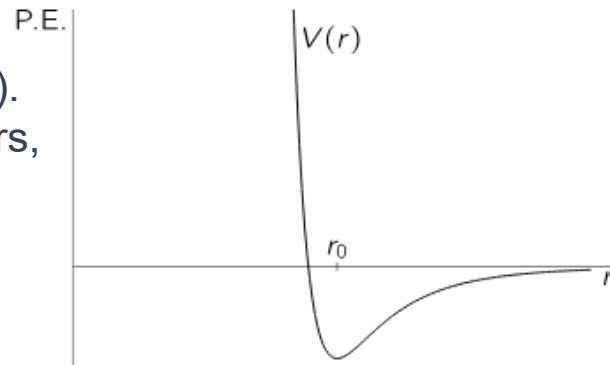
- Boltzmann's law:** the probability of finding molecules in a given spatial arrangement varies *exponentially* with the negative of the *potential energy* of that arrangement, divided by  $kT$ .

# Application: Evaporation of a liquid

- Suppose the potential energy function of each of two molecules (i and j) depends only on their separation,  $V(r_{ij})$ . The total potential energy would be the sum of all the pairs, in the full set of molecules. The probability of finding molecules in any particular combination is

$$\exp\left[-\sum_{i,j} V(r_{ij})/kT\right]$$

- For  $|V(r_0)| \ll kT$ , the exponential close to 1, the molecule can be anywhere. The potential does not make much difference for where the particle should be → **evaporation**
- For  $|V(r_0)| \gg kT$ , large positive exponent around  $r_0$ . In a given volume, molecules are likely to be at the distance of minimum energy than far apart → **condensation**



As the temperature falls, the atoms clump in lumps, and reduce to liquids, solids, and molecules, and as you heat them up they evaporate.

This is a *complicated* problem (due to a tremendous number of variables) sometimes referred to as the “**many-body problem**”, or “**condensed matter physics**”.

# The Distribution of Molecular Speeds

- Now we go on to discuss the distribution of **velocities**. We start by counting how many molecules are passing from below to above the plane  $h=0$  and  $h=h$ .

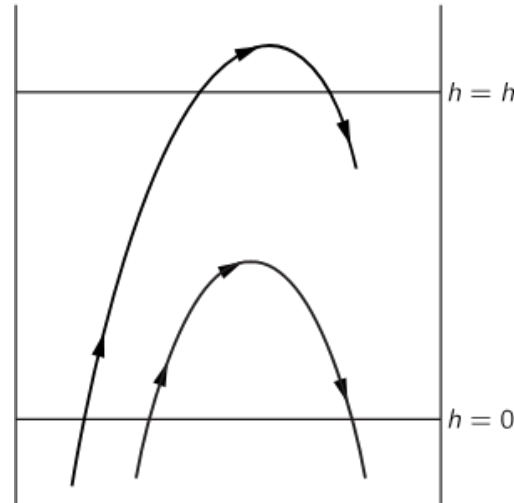
$$\left( \begin{array}{c} \text{Number passing } h = 0 \\ \text{with } v_z > u \end{array} \right) = \left( \begin{array}{c} \text{number passing } h = h \\ \text{with } v_z > 0 \end{array} \right) \quad mu^2/2 = mgh$$

- From the same temperature we know that the distribution of velocities is the same, we use  $n = n_0 e^{-mgh/kT}$  we find before and substitute with  $u$ , and find that

$$\frac{n_{>u}(0)}{n_{>0}(0)} = e^{-mgh/kT} = e^{-mu^2/2kT}$$

- Like the previous case, we can generalize the velocity to

$$n_{>u} \propto e^{-\text{kinetic energy}/kT}$$



We will continue the discussion next lecture..

# Chapter summary

- Temperature  $\leftrightarrow$  Kinetic energy
- Ideal Gas Law:  **$PV = Nk_B T$**
- Application: Isothermal expansion
- Check: Diatomic Gas
- The Boltzmann's law
- Distribution of Molecular Speeds

## Feynman Lectures Ch.39 Summary

Summary

Pressure  $P$  in gas is result of bombardment by molecules,  $N$  molecules, comes out  
 $PV = N \cdot \frac{2}{3}$  av. kinetic energy (of C.M.) of each molecule.

At temp  $T$  mean K.E. in each degree of freedom (independent direction of motion) is  $\frac{1}{2} kT$   $k = 1.38 \times 10^{-23}$  joules/K  $N_A = 6.025 \times 10^{23}$  objects/mole

K.E. of C.M. of molecule =  $\frac{1}{2} (m\overline{V_x^2} + m\overline{V_y^2} + m\overline{V_z^2}) = \frac{3}{2} kT$   $N_A k = R = 8.317$  joules/ $^{\circ}$ K.

**$PV = Nk_B T$**  For monoatomic gas  $PV = \frac{2}{3} U$  where  $U =$  total internal energy.

If  $PV = (\gamma - 1)U$  then on adiabatic (no heat in or out) compression  $PV^{\gamma} = \text{const.}$   
 $\gamma = \frac{5}{2}$  for monoatomic gas.