Kinetic theory

Collective behaviour of large systems
Statistical basis for the ideal gas equation
Deviations from ideality
Learning objectives

- Describe physical basis for the kinetic theory of gases
- Describe relationship between energy, molecular speed, and temperature
- Use Maxwell-Boltzmann distribution to predict trends in molecular speeds with temperature and mass
- Apply Graham’s law of diffusion
- Describe physical basis of the van der Waal’s equation and apply to real gases
Why gases exert pressure

- Gases are mostly empty space
- Gases contain molecules which have random motion
- Molecules have kinetic energy
- Molecules strike walls of container – collisions are perfectly elastic
- Collisions exchange momentum with container
- Pressure results from momentum change
- Energy (momentum) of molecules depends on temperature
Large collections of particles or people exhibit predictable behaviour

- Fluctuations in behaviour of a small group of particles are quite noticeable (pressure gauge readings fluctuate)
- Fluctuations in behaviour of a large group (a mole) of particles are negligible (pressure gauge reading constant)
- Large populations are statistically very reliable
Pressure and momentum

- Pressure = force/unit area \((F/A)\)
- Force = mass \(\times\) acceleration \((F = ma)\)
- Acceleration = rate of change of velocity \((a = \frac{dv}{dt})\)
- Force = rate of change of momentum \((F = mdv/dt)\)
- Collisions cause momentum change
- Momentum is conserved
Elastic collision of a particle with the wall

- Momentum lost by particle mass \( m \), velocity \( v = -2mv \)
- Momentum gained by wall per collision = \( 2mv \)
- Momentum conserved
  - \(-2mv + 2mv = 0\)
- Rate of momentum change = momentum change per collision \( \times \) collision frequency = \( \frac{2mv}{\Delta t} \)
Factors affecting collision rate

\[ P = \frac{\text{momentum change}}{\text{collision}} \times \frac{\text{no collisions}}{\text{time}} \times \frac{1}{\text{area}} \]

1. Particle velocity – the faster the particles the greater the momentum – the higher the frequency of collisions
2. Number – the more particles – the more collisions
3. Volume – the smaller the container, the more collisions per unit area

\[ P = 2mv \cdot \frac{vN_o}{V} = \frac{2mv^2N_o}{V} \]
Making refinements

- We only considered one wall – but there are six walls in a container
  - Multiply by 1/6
- Replace $v^2$ by the mean square speed of the ensemble (to account for fluctuations in velocity)

\[
P = \frac{1}{6} \cdot \frac{2mv^2 N_o}{V} = \frac{mv^2 N_o}{3V}
\]

\[
P = \frac{1}{3} \cdot \frac{m \langle v^2 \rangle N_o}{V}
\]
Boyle’s Law

- Rearranging the previous equation:

\[
PV = \frac{2}{3} P = \frac{1}{3} \frac{m\langle v^2 \rangle N_o}{V} \cdot N_o \langle E_k \rangle
\]

- Substituting the average kinetic energy

\[
\langle E_k \rangle = \frac{1}{2} m\langle v^2 \rangle
\]

- Compare ideal gas law \( PV = nRT \):

\[
\langle E_k \rangle = \frac{3}{2} RT
\]

- Average kinetic energy one mole of gas = \( 3RT/2 \)
Root mean square speed

- Total kinetic energy of one mole
  \[ E_k = \frac{1}{2} N_o m \langle v^2 \rangle = \frac{3}{2} RT \]
- But molar mass \( M = N_o m \)
  \[ v_{RMS} = \sqrt{\frac{3RT}{mN_o}} = \sqrt{\frac{3RT}{M}} \]
- Since the energy depends only on \( T \), \( v_{RMS} \) decreases as \( M \) increases
- Heavier molecules move slower
Speed and temperature

- Not all molecules move at the same speed or in the same direction
- Root mean square speed is useful but far from complete description of motion
- Description of distribution of speeds must meet two criteria:
  - Particles travel with an average value speed
  - All directions are equally probable
Maxwell meet Boltzmann: connecting the macroscopic with the microscopic

- The Maxwell-Boltzmann distribution describes the velocities of particles at a given temperature

\[ F(v) = Kv^2e^{-mv^2/2k_BT} \]

\[ K = 4\pi \left( \frac{m}{2\pi k_BT} \right)^{3/2} \]

- \( k_B \) = Boltzmann constant
- Area under curve = 1
- Curve reaches 0 at \( v = 0 \) and \( \infty \)
M-B and temperature

- **M-B T-dependence**
- As T increases $v_{\text{RMS}}$ increases
- Curve moves to right
- Peak lowers in height to preserve area
Boltzmann factor: transcends chemistry

- Energy of a particle
- From M-B distribution

\[ \varepsilon = \frac{mv^2}{2} \]

\[ \exp \left( -\frac{\varepsilon}{k_B T} \right) = \frac{1}{\exp \left( \frac{\varepsilon}{k_B T} \right)} \]

- Measures probability that particle has energy \( \varepsilon \) at thermal energy \( k_B T \)

\[ P(\varepsilon) \propto \exp \left( -\frac{\varepsilon}{k_B T} \right) \]

- As \( \varepsilon/k_B T \uparrow \), \( P \downarrow \)
Applying the Boltzmann factor

- Population of a state at a level $\varepsilon$ above the ground state depends on the relative value of $\varepsilon$ and $k_B T$
  - When $\varepsilon << k_B T$, $P(\varepsilon) = 1$
  - When $\varepsilon >> k_B T$, $P(\varepsilon) = 0$
- Thermodynamics, kinetics, quantum mechanics, spectroscopy, lasers...

\[
P(\varepsilon) \propto \exp\left(-\frac{\varepsilon}{k_B T}\right)
\]
Collisions and mean free path

- Collisions between molecules impede progress
- If $v = 200$ m/s time to cross room $\approx 0.05$ s
- Collisions make time much greater
- Diffusion and effusion are influenced by random motion
Diffusion

- The process by which gas molecules become assimilated into the population is diffusion.
- Diffusion mixes gases completely.
- Gases disperse: the concentration decreases with distance from the source.
Effusion and Diffusion

- High velocity of molecules leads to rapid mixing of gases and escape from punctured containers
- Diffusion is mixing of gases by motion
- Effusion is escape of gas from container through an opening
Graham’s Law

- Rate of effusion of gas is inversely proportional to square root of its mass
  \[ \text{Rate} \propto \frac{1}{\sqrt{m}} \]

- Compare two gases
  \[ \frac{\text{Rate}_1}{\text{Rate}_2} = \frac{\sqrt{m}_2}{\sqrt{m}_1} = \sqrt{\frac{m}_2}{m}_1 \]

- If \( m_2 > m_1 \), \( \text{rate}_1 > \text{rate}_2 \)
Living in the real world

- For many gases under most conditions, the ideal gas equation works well.
- Two differences between ideal and real:
  1. Real gases occupy nonzero volume.
  2. Molecules do interact with each other – collisions are non-elastic.
Consequences for the ideal gas equation

1. Nonzero volume means actual pressure is larger than predicted by ideal gas equation
   - Positive deviation

2. Attractive forces between molecules mean pressure exerted is lower than predicted – or volume occupied is less than predicted
   - Negative deviation
   - Note that the two effects offset each other
   - Negates consequences of deviation under wide range of conditions
Van der Waals equation: dealing with our deviancies

- Deviation due to finite molecule volume
  - Increases \( P \)
- Deviation due to inelastic collisions
  - Decreases \( P \)

\[
(P + \frac{an^2}{V^2})(V - nb) = nRT
\]

Correction for intermolecular interactions – decreases \( P \)
Correction for molecular volume – increases \( P \)
Real v ideal

- **At fixed temperature (300 K):**
  - $PV_{\text{obs}} < PV_{\text{ideal}}$ at low $P$
  - $PV_{\text{obs}} > PV_{\text{ideal}}$ at high $P$

- **Simulation**
Effects of temperature on deviations

- For given gas deviations from ideal vary with $T$
- As $T$ increases negative deviations from ideal vanish
- Explain in terms of van der Waals equation

\[
\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT
\]

\[
P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}
\]
Making sense with van der Waals

\[
\left( P + \frac{an^2}{V^2} \right)(V - nb) = nRT
\]

\[
P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}
\]

\[
\frac{PV}{RT} = n \left\{ \frac{V^2}{V - nb} - \frac{na}{RT} \right\}
\]
Interpreting real gas behaviors

- First term is correction for volume of molecules
  - Tends to increase $P_{\text{real}}$
- Second term is correction for molecular interactions
  - Tends to decrease $P_{\text{real}}$
- At higher temperatures, molecular interactions are less significant
  - First term increases relative to second term

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

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$