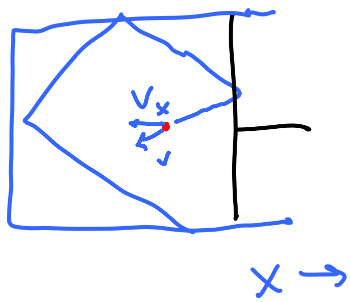
# Last Class

This is one of three model systems we will be using

- Ideal gas:

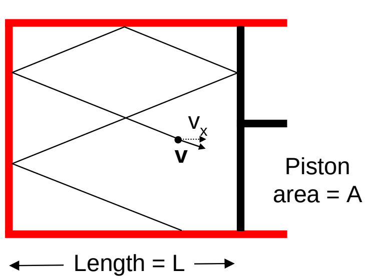
$$PV = nRT$$

$$PV = NkT$$




# Microscopic Model of Ideal Gas

- Assumptions
  - At any moment, the velocity of the molecule is **v** and the x-component is $v_x$
  - Collisions with the wall are always elastic (|v| is always constant)
  - Perfectly smooth surfaces: the molecule's path as it bounces is symmetrical about a line normal to the surface, just like bouncing light from a mirror



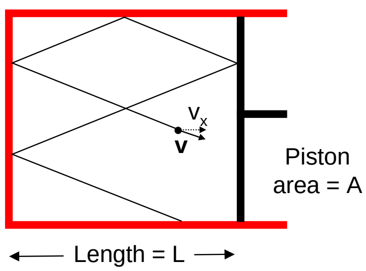

volume = L * A

# Microscopic Model of Ideal Gas

- What is the pressure of this molecule hitting the piston?

usually zero
except when molecule hits piston

Better question
→ what is average pressure?




# Ideal Gas Pressure

- Since pressure = force / unit area,

$$\bar{P} = \frac{\bar{f}_{x,\text{ on piston}}}{A} = -\frac{\bar{f}_{x,\text{ on molecule}}}{A}$$

$$f = m \cdot \left(\frac{\overline{\Delta v_x}}{\Delta t}\right)$$

$$\bar{P} = -\frac{m}{A}\left(\frac{\overline{\Delta v_x}}{\Delta t}\right)$$

take $\Delta t = 2L/v_x$

$$\Delta v_x = (-v_x) - (v_x) = -2v_x$$

$$\bar{P} = -\frac{m}{A}\left(\frac{-2v_x}{2L/v_x}\right) = \frac{m v_x^2}{A \cdot L} = \frac{m v_x^2}{V}$$

for N molecules

$$\overline{P}V = mv_{1x}^2 + mv_{2x}^2 + \ldots\ldots$$

$$PV = NkT = Nm\overline{v_x^2}$$

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT$$

# Energy versus Temperature

- Considering all three directions (x, y, z):

$$\overline{K}_{trans} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m\left(\overline{v_x^2 + v_y^2 + v_z^2}\right) = \frac{1}{2}m\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right)$$
$$= \frac{3}{2}kT$$

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- The temperature of a gas is proportional to the average translational kinetic energy of its molecules
- Boltzmann constant: A conversion factor between temperature and energy
  - At room temperature:
    $kT = (1.38 \times 10^{-23}$ J/K) (300 K) = $4.14 \times 10^{-21}$ J ← small energy for one molecule
  - An electron volt is the kinetic energy of an accelerated electron through a voltage difference of 1 volt
    (1 eV = $1.6 \times 10^{-19}$ J)
  - In eV, $kT = (8.62 \times 10^{-5}$ eV/K)(300 K) = 0.026 eV
    $\cong$ 1/40 eV

# Equipartition theorem

- At temperature T, the average energy of any quadratic degree of freedom is ½ $kT$
- For $N$ molecules,

number of molecules

degrees of freedom

$$U_{thermal} = N \cdot f \cdot \frac{1}{2}kT$$

total thermal energy

# Equipartition theorem

- At temperature T, the average energy of any quadratic degree of freedom is ½ $kT$
- For $N$ molecules,

$$U_{thermal} = N \cdot f \cdot \frac{1}{2} kT$$

- Quadratic degrees of freedom: forms of energy for which the formula is a quadratic function of a coordinate or velocity component

eg. $\frac{1}{2} m v_x^2$, $\frac{1}{2} I \omega_x^2$, $\frac{1}{2} k_s x^2$

- For monatomic gas particles, like helium gas

$f = 3 \rightarrow$ only translational motion in x, y, z

# More on equipartition of energy

- This is only for the thermal energy of the molecule
  - There are other types of energy in chemical bonds, rest mass energy ($mc^2$) etc.

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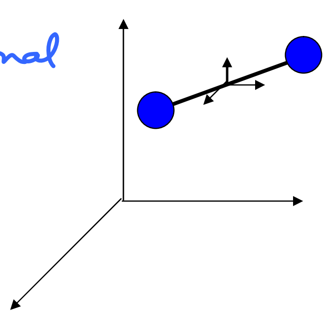
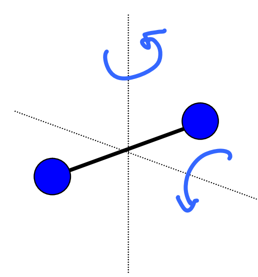
- This is only for the thermal energy of the molecule
  - There are other types of energy in chemical bonds, rest mass energy ($mc^2$) etc.
- How do we count the number of degrees of freedom?
  - No so easy.
  - A monatomic gas has three translational degrees of freedom (it can move in the x, y, and z directions), but no rotational degrees of freedom.
  - Quantum mechanics tell us so..
  - Semiclassically, if you consider an atom as a point-like object, it cannot have rotational inertia

# Diatomic molecule (rotation)

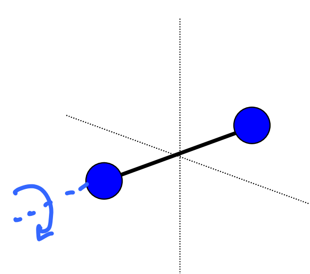
- Diatomic molecules such as $O_2$ or $N_2$ have two rotational degrees of freedom in addition to three translational degrees of freedom

translational
x, y, z





2 rotational degrees of freedom

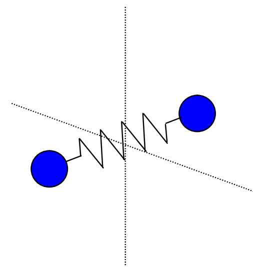


rotation about 3rd axis not counted

# Diatomic molecule (vibration)

- Two vibrational degrees of freedom

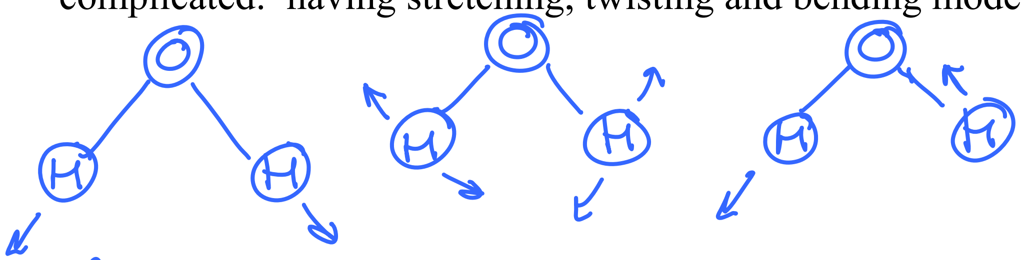
- $E_{total} = KE + PE$
  $= \frac{1}{2} mv^2 + \frac{1}{2} k_s x^2$
  (2 quadratic terms!)



kT contribution
for vibration

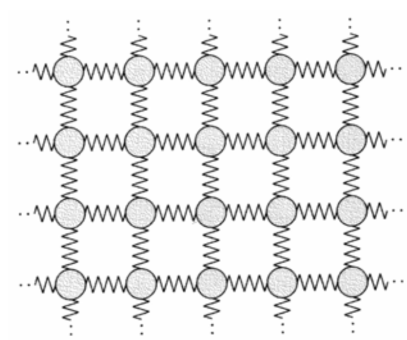
# Polyatomic molecules and solids

- Polyatomic molecules, such as $H_2O$ or $CO_2$, can get very complicated: having stretching, twisting and bending modes



fundamental modes

- Solids: each atom can vibrate in three directions
  – Giving six degrees of freedom per atom



3-D lattice

# Heat capacity

- Definition: The amount of heat needed to raise the temperature of an object, per degree temperature increase

accounts for work done by system

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

- The more the volume changes, the larger $C_P$ will be
- For solids and liquids, $\partial V/\partial T$ is usually small, but for gases it can be quite large.

# Heat capacity

- Example:
  - Suppose our system stores thermal energy only in quadratic degrees of freedom. Then, by the equipartition theorem:

$$U = \tfrac{1}{2} N f k T \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{Nfk}{2}$$

- For a monatomic gas, like He, $f$=3, so $C_V$ = 3/2 Nk = 3/2 nR (Usually, it is written per mole, $C_V$ = 3/2 R = 12.5 J/K)

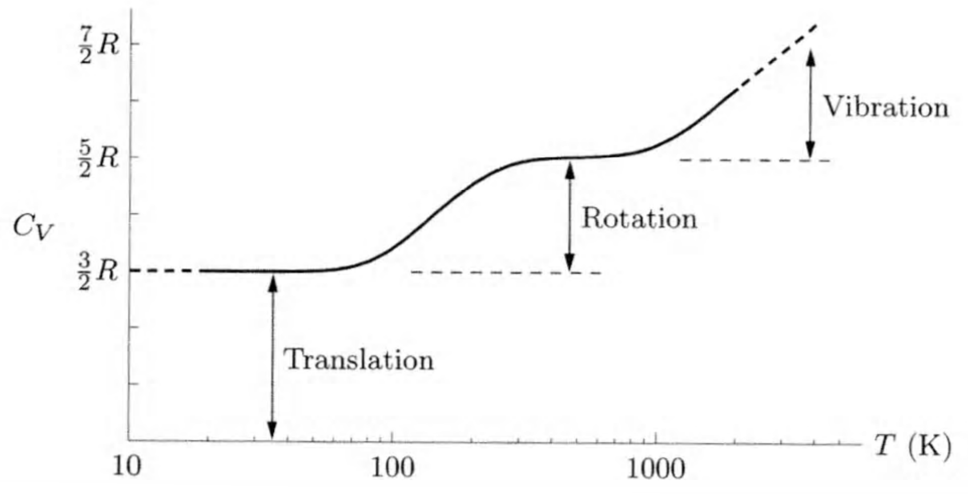
what about diatomic gas?

$C_V = \frac{7}{2} R$ per mole?

depends on temperature of system.

## Frozen degrees of freedom

- Example of $H_2$ molecule

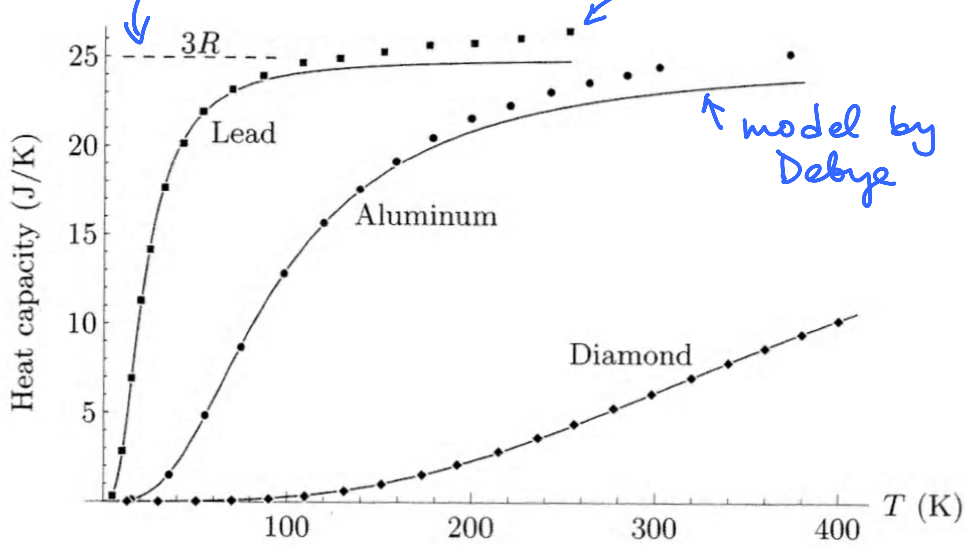



- Need Quantum and Statistical Mechanics!

## Another example

- For solids, $f$=6, $C_V$ = 3 R (per mole)
- Dulong and Petit Law

as measured




model by Debye