PHYS 262/266

George Mason University

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Chapter 18: Thermal Properties of Matter

Topics for Chapter

- Equations of State
- Ideal Gas Equation
- PV Diagrams
- Kinetic-Molecular Model of an Ideal Gas
- Heat Capacities
- Distribution of Molecular Speeds

Equations of State

- State Variables

  → physical variables describing the macroscopic state of the system:

  $$P,\ V,\ T,\ n \text{ (or } m\text{)}$$

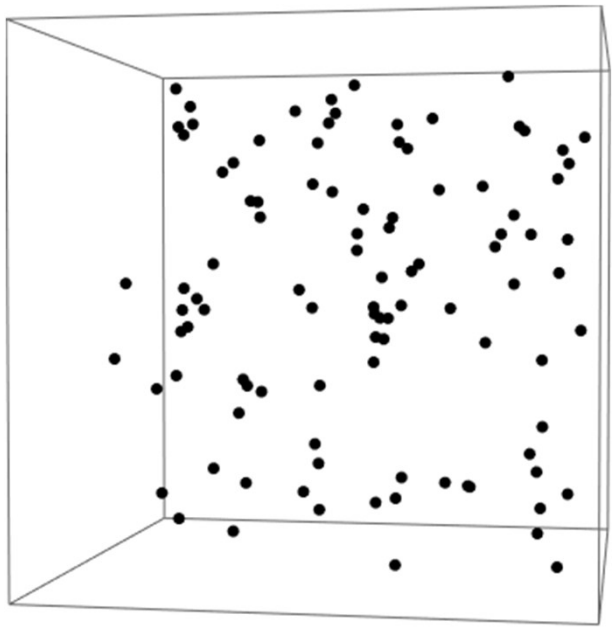
- Equation of State

  → a mathematical relationship linking these variables

Ideal Gas Law

- An Ideal Gas (diluted):
  - No molecular interactions besides elastic collisions
  - Molecular volume <<< volume of container

Most everyday gases ~ Ideal!



$$PV = nRT \qquad \text{OR} \qquad PV = NkT$$

$$R = 8.314 J/mol \cdot K$$

T has to be in K!

$$k = \frac{R}{N_A} = 1.381 \times 10^{-23} J/molecule \cdot K$$

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.

Molecular Interpretation of Temperature

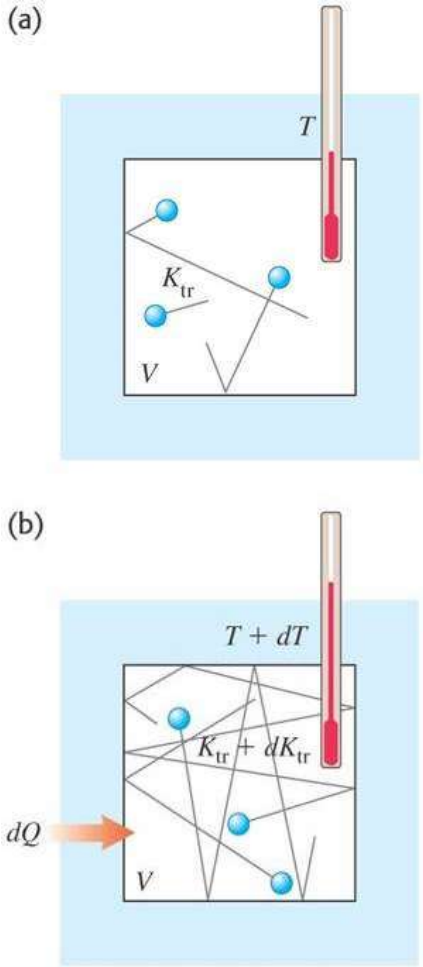
From Kinetic Theory for an Ideal Gas,

We linked the *average KE* of the molecules in the temperature T of the gas:

$$(KE)_{av} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT \quad \text{(per molecule)}$$

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

Heat Capacities of an Ideal Gas (at constant V)

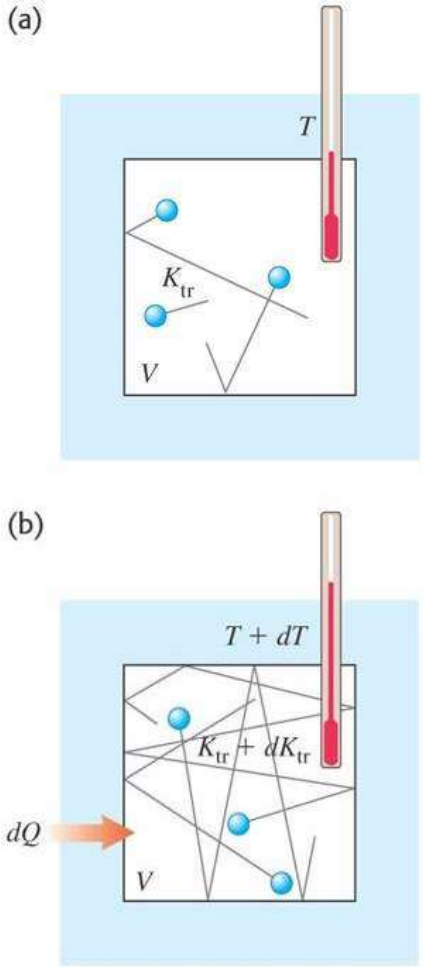


Using the Kinetic-Molecular model, one can calculate heat capacity for an *Ideal Gas*!

- For point-like molecules (monoatomic gases), molecular energy consists only of translational kinetic energy *KE*
- We just learned that *KE* is directly proportional to *T*.
- When an infinitesimal amount of heat d*Q* enters the gas, *dT* increases, and *d(KE)* increases accordingly,

$$d(KE) = \frac{3}{2} NkdT \quad (or = \frac{3}{2} nRdT)$$

Heat Capacities of an Ideal Gas (at constant V)



Then, from energy conservation,

$$dQ = d\left(KE\right)$$

So, $$dQ = d\left(KE\right) = \frac{3}{2}NkdT \quad (or = \frac{3}{2}nRdT)$$

Then, the definition of Heat Capacity $dQ = nC_V dT$,

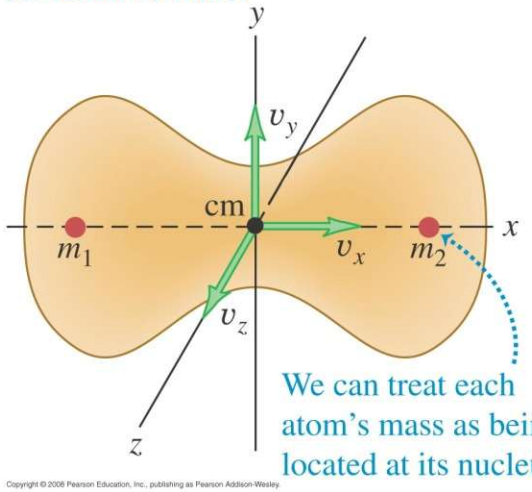
$$\rightarrow \; C_V = \frac{3}{2}R$$

Heat Capacity and Molecular Motion

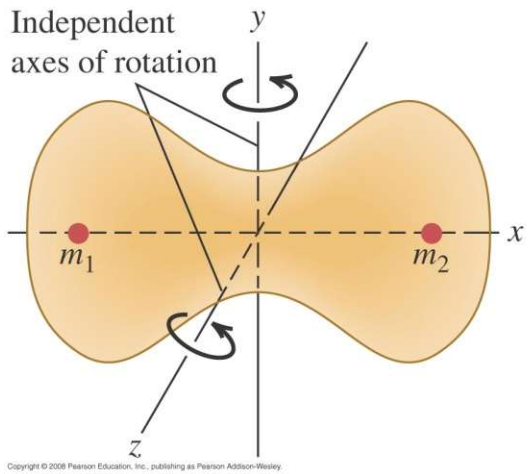
Heat capacity of a gas is related to its ability to absorb and store energy.

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

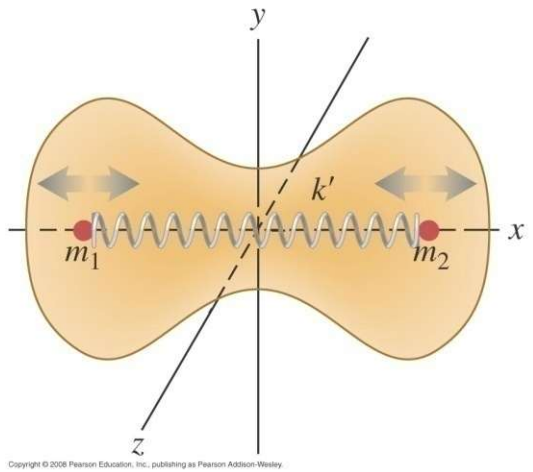
Translational motion. The molecule moves as a whole; its velocity may be described as the *x*-, *y*-, and *z*-velocity components of its center of mass.



Rotational motion. The molecule rotat-- about its center of mass. This molecule has independent axes of rotation.



Vibrational motion. The molecule oscillates as though the nuclei were connected by a spring.



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 $E_{tot} = 3/2\ NkT$ or $= 3/2\ nRT$

$$\langle E \rangle_{per\ molecule} = 3/2\, kT \qquad \rightarrow\ C_V = \frac{3}{2} R$$

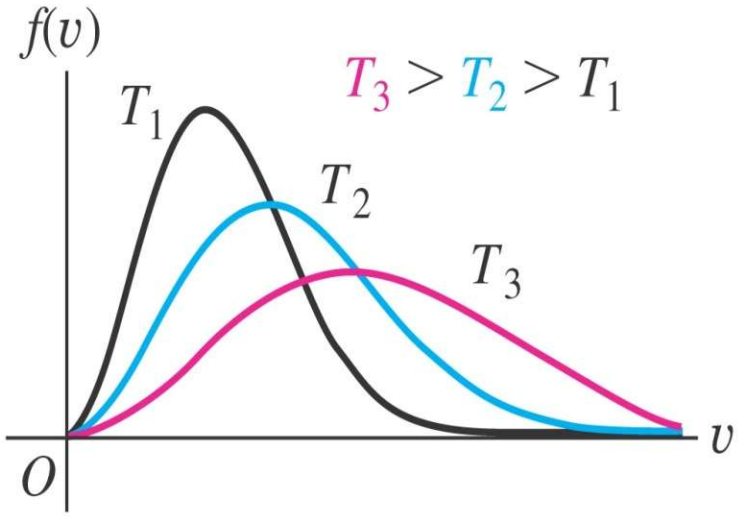
- Diatomic (*without* vibration): 3 trans dofs + 2 rotational dofs

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

$$\langle E \rangle_{per\ molecule} = 5/2\, kT \qquad \rightarrow\ C_V = \frac{5}{2} R$$

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.

- $f(v)\mathrm{d}v$ 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)

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!

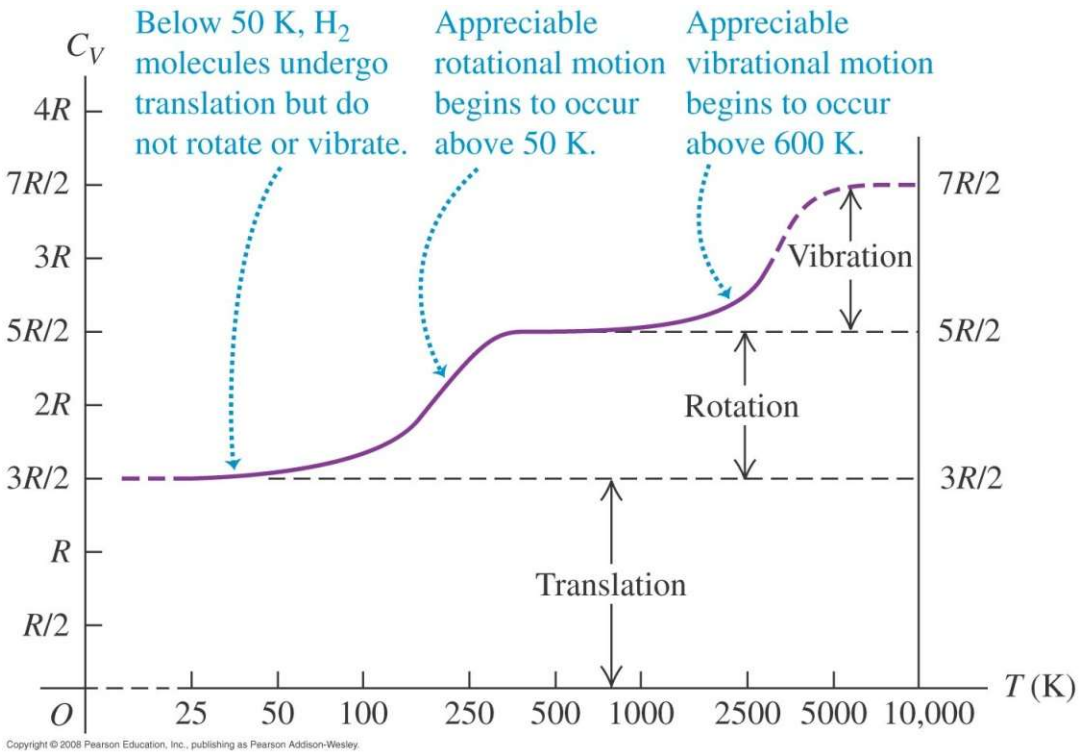
- Most Probable Speed - the maximum value of the distribution function $f(v)$:

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

Heat Capacities (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