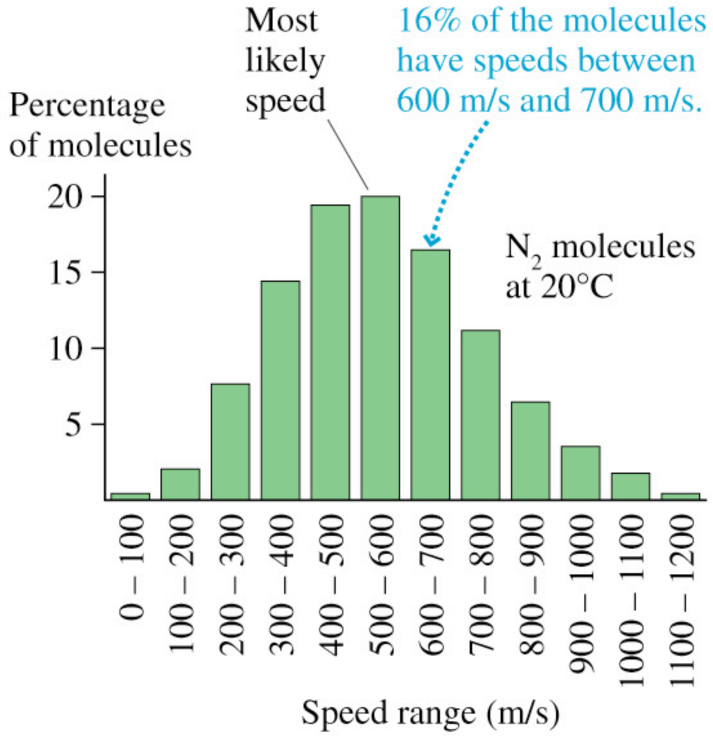
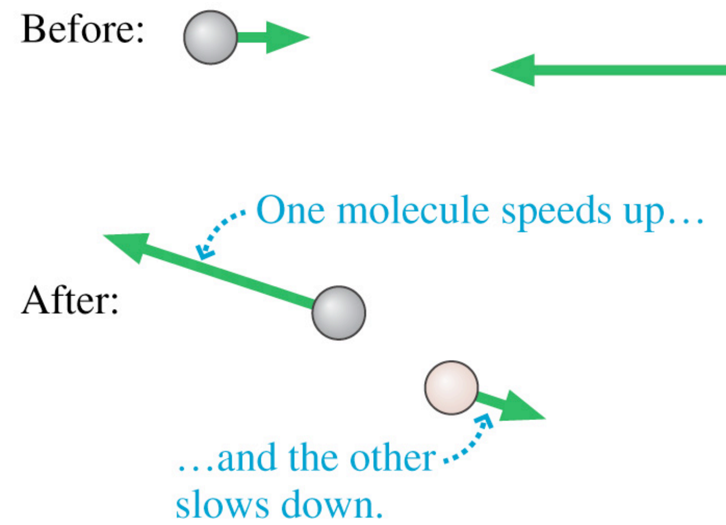
Lecture 13

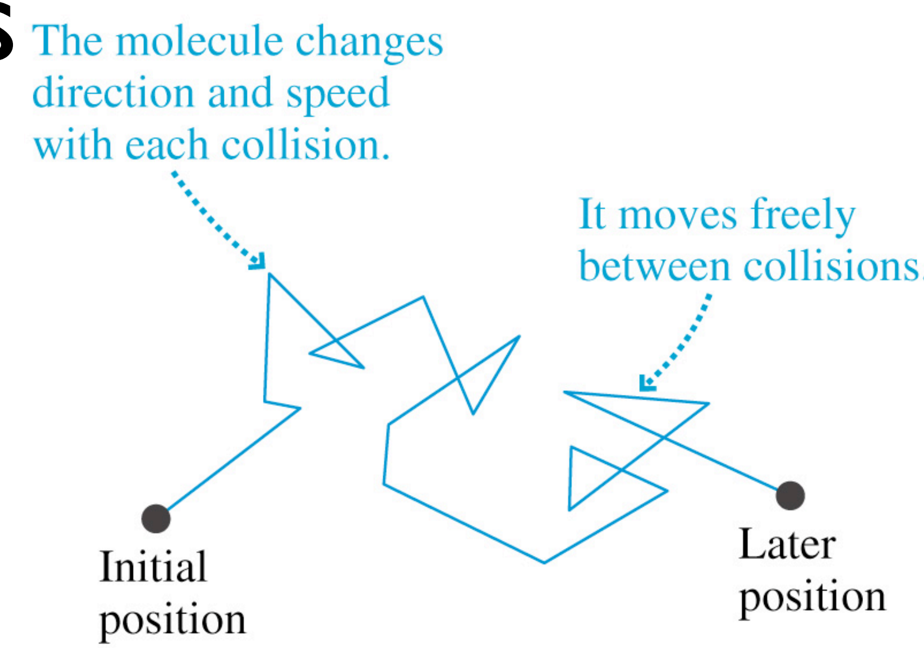
Chapter 18

- understand macroscopic properties (steady, predictable) such as p, heat transfer in terms of microscopic (random motion of molecules):
  connection between T and average translational kinetic energy of molecules
- predict molar specific heats of solids and gases
- 2nd law of thermodynamics: why heat energy “flows” from hot to cold...

Molecular collisions







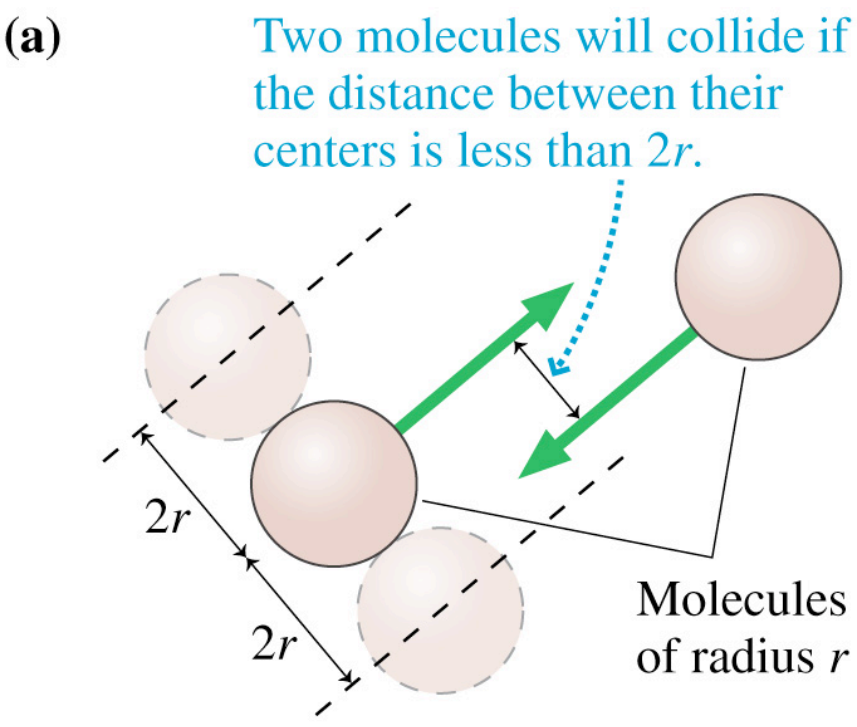
- can't keep track of individual molecules, but averages predictable/steady, e.g. distribution of speeds (molecules with speed in given range different each time, but number same)
- macroscopic properties (e.g. T) related to average behavior

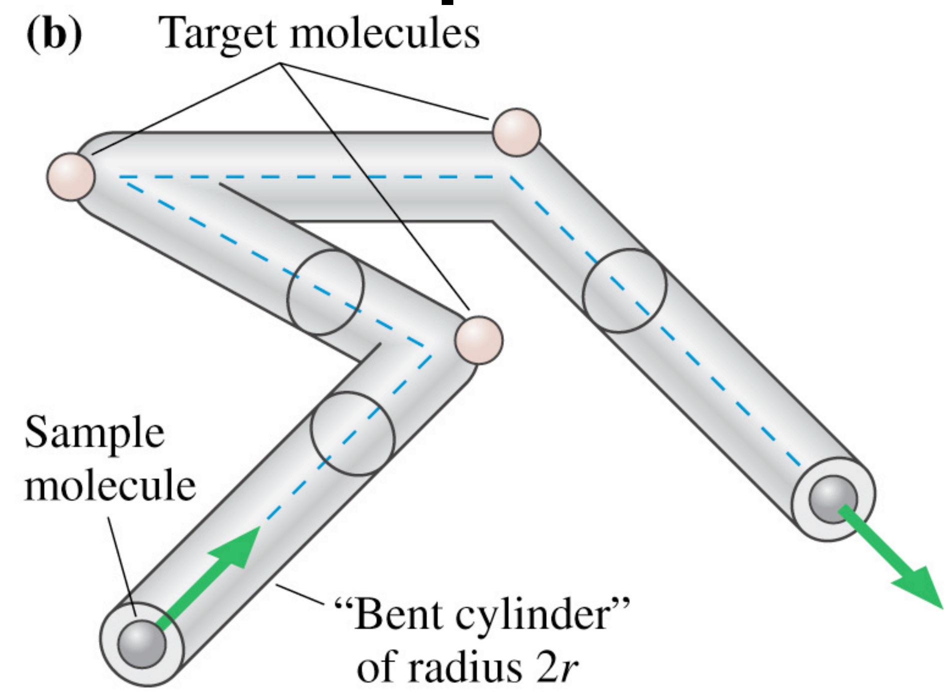
Mean Free Path

- zig-zag path: total distance travelled $\gg$ distance between initial and later position
- average distance between collisions: mean free path

$$\lambda = \frac{L}{N_{coll}}$$

Calculating mean free path





- molecules undergo hard-sphere collisions
- trajectory of molecule...bends due to collision...
- number of collisions, i.e., molecules in cylinder

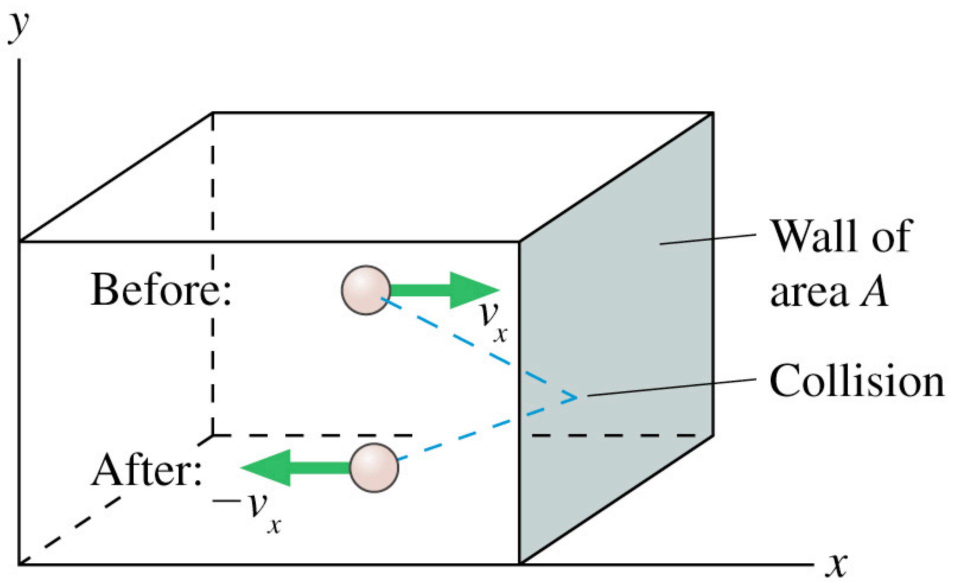
$$N_{coll} = \frac{N}{V} V_{cyl} = \frac{N}{V} \pi (2r)^2 L$$

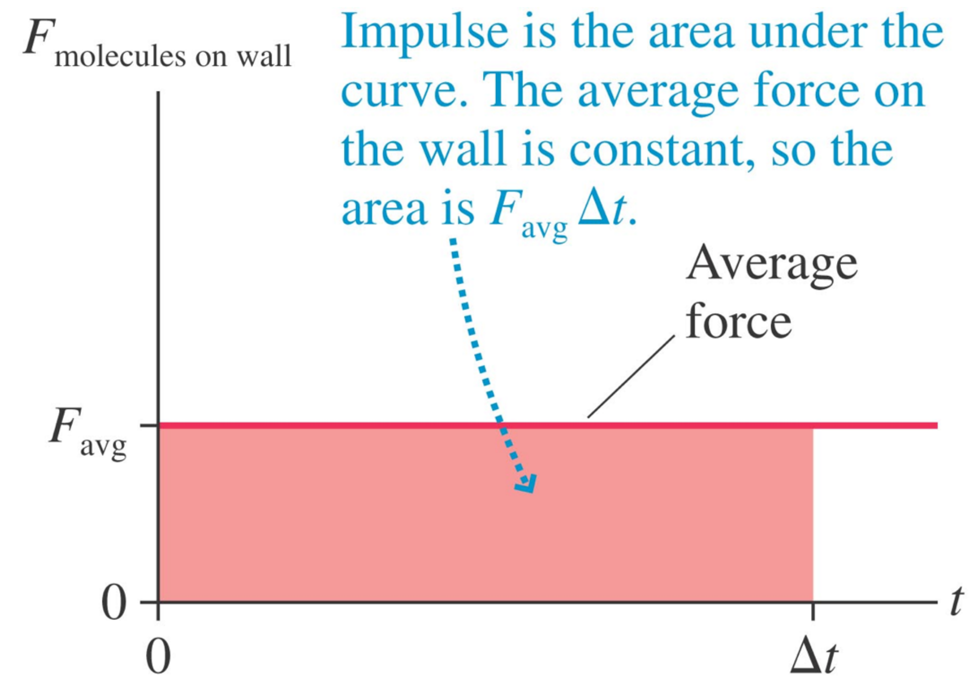
$$\Rightarrow \quad \lambda = \frac{1}{4\sqrt{2}\pi (N/V) r^2} \quad \text{(mean free path)}$$

target molecules not at rest

$r \approx 0.5(1) \times 10^{-10}$ m for mono (di)atomic gas

Pressure in a gas





- net forces exerted by collisions with wall...3 steps:
  1. Impulse due to single molecule
  2. Add impulses...
  3. Introduce average speed

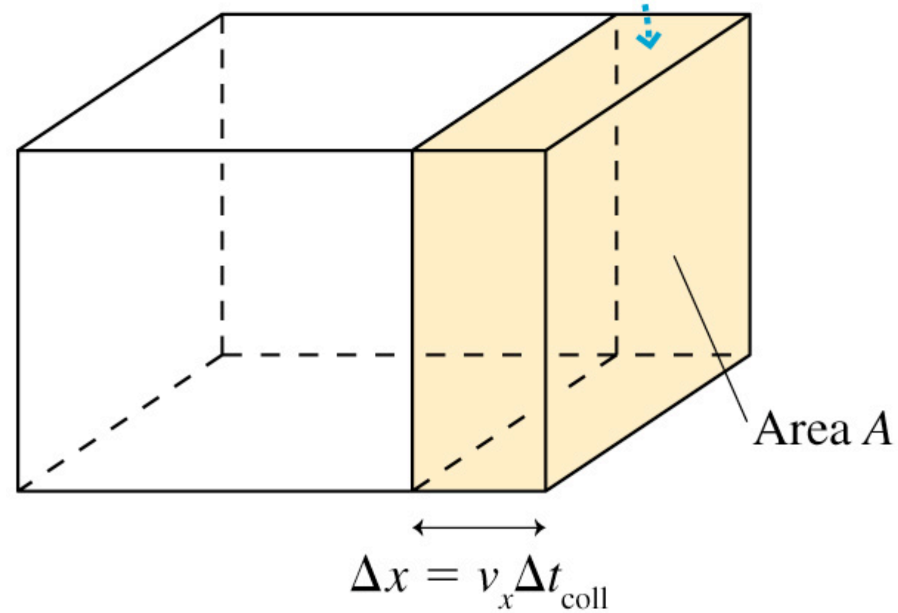
1. Impulse due to a single collision

$$\text{elastic collision: } v_x \rightarrow -v_x$$
$$\text{impulse: } (J_x)_{wall\ on\ molecule} = \Delta p = -2mv_x = -(J_x)_{molecule\ on\ wall}$$
$$N_{coll} \text{ during } \Delta t \ (same\ v_x)$$

2. Net impluse

$$J_{wall} = N_{coll} \times (J_x)_{molecule\ on\ wall} = 2N_{coll}mv_x$$
$$\text{Average force: } J_{wall} = F_{avg}\Delta t \Rightarrow F_{avg} = 2mv_x \frac{N_{coll}}{\Delta t}$$

Adding the Forces



$$F_{avg} = 2mv_x \frac{N_{coll}}{\Delta t} : \ \frac{N_{coll}}{\Delta t} \text{ (rate of collisions)}$$
$$\text{(assume } \Delta t \ll \text{ time between collisions)}$$

- molecules travel $\Delta x = v_x \Delta t$ during Δt

volume → ; half to right →

$$N_{coll} = \frac{N}{V}(A\Delta x)\frac{1}{2} \Rightarrow \text{rate of collisions} = \frac{1}{2}\frac{N}{V}v_x A$$

3. $F_{avg} = \frac{N}{V} A m \left(v_x^2\right)_{avg}$ ← all molecules don't have same speed

Root-Mean-Square Speed

average velocity (including sign), $(v_x)_{avg} = 0$

$(v^2)_{avg} = (v_x^2)_{avg} + (v_y^2)_{avg} + (v_z^2)_{avg}$

root-mean-square speed, $v_{rms} = \sqrt{(v^2)_{avg}}$

(close to average speed)

x-axis *not* special $\Rightarrow (v_x^2)\,avg = (v_y^2)\,avg = (v_z^2)\,avg$, i.e., $v_{rms}^2 = 3\,(v_x^2)_{avg}$

$\Rightarrow F_{avg} = \frac{1}{3}\frac{N}{V} m v_{rms}^2 A$

$$p = \frac{F}{A} = \frac{1}{3}\frac{N}{V} m {v_{\rm rms}}^2$$

- relate macroscopic p to microscopic physics!

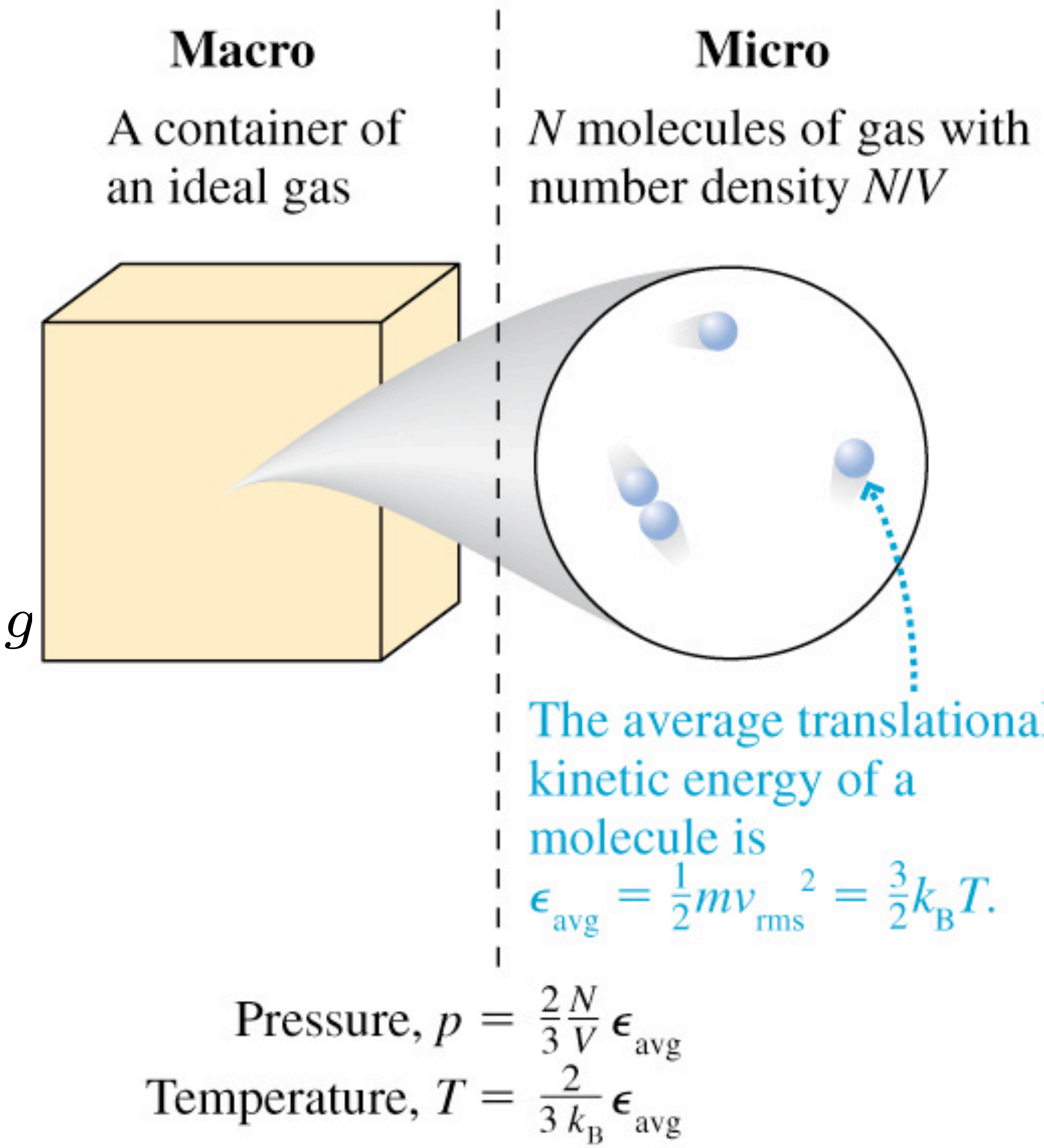
Temperature

- average translational kinetic energy of molecule (E is energy of system)

$$(\epsilon)_{avg} = \frac{1}{2}m\left(v^2\right)_{avg} = \frac{1}{2}mv_{rms}^2$$

Using $p = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}mv_{rms}^2\right) = \frac{2}{3}\frac{N}{V}\epsilon_{avg}$
and $pV = Nk_BT$ (ideal gas law),

$$\epsilon_{avg} = \frac{3}{2}k_BT \quad \text{(average translational kinetic energy)}$$



- $T = \frac{2}{3k_B}\epsilon_{avg}$:T is measure of average translational kinetic energy: motion stops at absolute zero

- collisions elastic: loss of energy reduces T, but T constant for isolated system

Using $\epsilon_{avg} = \frac{1}{2}mv_{rms}^2$ and $\epsilon_{avg} = \frac{3}{2}k_BT$,

$$v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

Example

- During a physics experiment, helium gas is cooled to a temperature of 10 K at a pressure of 0.1 atm. What are the (a) mean free path in the gas, (b) the rms speed of the atoms, and (c) the average energy per atom?

Thermal Energy and Specific Heat

- microscopic look at $E_{th} = K_{micro} + U_{micro}$

  kinetic of atoms (K_{micro}) bonds (U_{micro})

Monoatomic gases

- only translational kinetic energy:

  no bonds between 2 gas particles $\Rightarrow U_{micro} = 0$

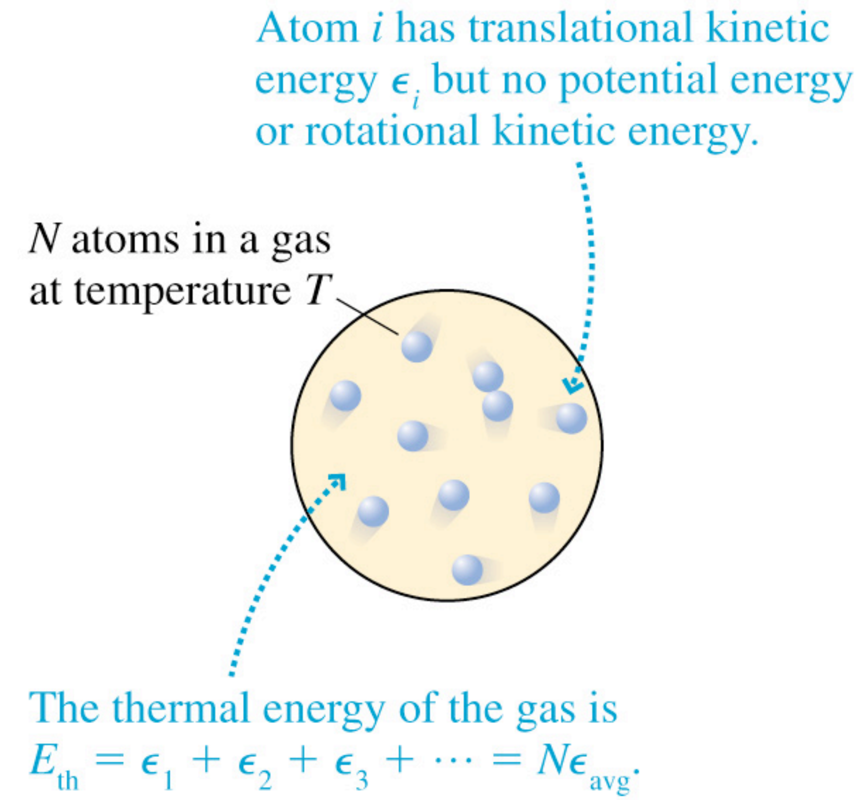
  $E_{th} = K_{micro} = \epsilon_1 + \epsilon_2 + ...\epsilon_N = N\epsilon_{avg}$

  Using $\epsilon_{avg} = \frac{3}{2}k_B T$, $E_{th} = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$ (thermal energy of a monotomic gas)

Equating $\Delta E_{th} = \frac{3}{2}nR\Delta T$ (microscopic: relate T to ϵ_{avg}) to $\Delta E_{th} = nC_V\Delta T$ (macroscopic: 1st law, i.e., $\Delta E_{th} = W + Q$ with $W = 0$ and definition of C_V),

- Macro/micro connection

$$C_V = \frac{3}{2}R = 12.5\ \text{J/mol K} \qquad \text{(monatomic gas)}$$



- agrees with experiment: (i) same for all monoatomic gases (ii) predict value

Equipartition Theorem

- 3 <u>in</u>dependent modes of energy storage

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_Z^2 = \epsilon_x + \epsilon_y + \epsilon_z$$

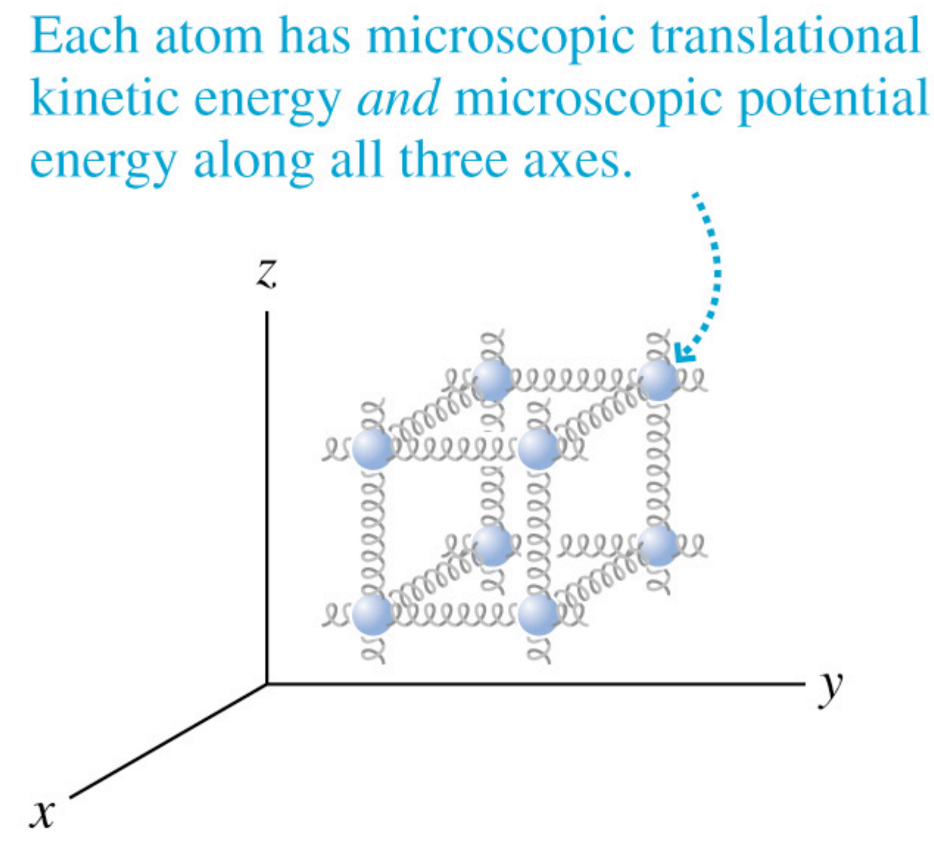
- other modes: 2 atoms vibrate (kinetic and potential); diatomic molecule can rotate (dumbbell)
- number of modes of energy storage: degrees of freedom
- statistical physics: thermal energy <u>equally</u> divided among all possible energy modes
- For N particles at temperature T, energy in each degree of freedom $= \frac{1}{2}Nk_BT = \frac{1}{2}nRT$

Solids

- 3 for vibrating + 3 for bonds compressing...

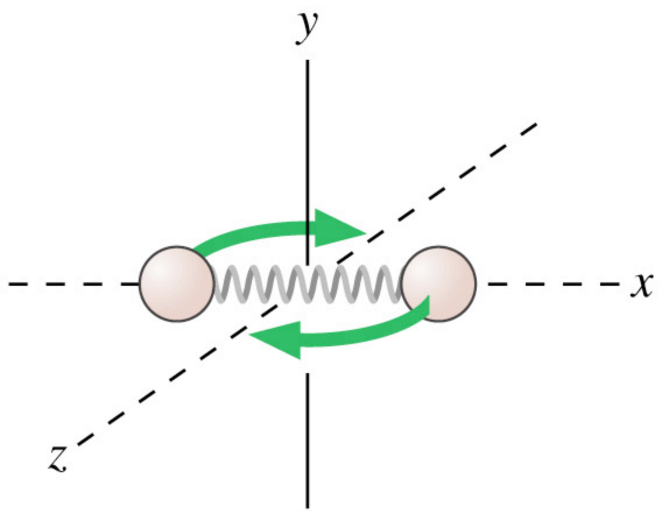
$$E_{th} = 3Nk_BT = 3nRT \quad \text{(thermal energy of a solid)}$$

Equating $\Delta E_{th} = 3nR\Delta T$ to $\Delta E_{th} = nC\Delta T$,
$C = 3R = 25.0$ J/mol/K

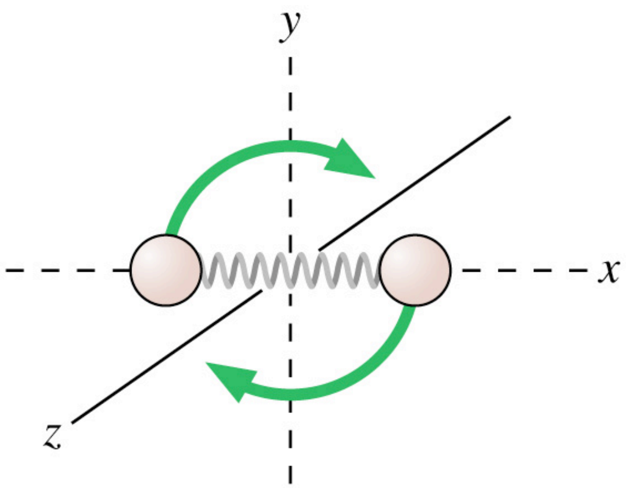


- agrees for elemental solids: not as much for gas: model not accurate + quantum effects

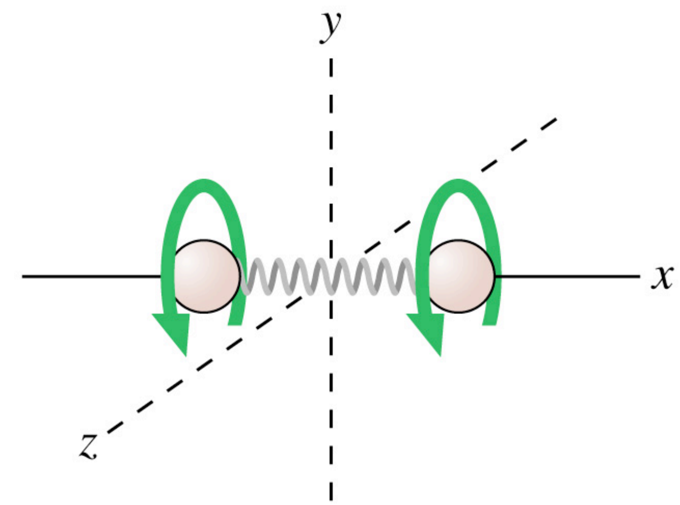
Diatomic molecules



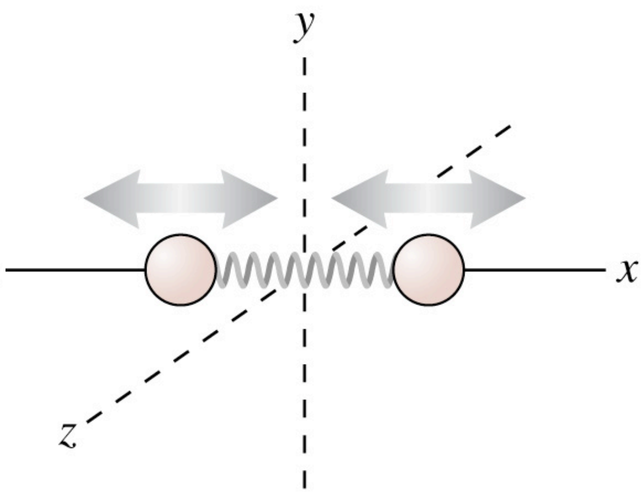
Rotation end-over-end about the y-axis



Rotation end-over-end about the z-axis



Rotation about its own axis



Vibration back and forth along the x-axis

- 3 for translational + 3 rotational + 2 vibrational d.o.f $\Rightarrow E_{th} = 4k_BT;\ C_V = 4R = 33.2$ J / mol / K?
  No! $C_V = 20.8$ J/mol/K $= \frac{5}{2}R \Rightarrow 5$ d.o.f.?
- classical Newtonian physics breaks down: quantum effects prevent 2 vibrational and 1 rotational mode from being active
- Usual T's

$$E_{\text{th}} = \frac{5}{2}Nk_BT = \frac{5}{2}nRT$$

$$C_V = \frac{5}{2}R = 20.8 \text{ J/mol K}$$

(diatomic gases)

only 3 translational

2 vibrational