Chapter 18

Thermal Properties of Matter (Microscopic models)

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University Physics, Twelfth Edition
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Topics for Chapter 18

• I. Ideal Gas Model & Ideal Gas Law
• II. Molecular speed distribution
• III. Equipartition of Energy Theorem
• IV. Molar heat capacity of gas and solid
Introduction

• A very simple microscopic model (ideal gas model) + application of classical mechanics (F=ma) + application of statistics was able to explain many macroscopic behavior of gas.

• We will study the conceptual idea behind the ideal gas model and explore its consequences (predictions).

• However, at “low” temperature, the classical mechanics predictions fail; quantum mechanics theory was invented.
I. Ideal Gas Model

- In this chapter, we will study the thermal properties of gases using an idealized model of molecular motions - called *Ideal Gas Model*.

**Ideal Gas Model:**
1. Point molecules
2. Molecules do not interact except when they collide

More realistic model:
1. Molecules have finite size
2. Molecules attract each other (that is why gas condenses into liquid when cooled)
When does a “real” gas behave like an ideal gas?

- When the molecules are far apart, that is, at very low molecular density because:
  - (1) Molecules look like point particles to each other when they are far apart.
  - (2) The attractive force between the molecules is negligible when they are far apart.

- How “low” is low density?

- When the average molecular separation $\gg$ size of molecule

*Implication: When molecular density is low, all gasses obey the ideal gas law and behave the same way.*
Ideal Gas Law

- Ideal Gas Model + classical mechanics => “Classical” Ideal Gas Law
- Ideal Gas Model + quantum mechanics => “Quantum” Ideal Gas Law

\[ PV = Nk_B T \] ("Classical" Ideal Gas Law; valid for \( T > \) few Kelvin)

- \( P \) = pressure of the gas
- \( V \) = volume of the gas
- \( N \) = number of gas "particles"
- \( k_B \) = Boltzmann's constant (universal constant)
  \[ \approx 1.38 \times 10^{-23} \text{ Joule/Kelvin} \] (What is the unit for \( PV \)?)
- \( T \) = temperatio of the gas in Kelvin

All gases (\( \text{H}_2, \text{He}, \text{N}_2, \text{etc} \)) obeys the same
Ideal Gas Law at "low" molecular density.

Note: \( N \) = number of gas "particles" NOT the number of atoms
Example: \( \text{H}_2 \) gas; each gas particle is two hydrogen atoms
forming one \( \text{H}_2 \) molecule.
Ideal Gas Law - an alternative version

• Since \(N\) is a very large number and \(k_B\) is a very small number, it is more convenient to work with the following version of the Ideal Gas Law:

\[
P V = N k_B T = \left( \frac{N}{N_A} \right) \left( N_A k_B \right) T \equiv nRT
\]

\(N_A = \text{Avogadro's number} \approx 6.02 \times 10^{23}\)

\(n = \left( \frac{N}{N_A} \right) = \text{number of moles of gas particles}\)

\(N_A k_B = R = \text{Gas constant}\)

\(\approx (6.02 \times 10^{23})(1.38 \times 10^{-23} \text{ Joule/Kelvin}) \approx 8.31 \frac{\text{J}}{\text{mole} \cdot \text{K}}\)

How many moles of gas particles are in 6 grams of \(\text{H}_2\) gas?
Number of moles and molar mass

Example: How many moles of gas particles are in 6 grams of H\textsubscript{2} gas?
The mass of two H atoms is essentially the mass of two protons (2m\textsubscript{p}).
The Avogadro number is defined such that the molar mass of H\textsubscript{2} is 2 grams.
That is \((6.02\times10^{23})(2m_p) \approx 2\) grams.

\[
n = \frac{\text{Total mass}}{\text{molar mass}} = \frac{6\text{ grams}}{2\text{ grams}} = 3\text{ moles}
\]

What is the molar mass of O\textsubscript{2}?
What is the molar mass of N\textsubscript{2}?
How many moles of gas particles are in 100 grams of air?
Example problem dealing with the Ideal Gas Law

- Example 1: A container has 60 grams of $\text{H}_2$ gas inside. The volume is 1 m$^3$ and the temperature is 300 K. What is the pressure?

Example 2: A container has 1000 grams of air inside. The volume is 1 m$^3$ and the temperature is 300 K. What is the pressure?
Graphical representation of Ideal Gas Law

- Plot Pressure vs. Volume for a fixed temperature (T) - the curve is called an isotherm.

  Easy to compress the gas at large volume

  Much harder to compress the gas at smaller volume

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

For each curve, $pV$ is constant and is directly proportional to $T$ (Boyle’s law).

$T_4 > T_3 > T_2 > T_1$

Easy to compress the gas at large volume
II. Molecular speed distribution

• Inside a container of gas, the molecules do not move at the same speed. However, we expect the average speed to increase with temperature.

(a)

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

(b)

Fraction of molecules with speeds from \( v_1 \) to \( v_2 \)

Fraction of molecules with speeds greater than \( v_A \)
The molecular speed distribution can be derived from statistical consideration (a branch of physics called statistical mechanics). For “classical” ideal gas, the molecular distribution is given by the Maxwell-Boltzmann distribution; valid for $T > \text{few Kelvin}$.

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}}$$

$$<v^2>_{\text{average}} = \frac{\int_0^\infty v^2 f(v)dv}{m} = \frac{3kT}{m}$$

Define: $v_{\text{rms}} = \sqrt{<v^2>_{\text{average}}} = \sqrt{\frac{3kT}{m}}$

$$<\text{kinetic energy}>_{\text{average}} = \frac{1}{2} m <v^2>_{\text{average}} = \frac{1}{2} m v_{\text{rms}}^2 = \frac{3kT}{2}$$

Total kinetic energy = $N <\text{kinetic energy}>_{\text{average}}$

$$= \frac{3}{2} NkT = \frac{3}{2} nRT = \frac{3}{2} PV \quad \text{(for ideal gas)}$$

Qualitative idea: Temperature is related to average kinetic energy per molecule (at least for ideal gas).
Molecular speed and kinetic energy - examples

• Given: Two moles of He gas and two moles of O\textsubscript{2} gas are at the same temperature (T=300K).

• (1) What are their total kinetic energies? Which one has a higher total kinetic energy?

• (2) Which one has a higher root-mean-square speed? What is the ratio of their root-mean-square speeds?
Equipartition of Energy Theorem

Equipartition of energy theorem relates the total energy of a substance to its temperature - "each degree of freedom" has \( \frac{1}{2} kT \) of energy (valid at "high" temperature.)

For examples:
Monatomic gas (e.g. He gas) -

total energy = translational kinetic energy  
\[ \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \]

\( \Rightarrow \) 3 degrees of freedom  \( \Rightarrow \) total energy = \( 3 \left( \frac{1}{2} kT \right) \)
Equipartition of Energy Theorem

Diatomic gas (e.g. H$_2$ gas)

total energy = translational K.E. + rotational K.E. =

\[
\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2
\]

\[ \Rightarrow 6 \text{ degrees of freedom} \]

Not quite! one of the rotation has zero momentum of inertia \((I_x = 0) \Rightarrow 5 \text{ degrees of freedom} \]

Not quite! The molecule can vibrate

\[ \Rightarrow \text{kinetic energy } + \text{potential energy} \]

\[ \Rightarrow 7 \text{ degrees of freedom} \]
IV. Molar specific heat

- An atom can absorb energy as the kinetic energy of its motion.
- A molecule can absorb energy in its translation, and also in its rotation and in the vibrations of the molecule.
- The more degree of freedom => need to absorb more heat to raise the temperature => higher molar heat capacity.

Table 18.1 Molar Heat Capacities of Gases

<table>
<thead>
<tr>
<th>Type of Gas</th>
<th>Gas</th>
<th>$C_V$ (J/mol \cdot K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monatomic</td>
<td>He</td>
<td>12.47</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>12.47</td>
</tr>
<tr>
<td>Diatomic</td>
<td>H$_2$</td>
<td>20.42</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>20.76</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>21.10</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>20.85</td>
</tr>
<tr>
<td>Polyatomic</td>
<td>CO$_2$</td>
<td>28.46</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>31.39</td>
</tr>
<tr>
<td></td>
<td>H$_2$S</td>
<td>25.95</td>
</tr>
</tbody>
</table>

Example: Monatomic gas - Energy (E) = $\frac{3}{2}nRT$

$Heat$ input $Q = \Delta E = \frac{3}{2}nR\Delta T$

$\Rightarrow$ Molar heat capacity = $\frac{3}{2}R$

$\approx \frac{3}{2}\left(\frac{8.31}{mole \cdot K}\right) \approx 12.47 \frac{J}{mole \cdot K}$

Diatomic gas - Energy (E) = $\frac{7}{2}nRT$

$\Rightarrow$ Molar heat capacity = $\frac{7}{2}R \approx 29.08 \frac{J}{mole \cdot K}$

See next slide!
Various degree of freedom “turns on” at different different temperature

(a) 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.

(b) Rotational motion. The molecule rotates about its center of mass. This molecule has two independent axes of rotation.

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

Below 50 K, $H_2$ molecules undergo translation but do not rotate or vibrate. Appreciable rotational motion begins to occur above 50 K. Appreciable vibrational motion begins to occur above 600 K.
Molar specific heat for solid

At high temperature, all solids have the same molar heat capacity because it is related to the number of degree of freedom (6 of them: 3 K.E. +3P.E.). \( C_v = 3R \approx 3 \times 8.31 \approx 25 \text{ J/mol.K} \) was confirmed by experiments (see figure and table on next slide).

The low temperature behavior was very puzzling at the beginning of the 20th century. Quantum mechanics was invented to explain the low temperature behavior of molar heat capacity of solid and other phenomena.
### Specific heat values

#### Table 17.3  Approximate Specific Heats and Molar Heat Capacities (Constant Pressure)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat, $c$ (J/kg · K)</th>
<th>Molar Mass, $M$ (kg/mol)</th>
<th>Molar Heat Capacity, $C$ (J/mol · K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>910</td>
<td>0.0270</td>
<td>24.6</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1970</td>
<td>0.00901</td>
<td>17.7</td>
</tr>
<tr>
<td>Copper</td>
<td>390</td>
<td>0.0635</td>
<td>24.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2428</td>
<td>0.0461</td>
<td>111.9</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2386</td>
<td>0.0620</td>
<td>148.0</td>
</tr>
<tr>
<td>Ice (near 0°C)</td>
<td>2100</td>
<td>0.0180</td>
<td>37.8</td>
</tr>
<tr>
<td>Iron</td>
<td>470</td>
<td>0.0559</td>
<td>26.3</td>
</tr>
<tr>
<td>Lead</td>
<td>130</td>
<td>0.207</td>
<td>26.9</td>
</tr>
<tr>
<td>Marble (CaCO₃)</td>
<td>879</td>
<td>0.100</td>
<td>87.9</td>
</tr>
<tr>
<td>Mercury</td>
<td>138</td>
<td>0.201</td>
<td>27.7</td>
</tr>
<tr>
<td>Salt (NaCl)</td>
<td>879</td>
<td>0.0585</td>
<td>51.4</td>
</tr>
<tr>
<td>Silver</td>
<td>234</td>
<td>0.108</td>
<td>25.3</td>
</tr>
<tr>
<td>Water (liquid)</td>
<td>4190</td>
<td>0.0180</td>
<td>75.4</td>
</tr>
</tbody>
</table>

Note: Although the specific heat (J/kg·K) for various solid are very different, the molar specific heat (J/mol·K) are very similar ~ 25 J/mol·K as predicted.