

Chapters 18

- Thermal properties of matter

Michael Wong – PHY 1122 Spring 2023

Learning Goals

- How to relate p , V , and T of a gas.
- How p and T are related to kinetic energy of molecules.
- Looking at heat capacities of a gas and what it reveals (microscopic picture)
- *Distribution of molecular speeds (some statistics).

Introduction

- In Ch. 18, we examine how **change in temperature affects matter**. We relate thermal properties from macroscopic to **microscopic** scale.
- Think about water vapor (or steam) in your kitchen.
 - Kettle boils water.
 - Microwave a potato.
 - Condensation on a glass.
 - Ice forming in a freezer.



Equations of state

- Quantities like **pressure**, **volume**, **temperature**, and amount of a substance are **state variables** because they describe the state of the substance.
- It's possible to describe the relationship between these variables using an **equation of state**.
 - If the relationship is too complicated, we must use graphs or tables.

- Eg. An approximate equation of state for a **solid**:

$$V = V_0(1 + \beta \Delta T - k \Delta p)$$

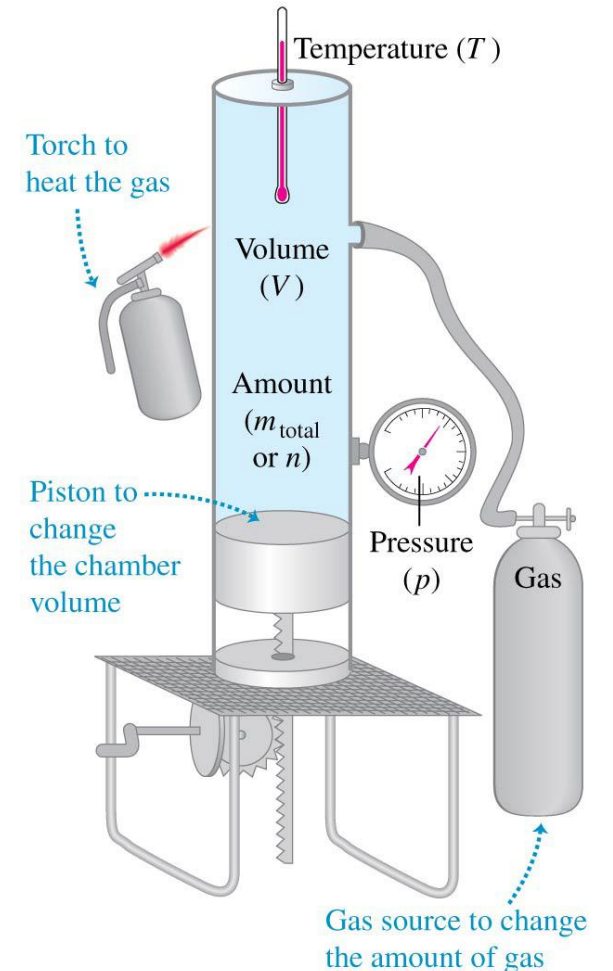
The Ideal-gas equation (law)

- The **ideal-gas equation** is another equation of state:

$$pV = nRT$$

where the n is the number of moles.

- # of moles n , mass m_{total} , and **molar mass** M (molecular weight) are related by: $m_{total} = nM$.
- Gay-Lussac:** $P \propto T$, **Charles:** $V \propto T$
Boyle: $P \propto 1/V$, **Avogadro:** $V \propto n$
- $R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$ is the **ideal gas constant**.



Ideal gas (cont.)

- We can express $pV = nRT$ in other useful ways.

- In terms of mass of the gas and molar mass:

$$pV = \frac{m_{total}}{M} RT$$

and from this equation we get an expression for **density** ρ :

$$\boxed{\rho} = \frac{m_{total}}{V} = \boxed{\frac{pM}{RT}}$$

- For a constant mass (or n) of an ideal gas, pV/T is constant:

$$\boxed{\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}} = \text{constant}$$

Ex. 18.1 – Volume of an Ideal Gas

$$1 \text{ atm} = 101.3 \text{ kPa} = 14.7 \text{ psi}$$

- At standard temperature and pressure (STP):

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(273.15 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = 0.0224 \text{ m}^3 = 22.4 \text{ L}$$

Ex. 18.3 – Mass of Air in a Scuba Tank

- An “empty” aluminum scuba tank contains 11.0 L of air at 21.0°C and 1 atm. When the tank is filled rapidly from a compressor, the air temperature is 42°C and the gauge pressure is $2.10 \times 10^7 \text{ Pa}$. What mass of air was added? Air is about 78% N_2 , 21% O_2 , and 1% miscellaneous; it has $M_{avg} = 28.8 \frac{\text{g}}{\text{mol}} = 28.8 \times 10^{-3} \frac{\text{kg}}{\text{mol}}$.

Gauge or absolute pressure

- **Ideal gas law uses the absolute pressure.**
- The **gauge pressure** is the difference between the absolute pressure and atmospheric pressure in a sealed container.
- Example: Flat tire has 1 atm pressure inside. Inflated tire has ~3 atm of pressure inside. Gauge pressure is (3-1=**2 atm**).
- Example: “empty” scuba tank has 1 atm pressure. Filled scuba tank has ~200 atm of pressure inside.

$$pV = nRT$$



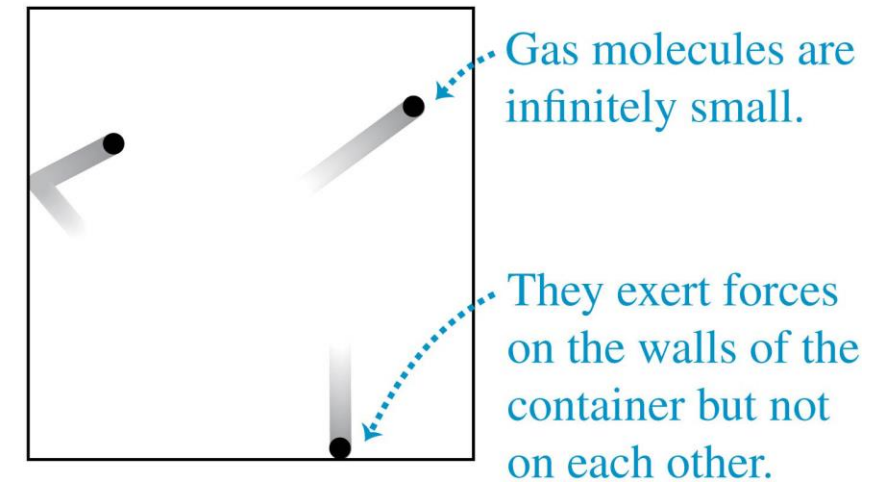
The van der Waals equation*

- The ideal gas equation ignores volumes of molecules and attractive forces between them (figure (a) below).
- The **van der Waals** equation is more realistic:

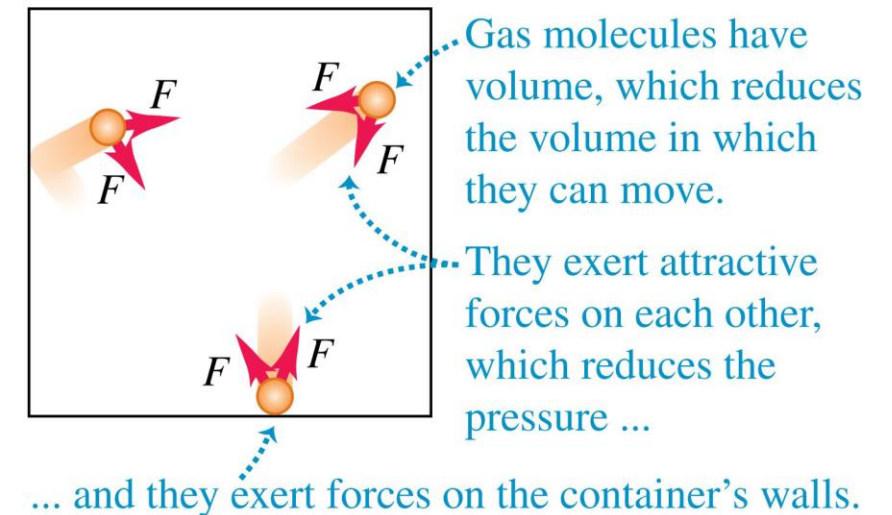
$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where a and b are different constants for different gases.

(a) An idealized model of a gas

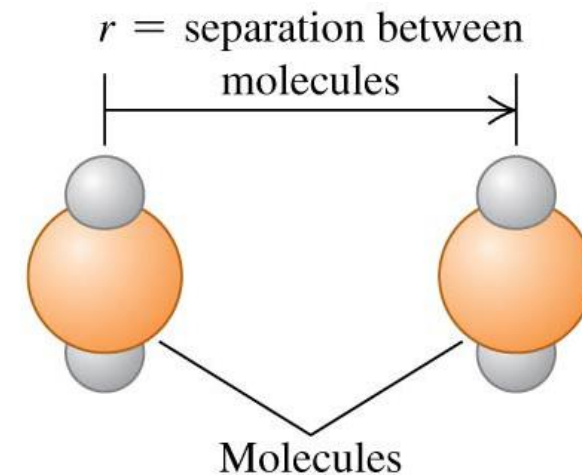


(b) A more realistic model of a gas



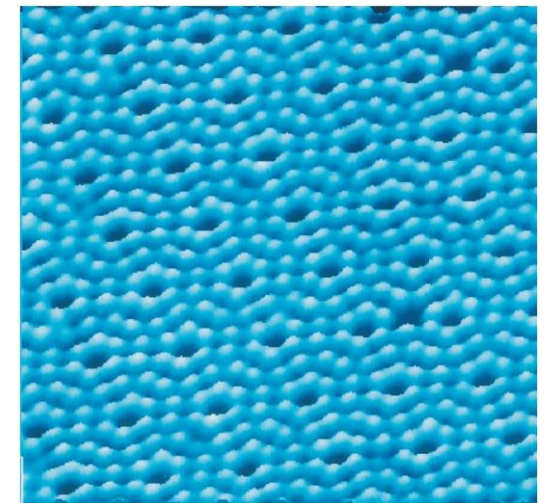
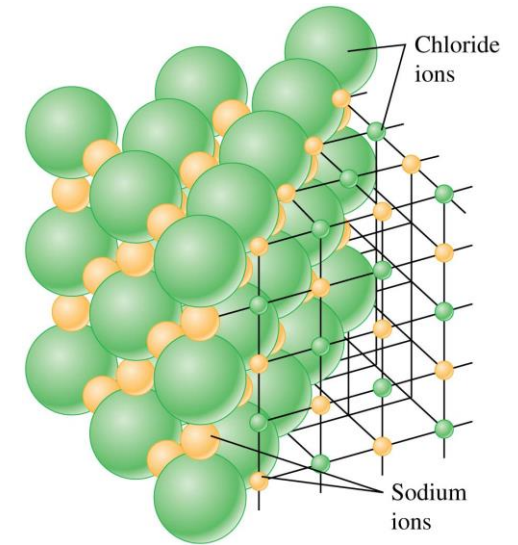
Molecules and intermolecular forces

- We'll now look at how molecular structure influences "bulk" behavior (density, heat capacities, equations of state, etc...)
- All chemical compounds are made of identical **molecules** which in turn are composed of atoms ($\sim 10^{-10}$ m in size).
- In solids and liquids, molecules are held together by **intermolecular forces**. In gases, they move nearly independently.
- The force between molecules depends on the distance r between them.



Molecular properties of matter

- In solid form, molecules move by vibrating about some fixed points within their *lattices*. (eg. NaCl – table salt).
- They can also make some interesting geometries like the diamond-cubic lattice of silicon (looks hexagonal at angle).
- In liquids, intermolecular distances are slightly larger than solid phase of same substance.
 - But with greater freedom of movement.
- In gas, molecules move independently.



Kinetic-molecular model of an ideal gas

- Using molecular structure (microscopic) to describe macroscopic properties of matter (volume, temp., etc...) for an ideal gas.
- This model is based on a large # of particles bouncing around in a closed container (separate document will be posted showing the derivation).
- Using the model we can determine:
 - Total translational kinetic energy of a set of molecules (or atoms).
 - Average trans. Kinetic energy of a *single* molecule.
 - Modified formula for the ideal gas law based on **number of molecules**.
 - The root-mean-square (rms) speed of a molecule.

Pressure, temperature, and molecular KE

- The **total translational kinetic energy** of a set of atoms or molecules:

$$\boxed{K_{tr} = \frac{3}{2} nRT} \quad \left(= \frac{3}{2} pV \right)$$

- The *average* K_{tr} of a **single molecule** also depends only on temperature:

$$\frac{K_{tr}}{N} = \boxed{\frac{1}{2} m(v^2)_{\text{avg}} = \frac{3}{2} kT}$$

where $\boxed{k = \frac{R}{N_A}} = 1.381 \times 10^{-23} \frac{\text{J}}{\text{molecule} \cdot \text{K}}$ is known as the **Boltzmann constant**.

- The ideal gas equation can also now be written as:

$$\boxed{pV = NkT}$$

Molecular speeds

- The **root-mean-square speed** of a single molecule is given by:

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} = \sqrt{\frac{3kT}{m}} \text{ or } = \sqrt{\frac{3RT}{M}}$$

- This represents the speed of a molecule that has an average value of translational kinetic energy in your system.
 - Slightly different (higher) than the average speed of any given molecule.
- Lighter molecules (like hydrogen) have faster v_{rms} and can escape into space. Heavier molecules (nitrogen and oxygen) are slower which is why our air is mostly N_2 and O_2 gas.

Ex. 18.6 – Molecular kinetic energy and v_{rms}

- (a) What is the average translational kinetic energy of an ideal gas molecule at 27°C?

$$\boxed{\frac{1}{2}m(v^2)_{\text{avg}}} = \frac{3}{2}kT = \boxed{6.21 \times 10^{-21} \text{ J}}$$

- (b) What is the total random translational kinetic energy of the molecules in 1 mole of this gas?

$$\boxed{K_{\text{tr}}} = \frac{3}{2}nRT = \boxed{3740 \text{ J}}$$

- (c) What is the rms speed of oxygen molecules at this temperature?

$$\boxed{v_{\text{rms}}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \boxed{484 \text{ m/s}}$$

Ex. 18.7 – Calculating rms and average speeds

- Five gas molecules have speeds of 500, 600, 700, 800, and 900 m/s.
 - What is the rms speed?
 - What is the *average* speed?

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} = \sqrt{\frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5}} = 714 \text{ m/s}$$

$$v_{\text{avg}} = \frac{500 + 600 + 700 + 800 + 900}{5} = 700 \text{ m/s}$$

In general, v_{rms} and v_{avg} are not the same. Roughly speaking, v_{rms} gives greater weight to the higher speeds than v_{avg} .

Heat capacities of gases

- Before, we introduced heat capacities as a way to measure energy transfer.
 - We can predict values of it based on kinetic-molecular theory.
- Heat is *energy* in transit: add heat, increase energy!
- If volume doesn't change, we can predict C_V (in $\frac{\text{J}}{\text{mol}\cdot\text{K}}$) which is the **molar heat capacity at constant volume**.
 - $C_V = Mc_V$ where c_V (in $\frac{\text{J}}{\text{kg}\cdot\text{K}}$) is specific heat capacity.

Heat capacities of gases

- Trans. kin. energy and heat depend on temperature:

$$K_{tr} = \frac{3}{2}nRT \quad , \quad Q = nC_V T$$

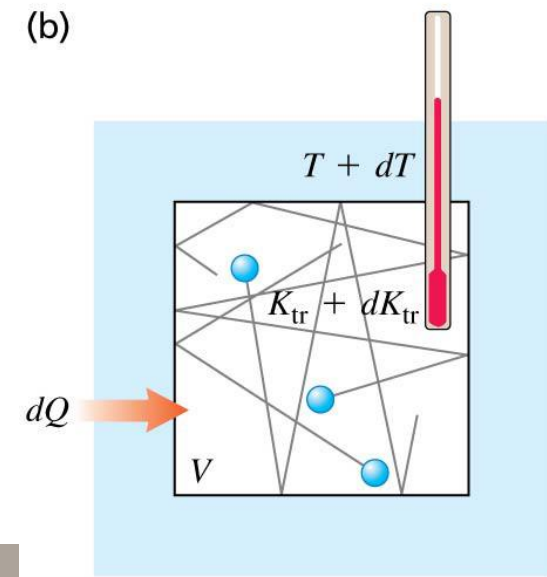
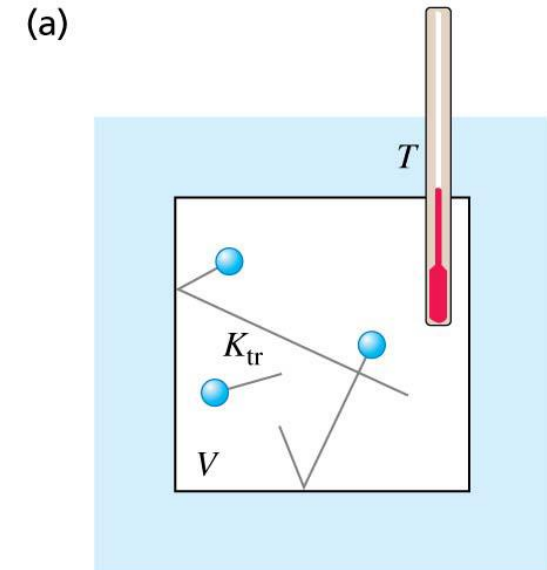
- If temp. changes by dT then energy changes by dK_{tr} .
– The heat also changes by $dQ \propto dT$.

- Let's assume K_{tr} is total molecular energy, then dK_{tr} and dQ are equal:

$$dK_{tr} = \frac{3}{2}nR dT$$

$$dQ = nC_V dT$$

$$\boxed{C_V = \frac{3}{2}R} = 12.47 \text{ J/mol} \cdot \text{K}$$



Heat capacities of gases

- This value of $C_V = 12.47 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ predicts correctly for the **monatomic gases** like He (~ 12.46) and Ar (~ 12.46).
 - But diatomic gases like H_2 , N_2 , and O_2 have $C_V = \sim 20.4 - 20.8 \frac{\text{J}}{\text{mol}\cdot\text{K}}$.
- The reason is that diatomic gases have more *degrees of freedom* than monatomic. Diatomic gases have two possible rotational axes.
The total kinetic energy per molecule is:

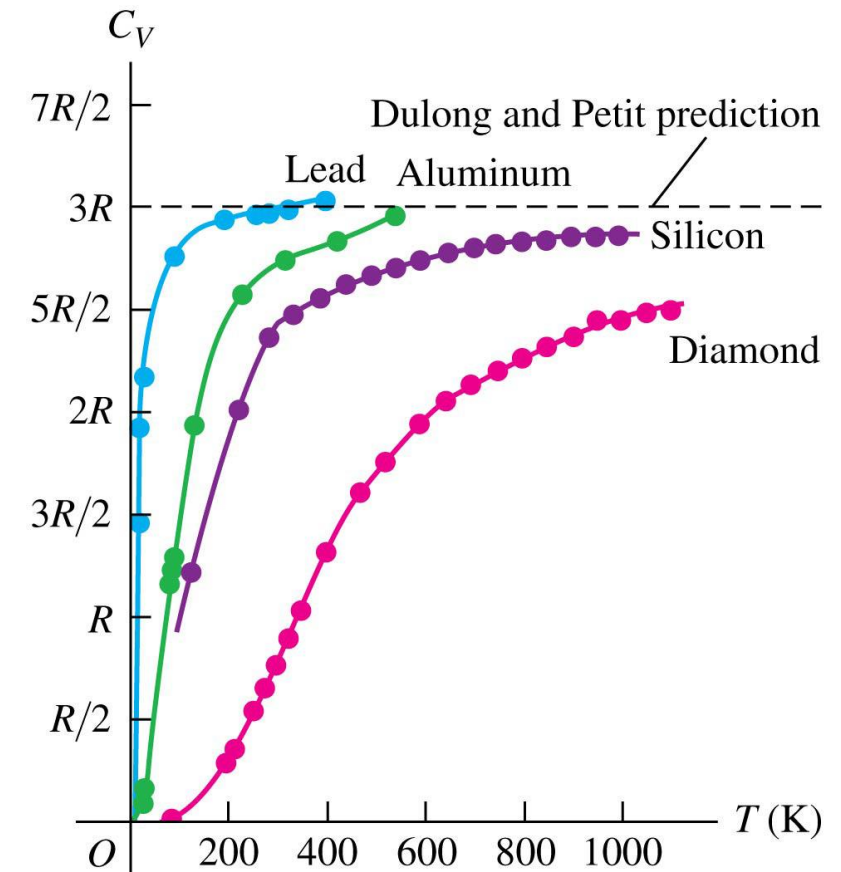
$$K_{tr+rot} = \frac{5}{2} kT$$

$$C_V = \frac{5}{2} R \quad (\text{for diatomic gas})$$

$$C_V = 20.79 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

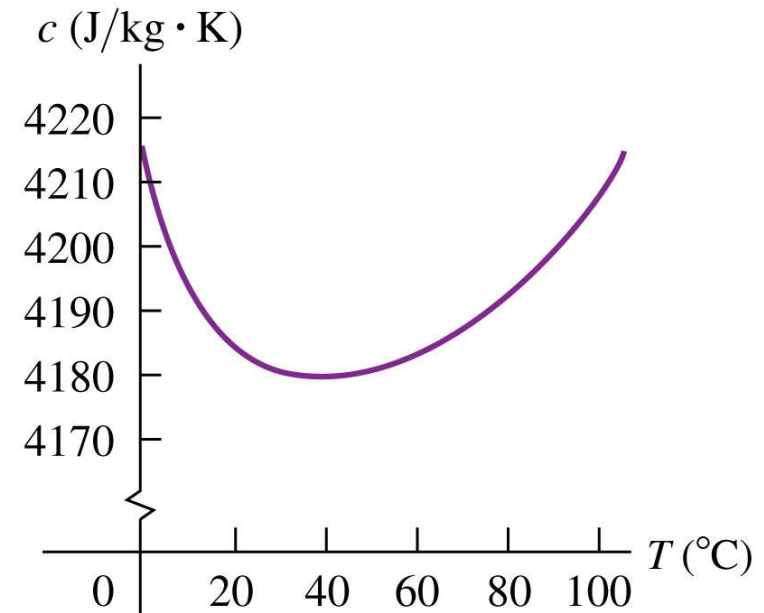
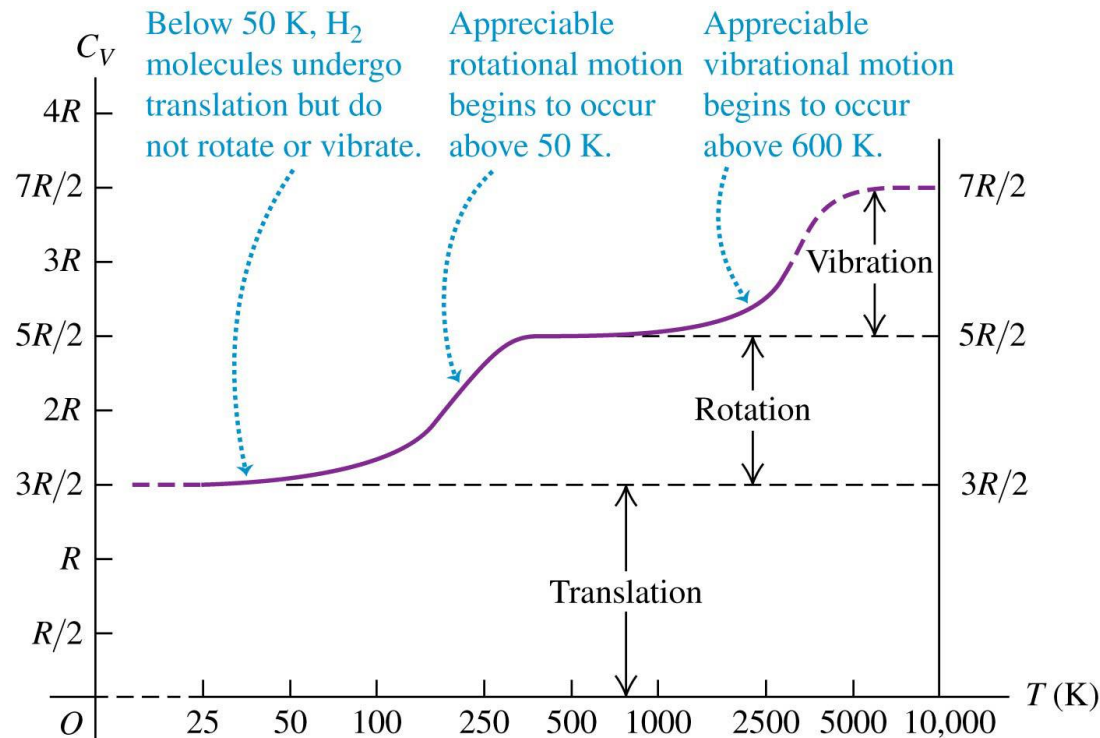
Heat capacities of (monatomic) solids

- For **monatomic solids**, atoms are bound to each other by interatomic forces.
- Each atom has translational and vibrational kinetic energy and also has elastic potential energy.
- The molar heat capacity at constant volume is: $C_V = 3R = 24.9 \frac{\text{J}}{\text{mol}\cdot\text{K}}$.
- Rule of Dulong and Petit (introduced in Ch. 17).



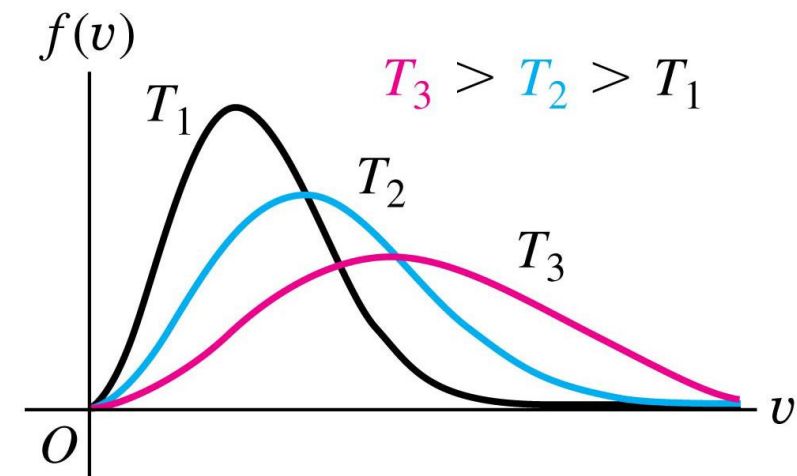
Heat capacities and temperature

- Heat capacities also tend to vary with temperature.
 - Examples: H_2 gas (left) and water (right).



Statistics of molecular speeds*

- Molecules in a gas don't all have the same speeds.
- A function $f(v)$ is called a **probability distribution function**.
 - In terms of speeds, $f(v)$ would give the probability of a molecule to have a speed within an interval.
- The peak of the curve represents the most probably speed v_{mp} .
 - As T increases, the peak shifts to higher v_{mp} .



As temperature increases:

- the curve flattens.
- the maximum shifts to higher speeds.