Statistical Mechanics, Kinetic Theory
Ideal Gas

8.01t
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Statistical Mechanics and Thermodynamics

• Thermodynamics Old & Fundamental
  – Understanding of Heat (i.e. Steam) Engines
  – Part of Physics Einstein held inviolate
  – Relevant to Energy Crisis of Today

• Statistical Mechanics is Modern Justification
  – Based on mechanics: Energy, Work, Momentum
  – Ideal Gas model gives observed thermodynamics

• Bridging Ideas
  Temperature (at Equilibrium) is Average Energy Equipartition - as simple/democratic as possible
Temperature and Equilibrium

• Temperature is Energy per Degree of Freedom
  – More on this later (Equipartition)

• Heat flows from hotter to colder object
  Until temperatures are equal
  Faster if better thermal contact
  Even flows at negligible $\Delta t$ (for reversible process)

• The Unit of Temperature is the Kelvin
  Absolute zero (no energy) is at 0.0 K
  Ice melts at 273.15 Kelvin (0.0 C)
  Fahrenheit scale is arbitrary
State Variables of System

• State Variables - Definition
  Measurable Static Properties
  Fully Characterize System (if constituents known)
  e.g. Determine Internal Energy, compressibility
  Related by Equation of State

• State Variables: Measurable Static Properties
  – Temperature - measure with thermometer
  – Volume (size of container or of liquid in it)
  – Pressure (use pressure gauge)
  – Quantity: Mass or Moles or Number of Molecules
    • Of each constituent or phase (e.g. water and ice)
Equation of State

• A condition that the system must obey
  – Relationship among state variables

• Example: Perfect Gas Law
  – Found in 18th Century Experimentally
  – \[ pV = NkT = nRT \]
  – \( K \) is Boltzmann’s Constant \( 1.38 \times 10^{-23} \, \text{J/K} \)
  – \( R \) is gas constant \( 8.315 \, \text{J/mole/K} \)

• Another Eq. Of State is van der Waals Eq.
  – You don’t have to know this.
PV = n R T = N k T

• P is the Absolute pressure
  – Measured from Vacuum = 0
  – Gauge Pressure = Vacuum - Atmospheric
  – Atmospheric = 14.7 lbs/sq in = 10^5 N/m

• V is the volume of the system in m^3
  – often the system is in cylinder with piston
  – Force on the piston does work on world

Does work on world
P=0 outside
PV = n RT = NkT

chemists vs physicists

• Mole View (more Chemical) = nRT
  – R is gas constant 8.315 J/mole/K

• Molecular View (physicists) = NkT
  – N is number of molecules in system
  – K is Boltzmann’s Constant 1.38x10^{-23} J/K
Using PV=nRT

• Recognize: it relates state variables of a gas

• Typical Problems
  – Lift of hot air balloon
  – Pressure change in heated can of tomato soup
  – Often part of work integral
Heat and Work are Processes

• Processes accompany/cause state changes
  – Work along particular path to state B from A
  – Heat added along path to B from A

• Processes are not state variables
  – Processes change the state!
  – But Eq. Of State generally obeyed
Ideal Gas Law Derivation: Assumptions

• Gas molecules are hard spheres without internal structure
• Molecules move randomly
• All collisions are elastic
• Collisions with the wall are elastic and instantaneous
Gas Properties

- $N$ number of atoms in volume
- $n_m$ moles in volume
- $m$ is atomic mass ($^{12}\text{C} = 12$)

- mass density 
  \[
  \rho = \frac{m_T}{V} = \frac{nm}{V} = \frac{n_m N_A m}{V}
  \]

- Avogadro’s Number 
  \[
  N_A = 6.02 \times 10^{23} \text{ molecules} \cdot \text{mole}^{-1}
  \]
Motion of Molecules

• Assume all molecules have the same velocity (we will drop this latter)

• The velocity distribution is isotropic
Collision with Wall

- Change of momentum
  \[ \vec{i}: \Delta p_x = -mv_{x,f} - mv_{x,0} \]
  \[ \vec{j}: \Delta p_y = mv_{y,f} - mv_{y,0} \]

- Elastic collision
  \[ v_{y,f} = v_{y,0} \]
  \[ v_x = v_{x,f} = v_{x,0} \]

- Conclusion
  \[ \vec{i}: \Delta p_x = -2mv_x \]
Momentum Flow Tube

- Consider a tube of cross-sectional area $A$ and length $v_x \Delta t$

- In time $\Delta t$ half the molecules in tube hit wall

- Mass enclosed that hit wall: $\Delta m = \frac{\rho}{2} \text{Volume} = \frac{\rho}{2} A v_x \Delta t$
Pressure on the wall

- Newton’s Second Law
  \[ \vec{F}_{\text{wall, gas}} = \frac{\Delta \vec{p}}{\Delta t} = \frac{-2 \Delta m v_x}{\Delta t} \hat{i} = -\frac{2 \rho A v_x^2 \Delta t}{2 \Delta t} \hat{i} = -\rho A v_x^2 \hat{i} \]

- Third Law
  \[ \vec{F}_{\text{gas, wall}} = -\vec{F}_{\text{wall, gas}} = \rho A v_x^2 \hat{i} \]

- Pressure
  \[ P_{\text{pressure}} = \frac{|\vec{F}|}{A} = \rho v_x^2 \]
Average velocity

- Replace the square of the velocity with the average of the square of the velocity
  \[ (v_x^2)_{\text{ave}} \]

- Random motions imply
  \[ (v^2)_{\text{ave}} = (v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}} = 3(v_x^2)_{\text{ave}} \]

- Pressure
  \[ P_{\text{pressure}} = \frac{1}{3} \rho (v^2)_{\text{ave}} = \frac{2}{3} \frac{n_m N A}{V} \frac{1}{2} m (v^2)_{\text{ave}} \]
Degrees of Freedom in Motion

- Three types of degrees of freedom for molecule
  1. Translational
  2. Rotational
  3. Vibrational

- Ideal gas Assumption: only 3 translational degrees of freedom are present for molecule with no internal structure
Equipartition theorem: Kinetic energy and temperature

• Equipartition of Energy Theorem

\[
\frac{1}{2} m \langle v^2 \rangle_{ave} = \frac{(# \text{degrees of freedom})}{2} kT = \frac{3}{2} kT
\]

• Boltzmann Constant \( k = 1.38 \times 10^{-23} J \cdot K^{-1} \)

• Average kinetic of gas molecule defines kinetic temperature
Ideal Gas Law

- **Pressure**

\[
p_{\text{pressure}} = \frac{2}{3} \frac{n_m N_A}{V} \frac{1}{2} m \left( \langle v^2 \rangle \right)_{\text{ave}} = \frac{2}{3} \frac{n_m N_A}{V} \frac{3}{2} kT = \frac{n_m N_A}{V} kT
\]

- **Avogadro’s Number**

\[N_A = 6.022 \times 10^{23} \text{ molecules} \cdot \text{mole}^{-1}\]

- **Gas Constant**

\[R = N_A k = 8.31 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}\]

- **Ideal Gas Law**

\[pV = n_m RT\]
Ideal Gas Atmosphere

• Equation of State \( PV = n_m RT \)

• Let \( M_{\text{molar}} \) be the molar mass.

• Mass Density \( \rho = \frac{n_m M_{\text{molar}}}{V} = \frac{M_{\text{molar}}}{RT} P \)

• Newton’s Second Law

\[
A \left( P(z) - P(z + \Delta z) \right) - \rho g A \Delta z = 0
\]
Isothermal Atmosphere

• Pressure Equation

\[ \frac{P(z + \Delta z) - P(z)}{\Delta z} = \rho g \]

• Differential equation

\[ \frac{dP}{dz} = -\rho g = -\frac{M_{\text{molar}} g}{RT} P \]

• Integration

\[ \int_{P_0}^{P(z)} \frac{dp}{p} = -\int_{z=0}^{z} \frac{M_{\text{molar}} g}{RT} dz' \]

• Solution

\[ \ln \left( \frac{P(z)}{P_0} \right) = -\frac{M_{\text{molar}} g}{RT} z \]

• Exponentiate

\[ P(z) = P_0 \exp \left( -\frac{M_{\text{molar}} g}{RT} z \right) \]