Phases of Matter (reading phase diagrams)

At \( p \) and \( T \) values above the critical point, the material properties change smoothly with changing \( p \) or \( T \), rather than undergoing a phase change.

At the triple point, solid, liquid, and vapor coexist.
Critical Point and Liquid-Gas Coexistence
Kinetic-Molecular Model of an Ideal Gas

Macroscopic description of gases

\[ P, \ V, \ T \]

Ideal Gas Law

Microscopic description of gas molecules

\[ v, \ p, \ F, \ KE \]

Newton’s Eq.

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.
  - \(\rightarrow\) both KE and momentum are conserved.

[Link to PhET simulation: http://phet.colorado.edu/en/simulation/gas-properties]
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.
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 $v_i$:

\[
\Delta(mv) = P_f - P_i = mv_x - (-mv_x) = 2mv_x
\]

2. Duration, $\Delta t$, 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:

\[ F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \]

4. With \( N \) molecules, total force on wall in \( \Delta t \):

\[
F_{\text{tot}} = \sum_{i=1}^{N} F_i = m \frac{1}{L} \left( v_{1x}^2 + v_{2x}^2 + \cdots + v_{N_x}^2 \right) \\
= mN \frac{1}{L} \left( \frac{1}{N} \sum_{i=1}^{N} v_{ix}^2 \right) = mN \frac{1}{L} \left( v_{x}\right)_{\text{av}}
\]

Note: \( \left( v_{x}\right)_{\text{av}} \neq \left( v_{x}\right)_{\text{av}}^2 \)

\( \rightarrow \) Fixed Invariant distribution implies \( (\cdot)_e \) will be the same when experiment is repeated.
Pressure of an Ideal Gas

5. Random direction (isotropic) assumption:

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

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

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

\[ PV = \frac{2}{3} N \left( \frac{1}{2} m \langle v^2 \rangle_{av} \right) = \frac{2}{3} N \langle KE \rangle_{av} \]

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: \[ \frac{2}{3} N \left( KE \right)_{av} = NkT \]

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

\[ K_{tr} = \frac{3}{2} NkT \text{ (all molecules in V)} \] (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.”
Distribution of Molecular Speeds

- Within an ideal gas, molecules move with a diversity of speeds.
- A mathematical rigorous way to describe this statistically is through a distribution function $f(v)$.

Properties:
- $f(v) \sim 0$, $v \sim 0$
- $f(v) \to 0$, $v \to$ large
- $f(v)$ largest at mid-range
Maxwell-Boltzmann Distribution

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

- \( f(v)dv \) gives the probability of finding molecules with speed in range \([v,v+dv]\).
- Diff averages with respect to the distribution of molecular speeds can be calculated using \( f(v) \):
  1. \( \nu_{av} = \int_0^\infty v f(v) dv \) (avg of \( v \))
  2. \( (\nu^2)_{av} = \int_0^\infty \nu^2 f(\nu) d\nu \) (avg of \( \nu^2 \))
Example: Test Scores

4 Test Scores: \( s_i = \{65, 80, 80, 95\} , i = 1, \ldots, 4 \)

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

\[ S_{av} = \frac{1}{4} (65) + \frac{2}{4} (80) + \frac{1}{4} (95) = 80 \quad \text{weighted average} \]

\[ S_{av} = \sum f_i s_i \quad \text{where } f_i \text{ gives the fraction of occurrence of } s_i \]

\[ v_{av} = \int_{0}^{\infty} f(v)vdv \quad \text{where } f(v)dv \text{ gives the fraction of molecules moving with speed } [v,v+dv] \]
Example: Test Scores

4 Test Scores: \( s_i = \{65, 80, 80, 95\}, i = 1, \ldots, 4 \)

Simple Avg: 

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

\[
(S^2)_{av} = \frac{1}{4} (65^2) + \frac{2}{4} (80^2) + \frac{1}{4} (95^2) = 6512.5
\]

\[
(S^2)_{av} = \sum f_i s_i^2 \quad \neq \quad (S_{av})^2 = 80^2 = 6400
\]

\[
(v^2)_{av} = \int_{0}^{\infty} f(v)v^2 dv \neq (v_{av})^2
\]
Statistical Description of Molecular Speed

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

- Root Mean Square (RMS) speed:
  \[ v_{rms} = \sqrt{\langle v^2 \rangle_{av}} = \sqrt{\frac{3kT}{m}} \]
  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 \( f(v) \):
  \[ v_{mp} = \sqrt{\frac{2kT}{m}} \]
Mean Free Path for Gas Molecules

Assumptions:
- Molecule with finite radius $r$ (note: point-like particles do not collide)
- The number density (# per unit vol) is given by $N/V$.
- Molecules move at an average speed $v$ (assuming this average to be $v_{rms}$).

For simplicity, let assume that the redder shaded molecule is the only one which is moving and to the right with speed $v$.

Then within a time interval $dt$, the number of molecules that it might collide will be given by:

$$dn = \left( \frac{\text{effective volume}}{\text{indicated (blue)}} \right) (\text{number density})$$

$$= \left( \pi \cdot 4r^2 \cdot vdt \right) (N/V) \quad \text{(we take } v = v_{rms})$$

Thus, the number of collisions/unit time is,

$$\frac{dn}{dt} = \frac{4\pi r^2 vN}{V}$$
Mean Free Path for Gas Molecules

To take into account that other molecules besides the red one are also moving, the estimated collision rate should be higher and it can be shown that this mean collision rate will be larger by $\sqrt{2}$. So,

$$\frac{dn}{dt} = \frac{4\pi \sqrt{2} r^2 v N}{V}$$

The average time between collisions (mean free time) is then the reciprocal of this value,

$$t_{\text{mean}} = \frac{V}{4\pi \sqrt{2} r^2 v N}$$

And, the **mean free path** will be,

$$\lambda = vt_{\text{mean}} = \frac{V}{4\pi \sqrt{2} r^2 N} \quad \text{or} \quad \lambda = \frac{kT}{4\pi \sqrt{2} r^2 P}$$

(we used $PV = NkT$)
Derivation of the $\sqrt{2}$ Factor

Key Idea: If all the molecules are moving, the relevant quantity for consideration should be the relative velocity between a pair of molecules.

Again, we take the average of this relative velocity to be the root-mean-square value:

$$\left( v_{rel}^2 \right)_{av} = \left( (v_2 - v_1) \cdot (v_2 - v_1) \right)_{av}$$

$$= \left( v_2 \cdot v_2 - 2v_2 \cdot v_1 + v_1 \cdot v_1 \right)_{av}$$

$$= \left( v_2 \cdot v_2 \right)_{av} - 2\left( v_2 \cdot v_1 \right)_{av} + \left( v_1 \cdot v_1 \right)_{av}$$

Note: $v_1$ and $v_2$ are in random relative directions!

$$\Rightarrow \left( v_2 \cdot v_1 \right)_{av} = 0$$
Derivation of the $\sqrt{2}$ Factor

This gives, 
\[
(v_{rel}^2)_{av} = (v_2 \cdot v_2)_{av} - 2(v_2 \cdot v_1)_{av} + (v_1 \cdot v_1)_{av}
\]

\[
= (v_2^2)_{av} + (v_1^2)_{av} = 2(v^2)_{av}
\]

Again, random direction assumption implies these two averages to be the same!

Taking the square root of the above equation,

\[
(v_{rel})_{rms} = \sqrt{(v_{rel}^2)_{av}} \quad \text{or} \quad \sqrt{2(v^2)_{av}} = \sqrt{2}v_{rms}
\]

Thus, 
\[
\frac{dn}{dt} = \frac{4\pi r^2 vN}{V} \quad \text{should be written as} \quad \frac{dn}{dt} = \frac{4\pi r^2 \sqrt{2}vN}{V}
\]
\( \nu_{\text{rms}} \) and \( \lambda \) Example: 18.6 & 18.8

18.6: a) What is the average translational KE of an ideal gas molecule at 27\(^\circ\)C?

Kinetic Theory \( \Rightarrow \) 

\[
KE_{\text{per molecule}} = \frac{3}{2} kT = \frac{3}{2} \left( 1.38 \times 10^{-23} \text{ J} / \text{K} \right) \left( 273.15 + 27 \right) \text{K} = 6.21 \times 10^{-21} \text{ J}
\]

b) What is the root-mean-square speed \( \nu_{\text{rms}} \) of O\(_2\) at this \( T \)?

\[
\nu_{\text{rms}} = \sqrt{\frac{3kT}{m_{O_2}}} = \sqrt{\frac{3 \left( 1.38 \times 10^{-23} \text{ J} / \text{K} \right) \left( 300 \text{K} \right)}{5.31 \times 10^{-26} \text{ kg}}} = 484 \text{ m/s}
\]

18.8: a) Evaluate the mean free path \( \lambda \) of an air molecule at 27\(^\circ\)C.

\[
\lambda = \frac{kT}{4\pi\sqrt{2}r^2p} = \frac{\left( 1.38 \times 10^{-23} \text{ J} / \text{K} \right) \left( 300 \text{K} \right)}{4\pi\sqrt{2} \left( 2.0 \times 10^{-10} \text{ m} \right)^2 \left( 1.01 \times 10^5 \text{ Pa} \right)} = 5.8 \times 10^{-8} \text{ m} \quad \left( r \sim 2 \times 10^{-10} \text{ m} \right)
\]

D\(_{\text{perfume}}\)

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,

$$dK_{tr} = \frac{3}{2} N k dT \quad \text{(or} \quad \frac{3}{2} n R dT)$$
Heat Capacities of Gases

- From definition of molar heat capacity, we also know:
  \[ dQ = nC_v dT \]

- From energy conservation, requiring \( dQ = dK_{tr} \) \((no work)\) gives,
  \[ nC_v dT = \frac{3}{2} nR dT \]

- **Monoatomic ~ Ideal Gas**
  (matches well with prediction)

\[ C_v = \frac{3}{2} R \quad (=12.47 \text{J/mol}\cdot\text{K}) \]

---

**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>
Heat Capacity (diatomic)

**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 rotates 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.

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 \textbf{degree of freedom} ("separate mechanisms in storing energy") will contribute \(\frac{1}{2} kT\) to the total average energy per molecule.

- **Monoatomic**: 3 translational dofs \(\rightarrow\) 3 \(\left(\frac{1}{2} kT\right)\)
  This gives \(E_{\text{tot}} = \frac{3}{2} NkT\) (same as before).

- **Diatomic (without vibration)**: 3 trans dofs + 2 rotational dofs
  This gives \(E_{\text{tot}} = \frac{5}{2} NkT\) or \(= \frac{5}{2} nRT\).
  Again, consider an infinitesimal energy change, we have
  \(nC_vdT = \frac{5}{2} nRdT\), and this gives \(C_v = \frac{5}{2} R\).
Heat Capacities (real gases, e.g., $\text{H}_2$)

- 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.

$\Rightarrow$ For normal $T$ range, one takes $C_v = \frac{5}{2} R$ for $\text{H}_2$ gas.