Typical Usage for the Ideal Gas Law

- For a fixed amount of gas (nR=const)

$$\frac{PV}{T} = nR = const$$

- So, if we have a gas at two different states 1(before) and 2 (after), their state variables are related simply by:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

We can use this relation to solve for any unknown variables with the others being given.

Example 18.2

In an automobile engine, a mixture of air/gasoline is being compressed before ignition.

- Typical compression ration 1 to 9
- Initial $P = 1$ atm and $T = 27\ ^{o}C$

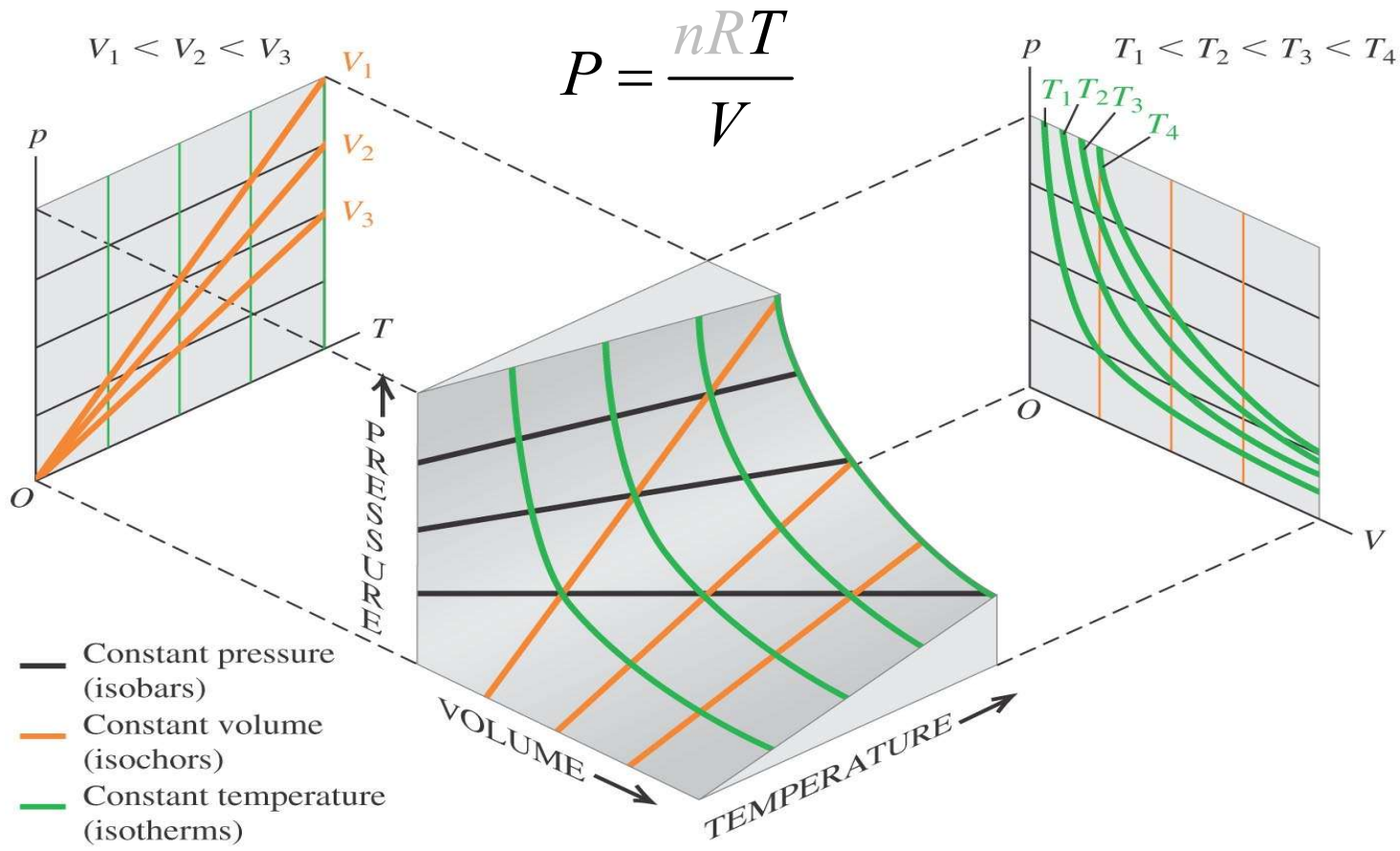
note

Find the temperature of the compressed gas if we are given the pressure after compression to be 21.7atm.

http://complex.gmu.edu/www-phys/phys262/soln/ex18.2.pdf

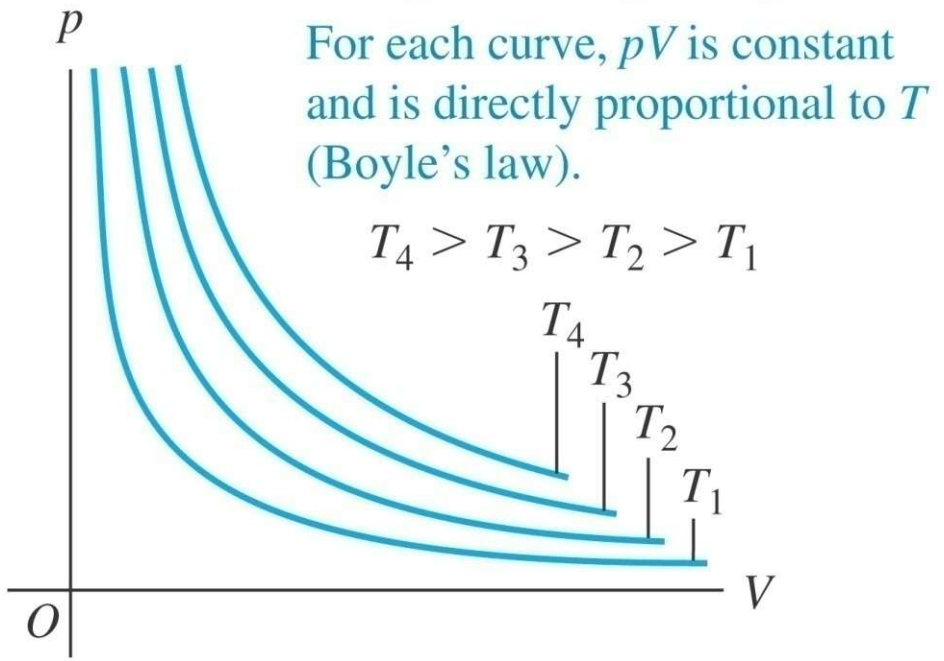
The Ideal Gas Law (graphical view)

P, V, T relationship in the Ideal Gas Law can be visualize graphically as a surface in 3D.



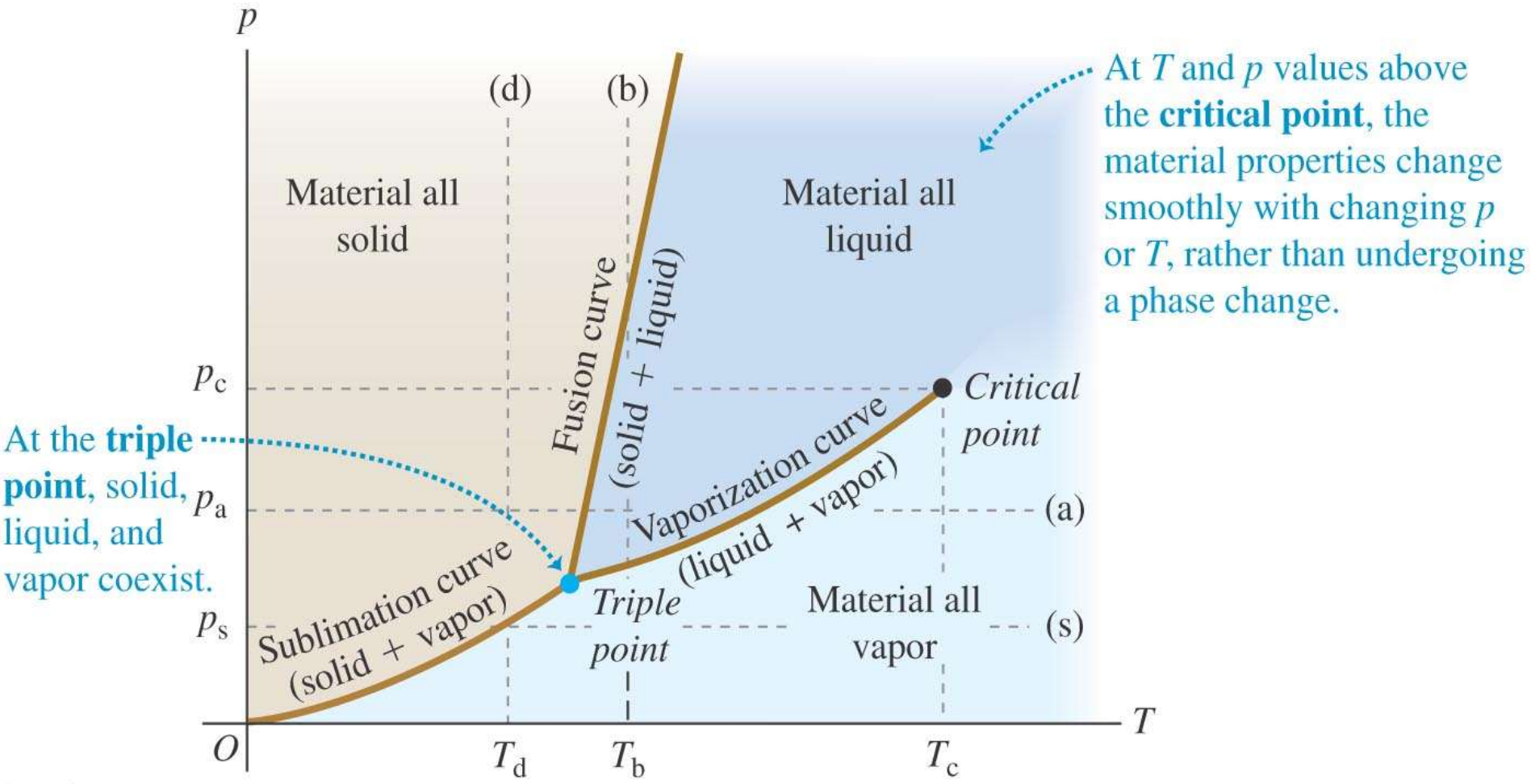
PV Diagrams

- 2D projections of the previous 3D surface.
- Evolution of a gas at *constant T* will move along these curves called *isotherms*.



Gives P vs. V at a various T: $P = (nRT)\frac{1}{V}$

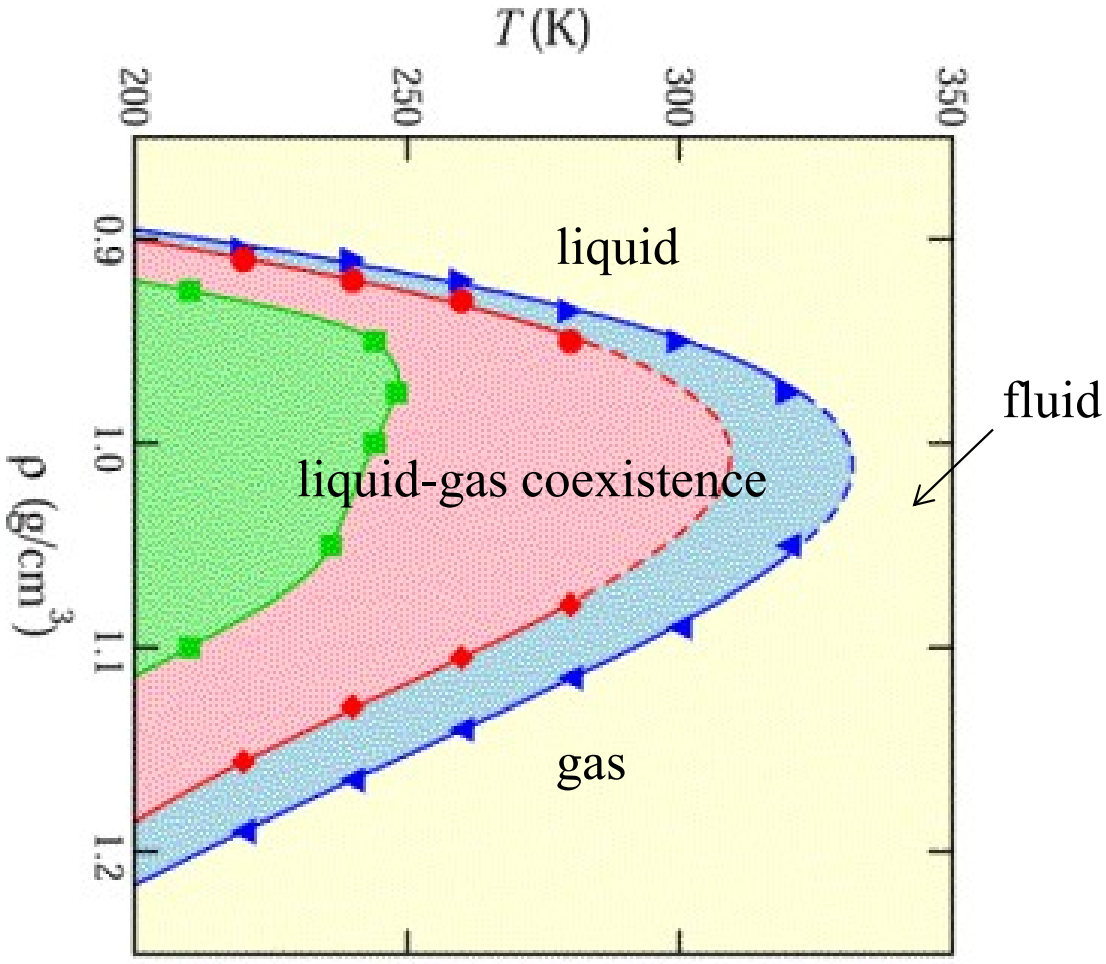
Phases of Matter (reading phase diagrams)



video

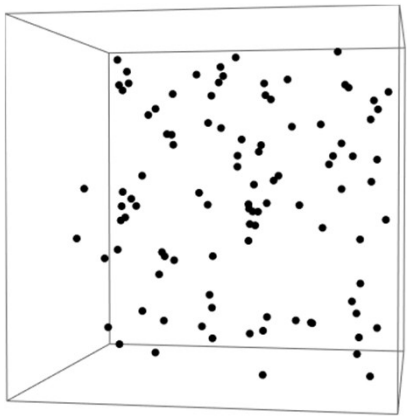
https://www.youtube.com/watch?v=ei8V5cWZebU

Critical Point and Liquid-Gas Coexistence



Kinetic-Molecular Model of an Ideal Gas

Macroscopic description of gases



Microscopic description of gas molecules

P, V, T
Ideal Gas Law

Kinetic Theory

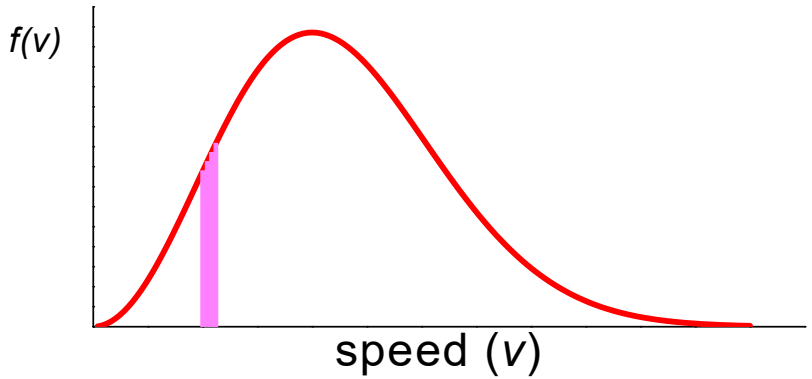
v, **p**, **F**, KE
Newton's Eqs

- An example of a successful theoretical linkage between the "micro" and "macro" descriptions for an ideal gas.
- Explicit expressions of *P* & *T* in terms of microscopic quantities!

Kinetic Theory (assumptions)

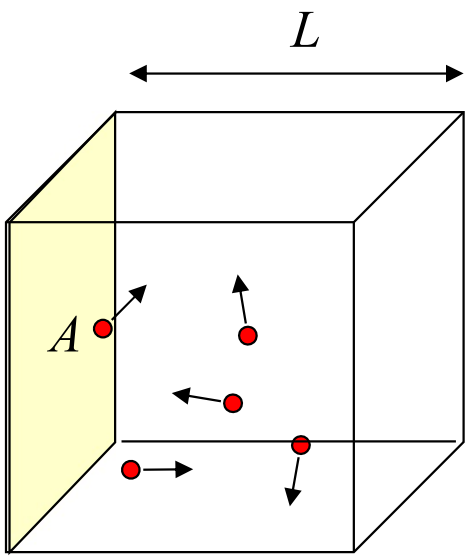
- A very *large # N* of *identical* molecules each with mass *m* in a container with volume *V*
- Molecules behaves as *point particles*:
  - Molecule sizes << avg separate bet particles & dim of container
- Molecules moves according to Newton's laws and they move randomly with equal probability in all directions and with a fixed **distribution** *f(v)* (histogram) of speed *v*

  "Fraction of molecules moving in a given range of speeds stays the same"

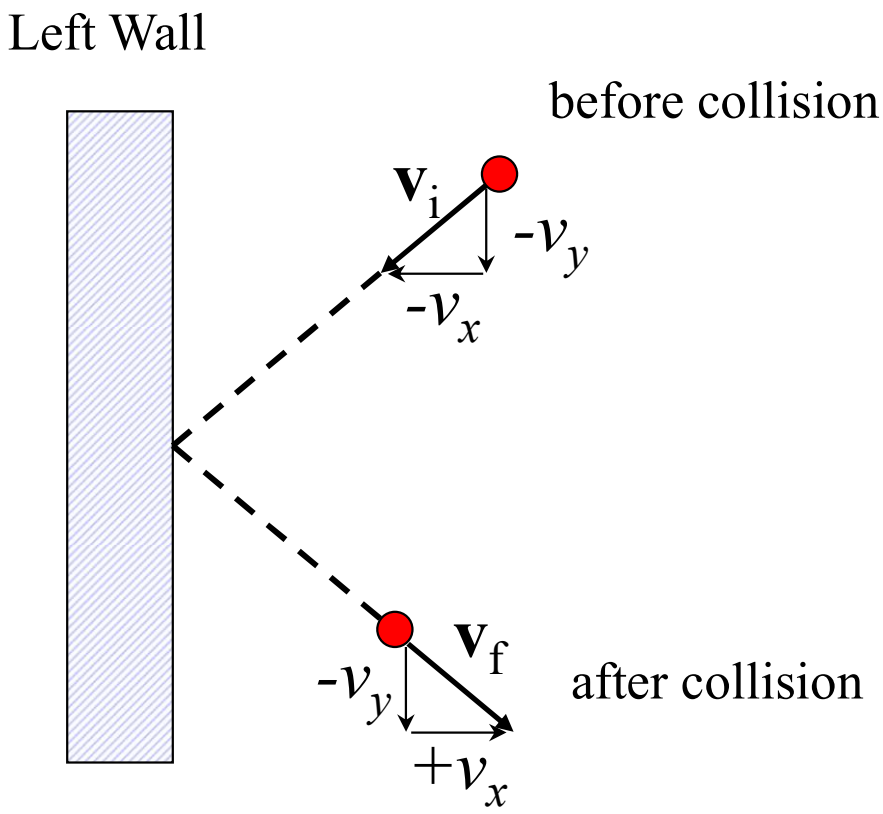


- Molecules interact only with the walls thru elastic collisions and the container walls are perfectly rigid and infinitely massive
  - → both KE and momentum are conserved

Kinetic Theory (model)



Idea Gas in a box with $V=AL$



- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

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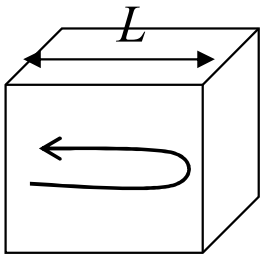
Pressure Exerted by an Ideal Gas

"Pressure on the left wall due to molecular collisions"

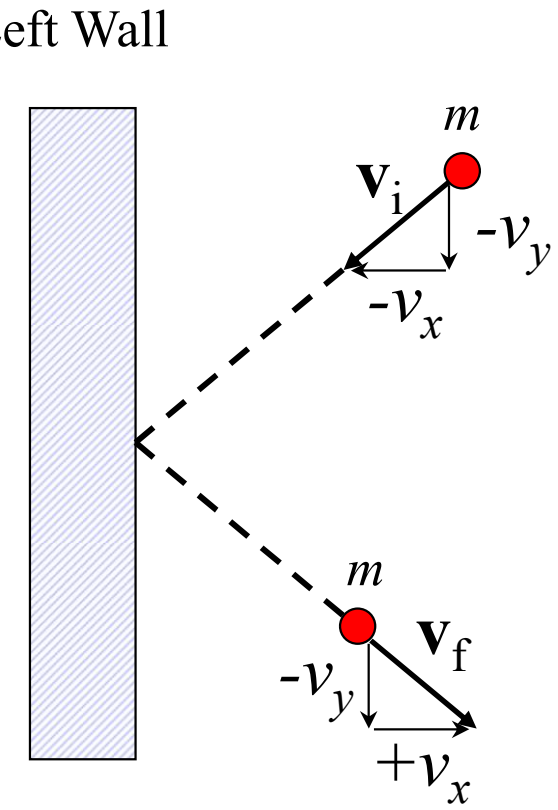
1. Momentum change in x-dir by a molecule moving to the left at $\mathbf{v}_i$:

$$\Delta(m\mathbf{v}) = P_f - P_i = mv_x - (-mv_x) = 2mv_x$$

2. Duration, Δt, that this molecule takes (on average) to collide with the left wall again (diluted gas),



$$\Delta t = \frac{2L}{v_x}$$



Pressure Exerted by an Ideal Gas

3. Force exerted by this molecule on the left wall:

$$F = \frac{\Delta(m\mathbf{v})}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

4. With N molecules, total force on wall in Δt:

$$F_{tot} = \sum_{i=1}^{N} F_i = \frac{m}{L}\left(v_{1x}^2 + v_{2x}^2 + \cdots + v_{Nx}^2\right)$$

$$= \frac{m}{L} N \left(\frac{1}{N}\sum_{i=1}^{N} v_{ix}^2\right) = \frac{mN}{L}\left(v_x^2\right)_{av} \qquad Note: \quad \left(v_x^2\right)_{av} \neq \left(v_x\right)_{av}^2$$

→ Fixed *Invariant* distribution implies $(\bullet)_{av}$ will be the same when experiment is repeated.

Pressure of an Ideal Gas

5. Random direction (isotropic) assumption:

   $(v_x^2)_{\text{av}} = (v_y^2)_{\text{av}} = (v_z^2)_{\text{av}}$ (x, y, z are the same)

   Since $v^2 = \|\vec{v}\|^2 = v_x^2 + v_y^2 + v_z^2$, we have $(v^2)_{\text{av}} = 3(v_x^2)_{\text{av}}$

   This gives, $F_{tot} = \frac{mN}{L}\frac{(v^2)_{av}}{3}$

6. Finally, the pressure on the wall is:

$$P = \frac{F_{tot}}{A} = \frac{mN}{AL}\frac{(v^2)_{av}}{3} = \frac{1}{3}\frac{Nm(v^2)_{av}}{V}$$

Pressure of an Ideal Gas

Rewriting, we have

(avg trans. KE per molecule)

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \left(v^2 \right)_{av} \right) = \frac{2}{3} N \left(KE \right)_{av}$$

- This tells us that P inside a container with a fixed V:
  - is proportional to the # of molecules N
  - is proportional to the **avg.** translational KE of molecules

(These are microscopic properties of the gas.)

Molecular Interpretation of Temperature

From before: $PV = \frac{2}{3} N \left(KE \right)_{av} \left(= \frac{2}{3} K_{tr} \right)$

From Idea Gas Law: $PV = NkT$ (Recall k – Boltzmann Constant)

For both of these to be true, we need to have: $\frac{2}{3} \cancel{N} \left(KE \right)_{av} = \cancel{N} kT$

$$\left(KE \right)_{av} = \frac{3}{2} kT \quad \text{(per molecule)}$$

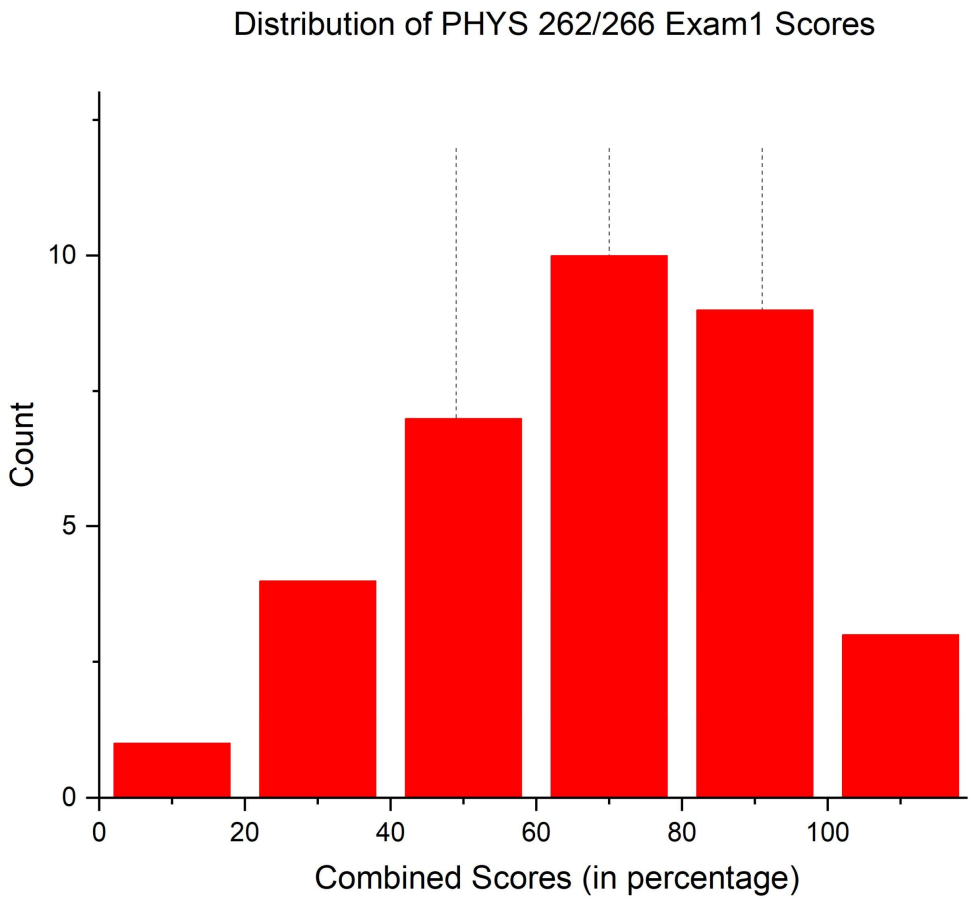
$K_{tr} = \frac{3}{2} NkT$ (all molecules in V)

(Note: K_{tr} in your book is the avg *total* *KE* for **all** molecules in volume *V*.)

"Temperature is a direct measure of the **average** translational KE of the molecules in an ideal gas."

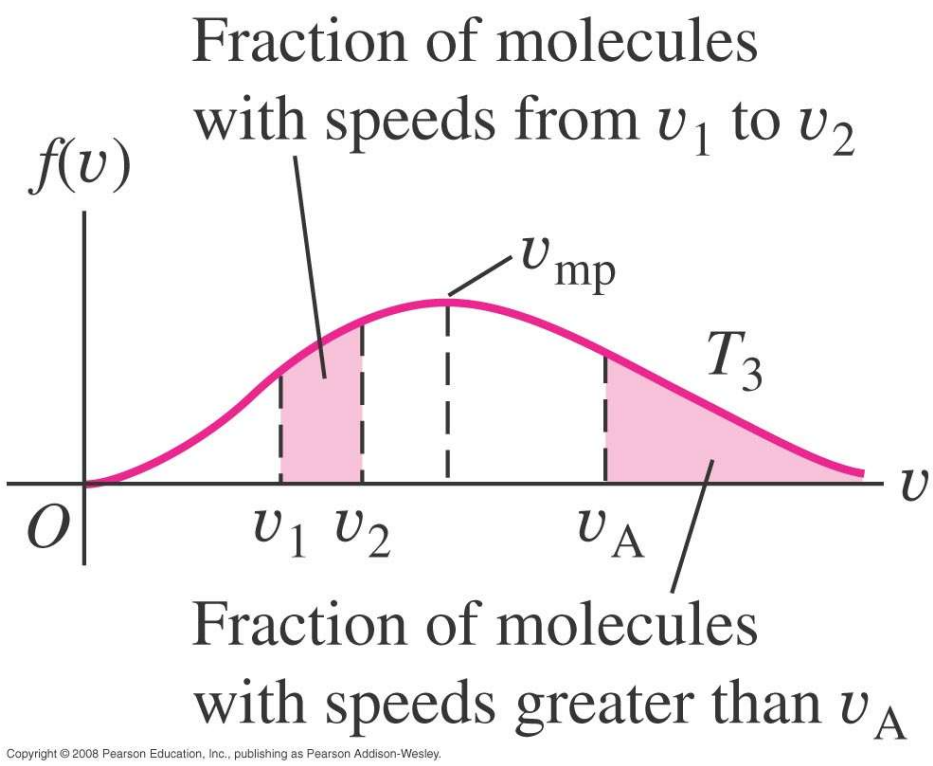
Histogram and Distribution

We all are familiar with the concept of using a histogram to represent a collection of different test scores.



Distribution of Molecular Speeds

- Within an ideal gas, molecules moves with a diversity of speeds
- A mathematical rigorous way to describe this statistically is thru a **distribution function** $f(v)$.
- Properties:
  - $f(v) \sim 0,\ v \sim 0$
  - $f(v) \rightarrow 0,\ v \rightarrow$ *large*
  - $f(v)$ *largest at mid-range*
  - $f(v)$ *fixed in time*



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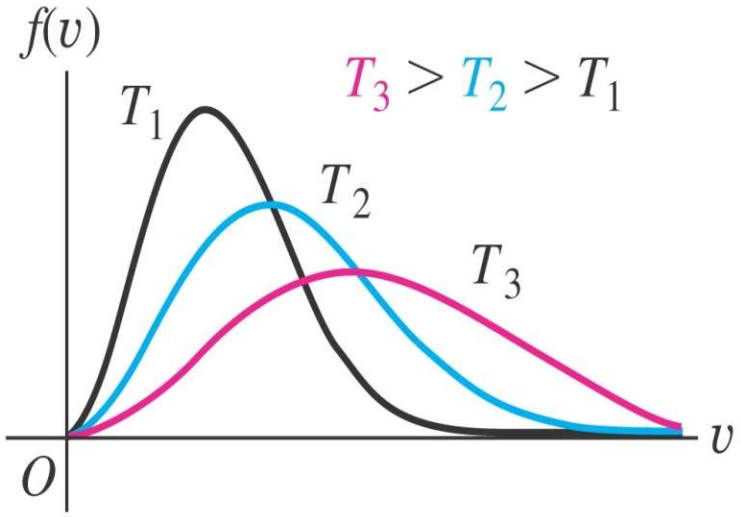
Maxwell-Boltzmann Distribution

$$f(\upsilon) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \upsilon^2 e^{-m\upsilon^2/2kT}$$



As temperature increases:
- the curve flattens.
- the maximum shifts to higher speeds.

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- $f(v)\mathrm{d}v$ gives the probability of finding molecules with speed in range $[v, v+\mathrm{d}v]$.
- Diff averages with respect to the distribution of molecular speeds can be calculated using $f(v)$:

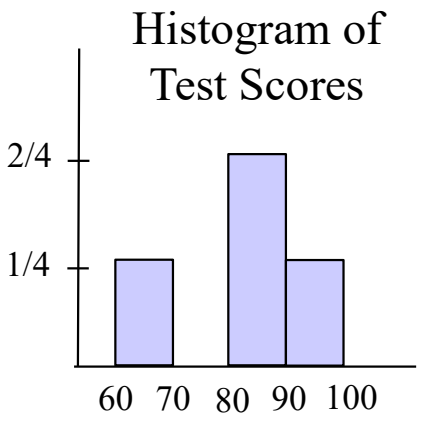
1. $v_{av} = \int_0^\infty v f(v) dv$ (avg of v)

2. $(v^2)_{av} = \int_0^\infty v^2 f(v) dv$ (avg of v^2)

Example: Test Scores

4 Test Scores: $s_i = \{65, 80, 80, 95\}, i = 1, \cdots, 4$

Simple Avg: $$s_{av} = \frac{1}{N}\sum_{i=1}^{N} s_i = \frac{1}{4}(65 + 80 + 80 + 95)$$



$$s_{av} = \frac{1}{4}(65) + \frac{2}{4}(80) + \frac{1}{4}(95) = 80$$

weighted average

$$s_{av} = \sum f_i s_i$$

where f_i gives the fraction of occurrence of s_i

$$v_{av} = \int_0^{\infty} f(v) v dv$$

where $f(v)dv$ gives the fraction of molecules moving with speed $[v, v + dv]$

Example: Test Scores

4 Test Scores: $s_i = \{65, 80, 80, 95\}, i = 1, \cdots, 4$

Simple Avg: $\left(S^2\right)_{av} = \frac{1}{N}\sum_{i=1}^{N} s_i^2 = \frac{1}{4}\left(65^2 + 80^2 + 80^2 + 95^2\right)$

$$\left(S^2\right)_{av} = \frac{1}{4}\left(65^2\right) + \frac{2}{4}\left(80^2\right) + \frac{1}{4}\left(95^2\right) = 6512.5$$

$$\left(S^2\right)_{av} = \sum f_i s_i^2 \quad \neq \quad \left(S_{av}\right)^2 = 80^2 = 6400$$

$$(v^2)_{av} = \int_0^{\infty} f(v) v^2 dv \neq (v_{av})^2$$

Statistical Description of Molecular Speed

- Average speed (mean value): $v_{av} = \sqrt{\frac{8kT}{\pi m}}$

- Root Mean Square (RMS) speed: $v_{rms} = \sqrt{\left(v^2\right)_{av}} = \sqrt{\frac{3kT}{m}}$

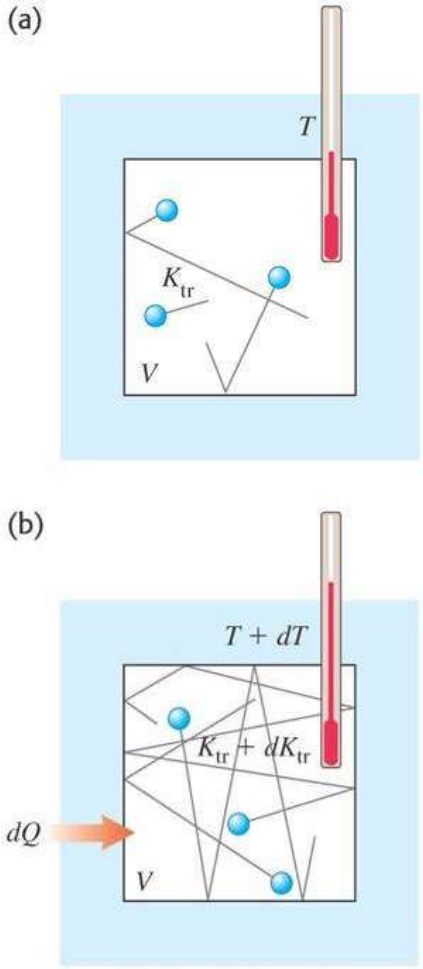
  Note: v_{av} does not equal v_{rms} !

In addition to simple "mean" and "median", there are other ways to statistically describe the "average" values for a distribution of molecules moving at different speeds!

- Most Probable Speed - the maximum value of the distribution function $f(v)$:

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

Heat Capacities of Gases (at constant V)



Using the Kinetic-Molecular model, one can calculate heat capacity for an *Ideal Gas*!

- For point-like molecules (monoatomic gases), molecular energy consists only of translational kinetic energy K_{tr}
- We just learned that K_{tr} is directly proportional to T.
- When an infinitesimal amount of heat dQ enters the gas, dT increases, and dK_{tr} increases accordingly,

$$dK_{tr} = \frac{3}{2} NkdT \quad (or = \frac{3}{2} nRdT)$$

Heat Capacities of Gases

- From definition of molar heat capacity, we also know:

$$dQ \equiv nC_v dT$$

- From mech-equivent of heat, requiring $dQ = dK_{tr}$ (*no work*) gives,

$$nC_v dT = \frac{3}{2} nRdT$$

- *Monatomic* ~ Ideal Gas

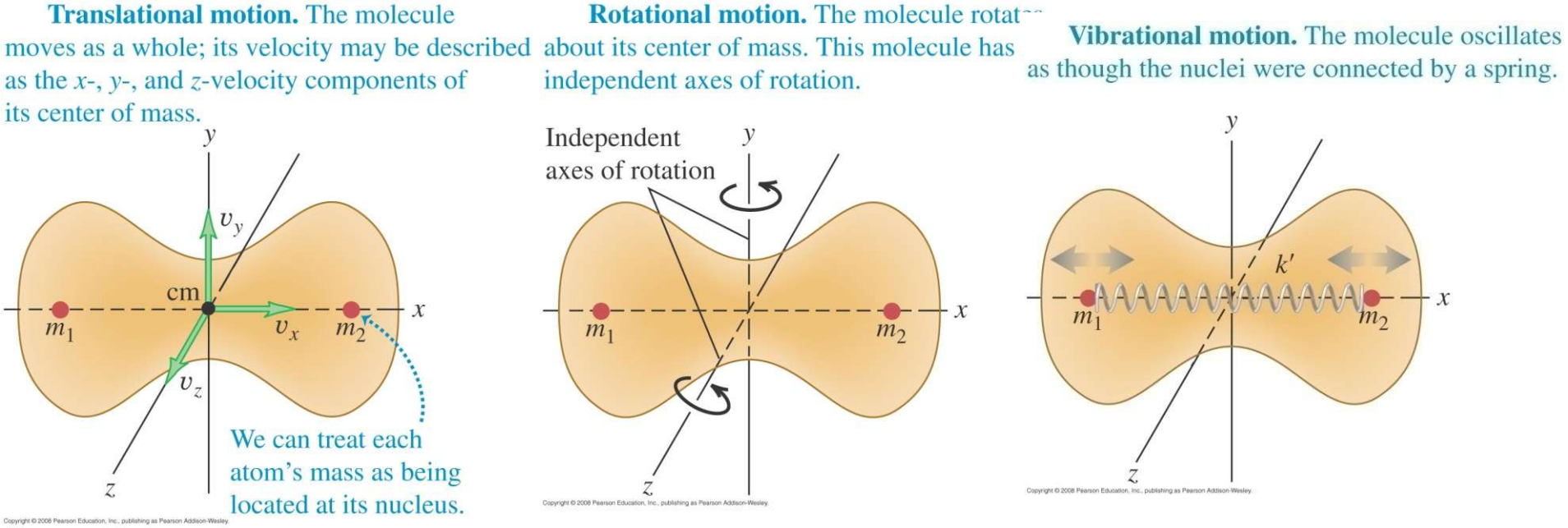
(matches well with prediction)

$$\Rightarrow \quad C_v = \frac{3}{2} R \quad (= 12.47 J/mol \cdot K)$$

Table 18.1 Molar Heat Capacities of Gases

Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O_2	21.10
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

Heat Capacity (diatomic)



A *diatomic* molecule can absorb energy into its translational motion, its rotational motion and in its vibrational motions.

Equipartition of Energy

This principle states that each **degree of freedom** ("separate mechanisms in storing energy") will contribute (½ kT) to the total average energy per molecule.

- Monoatomic: 3 translational dofs → 3 (½ kT)

  This give E_{tot}= 3/2 NkT (same as before).

- Diatomic (*without* vibration): 3 trans dofs + 2 rotational dofs

  This give E_{tot}= 5/2 NkT or = 5/2 nRT.

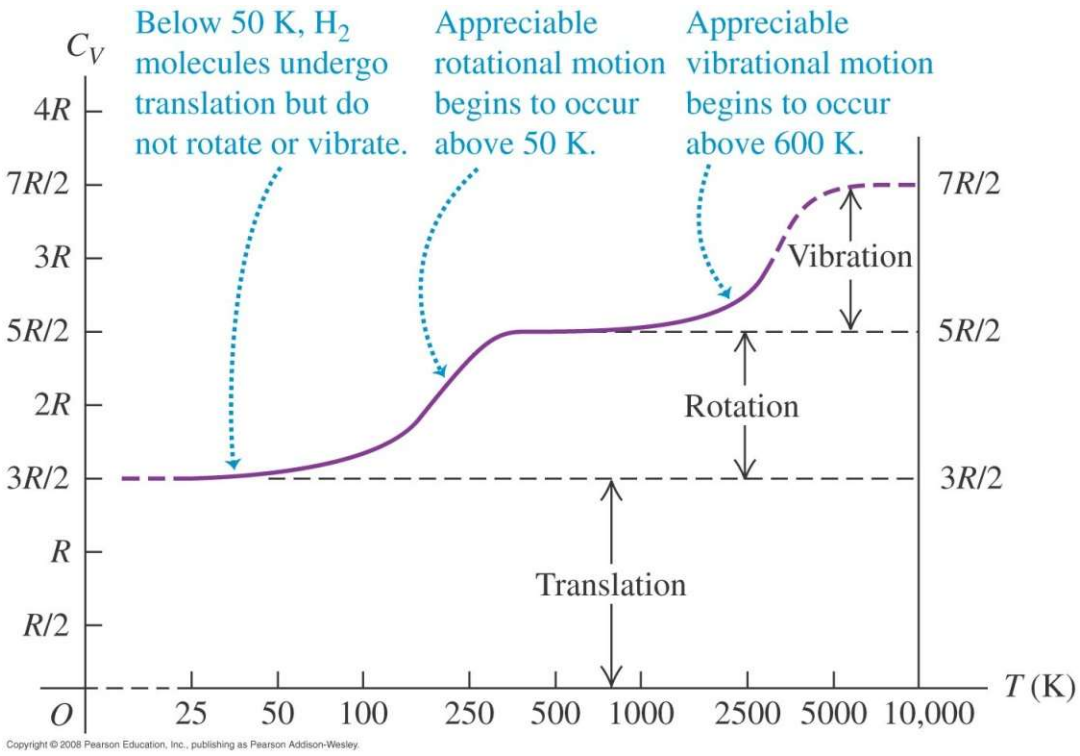
  Again, consider an infinitesimal energy change, we have

  $nC_v dT = \frac{5}{2} nRdT$, and this gives $C_v = 5/2\ R$.

Heat Capacities (real gases, e.g., H_2)

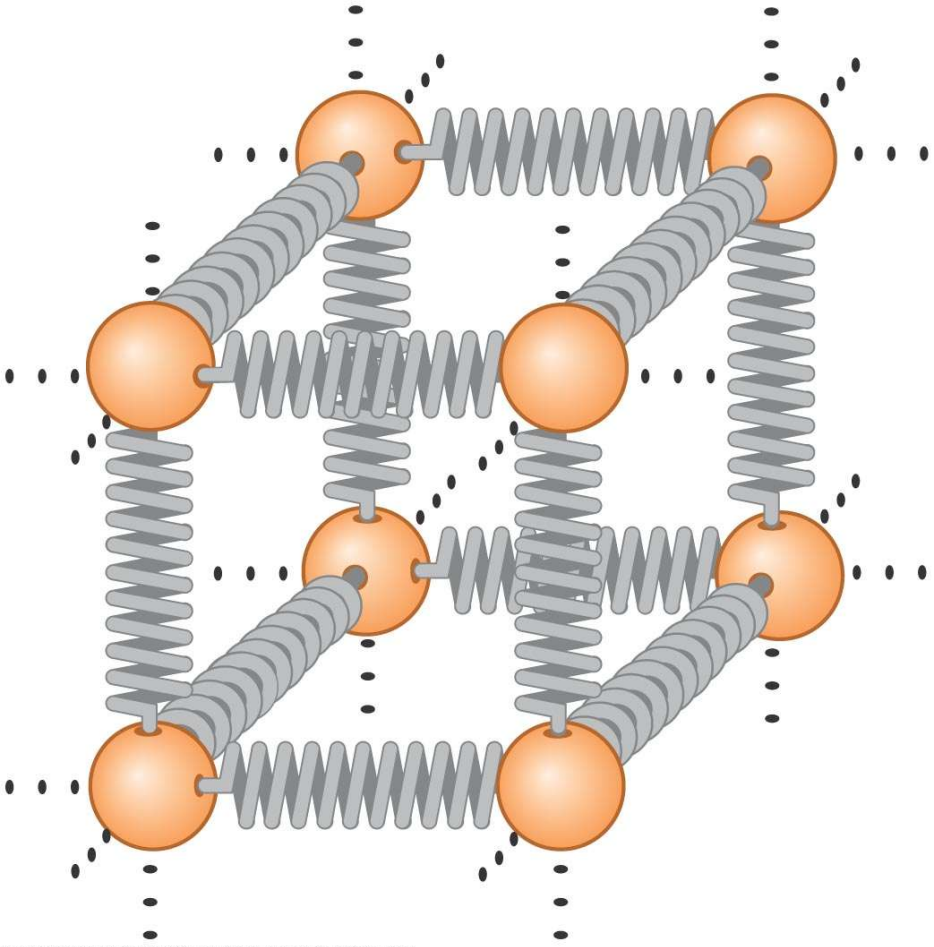
- At low T, only 3 translational dofs can be activated
- At higher T, additional rotational dofs can be activated
- At higher T still, vibrational dofs might also get activated

Heat capacity for a H_2 gas



→ For normal T range, one take $C_v = \frac{5}{2}R$ for H_2 gas

Heat Capacities of Ideal Solids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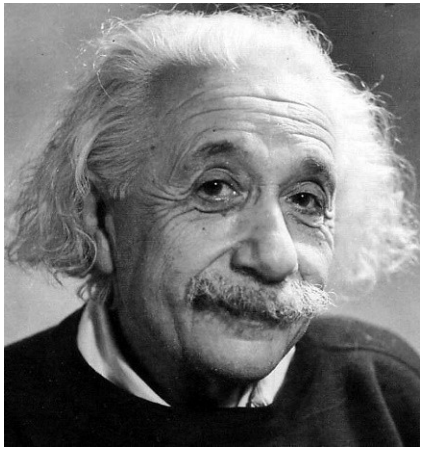
- Atoms are connected together by springs
- Assume harmonic motions for these springs (Hooke's law)
- For each spatial direction, there are two dofs (vibrational KE, vibrational PE) and we have 3 dims
- For the entire solid, we have 3/2 kT (KE) + 3/2 kT (PE) → $E_{tot} = 3kT$

→ $C_v = 3R$

Dulong Petit Prediction and Improvements

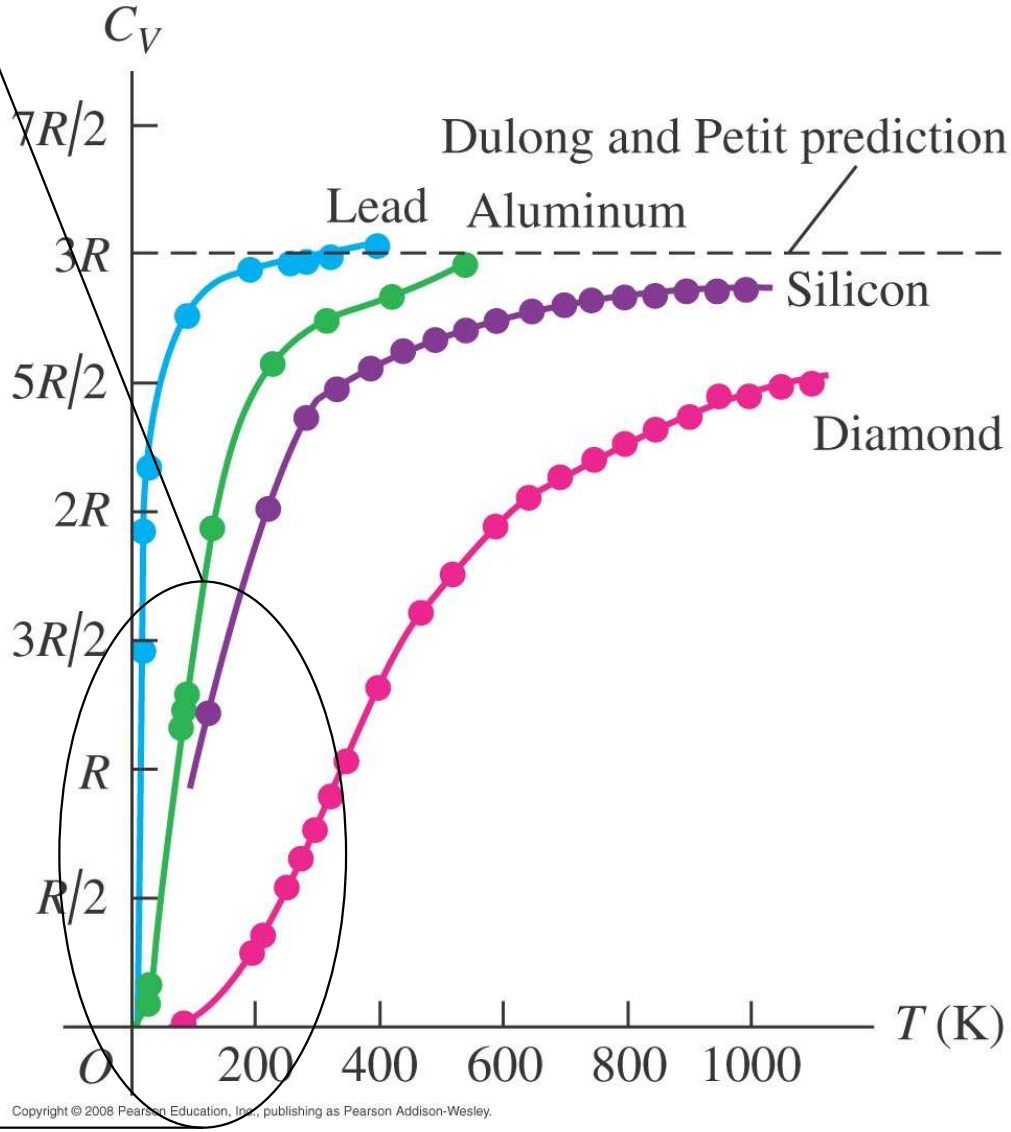


Einstein: treating atoms as QM HMOs…

$$C_v \to 0$$

Debye: extension by including low-*f* phonons…

$$C_v \sim T^3$$



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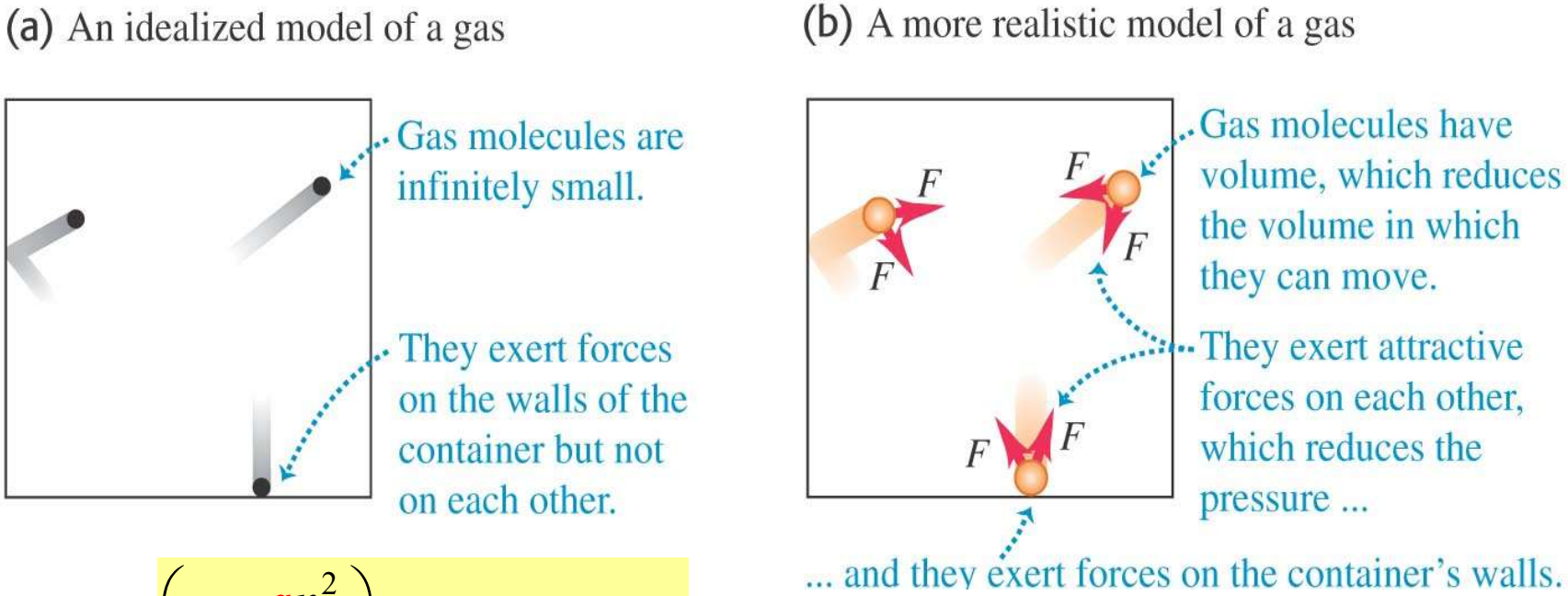
The van der Waals Equation

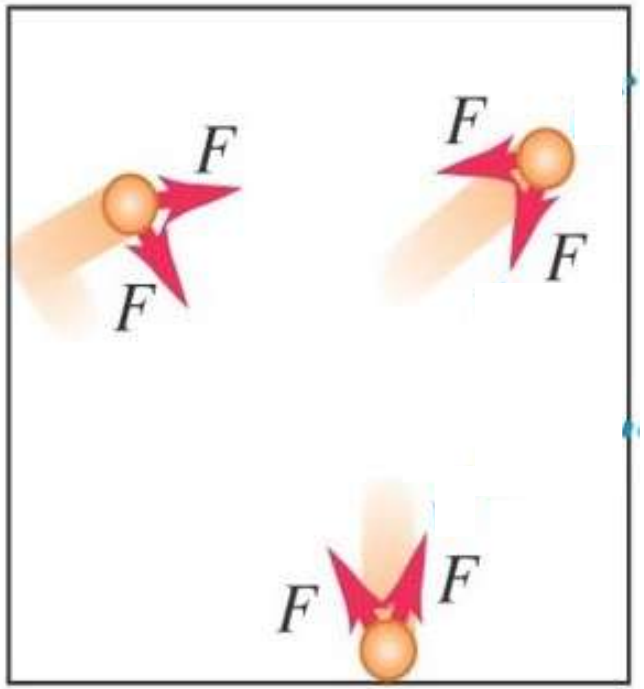
A more realistic Equation of States for gases which includes corrections for the facts that molecules are not point particles, that they have volume, and for the attraction/repulsion that naturally exists between the adjacent atoms/molecules.



$$\left(P+\frac{an^2}{V^2}\right)\left(V-bn\right)=nRT$$

Notes on Van Der Waals

- The volume parameter *b*:
  - It makes sense that real gas as finite size hard spheres will reduce the total volume of the gas by a term which is proportional to the number of mole *n*.

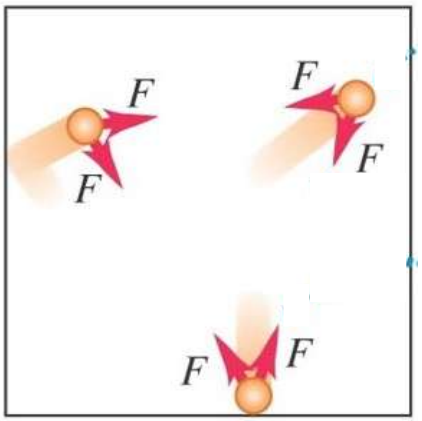


$$P = \frac{nRT}{V_{eff}} = \frac{nRT}{(V - bn)}$$

Notes on Van Der Waals

- The intra-molecular force parameter *a*:
  - Intra-molecular force tends to *reduce* the pressure of the gas onto the wall by pulling the molecules toward the interior of the container
  - This intra-molecular force acts in pairs (to the lowest order of approximation)

    → depends on the number of *pairs* of molecules within this unit volume
  - For N molecules, # pairs = $N(N\text{-}1)/2$; for N large, ~ N^2
    The count of molecular pairs (in mole) within an unit volume ~ $(n/V)^2$



$$P = \frac{nRT}{(V - nb)} - a\left(\frac{n}{V}\right)^2$$

$$\rightarrow \quad \left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$