Chapter 12: Kinetic Theory

Comprehensive Study Notes

Class 11 Physics - NCERT Based

EXAM SPRINT - Complete Coverage for JEE and NEET Examinations

12.1 INTRODUCTION

Historical Development

Boyle's Discovery (1661): First gas law established **Pioneers**: Boyle, Newton - early atomic particle theories **Modern Development**: Maxwell, Boltzmann (19th century)

Key Principles of Kinetic Theory

1. **Gases consist of rapidly moving atoms/molecules**
2. **Inter-atomic forces negligible** (short range forces important only in solids/liquids)
3. **Explains macroscopic properties** through molecular motion

Success of Kinetic Theory

- Molecular interpretation of pressure and temperature
- Consistency with gas laws and Avogadro's hypothesis
- Explains specific heat capacities
- Relates measurable properties (viscosity, conduction, diffusion) to molecular parameters
- Provides estimates of molecular sizes and masses

12.2 MOLECULAR NATURE OF MATTER

Feynman's Atomic Hypothesis

Quote: "Matter is made up of atoms" - most significant discovery **Complete Statement**: All things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.

Historical Atomic Concepts

Ancient India (Kanada - 6th century BC)

- **Vaiseshika School**: Detailed atomic picture
- **Paramanu**: Sanskrit word for smallest particle
- **Four Types**: Bhoomi (Earth), Ap (Water), Tejas (Fire), Vayu (Air)
- **Size Estimation**: Close to modern atomic size ($\sim 10^{-10}$ m) in Lalitavistara

Ancient Greece (Democritus - 4th century BC)

- **Atom**: Greek word meaning "indivisible"
- **Physical Differences**: Shape, size determining substance properties
- **Water atoms**: Smooth and round (flows easily)
- **Earth atoms**: Rough and jagged (hard substances)
- **Fire atoms**: Thorny (causes burns)

Modern Atomic Theory

John Dalton's Contribution: Scientific atomic theory

- **Law of Definite Proportions**: Fixed mass ratios in compounds
- **Law of Multiple Proportions**: Small integer ratios for different compounds

- **Atomic Structure**: Identical atoms within elements, different between elements

Molecular Distances and States

State	Interatomic Distance	Key Characteristics
Solids	~2 Å	Tightly packed, rigidly fixed
Liquids	~2-3 Å	Close but mobile, can flow
Gases	~tens of Å	Far apart, freely moving

Mean Free Path

Definition: Average distance a molecule travels without colliding

- **In gases**: ~thousands of angstroms
- **Significance**: Enables long-distance molecular motion

Intermolecular Forces

- **Long-range attraction**: Acts at few angstroms
- **Short-range repulsion**: Acts when atoms come very close
- **Gas behavior**: Forces negligible except during collisions

Current Understanding

Beyond Atoms:

- Atoms → Nucleus + Electrons
- Nucleus → Protons + Neutrons
- Protons/Neutrons → Quarks
- Quarks → Possibly strings

12.3 BEHAVIOUR OF GASES

Ideal Gas Properties

Advantages of studying gases:

1. Molecules far apart
2. Mutual interactions negligible (except during collisions)
3. Simple mathematical relationships

Gas Laws - Mathematical Formulation

Basic Gas Equation

PV = KT (for given sample) ...(12.1)

- P: Pressure
- V: Volume
- T: Absolute temperature (Kelvin)
- K: Constant for given sample, proportional to number of molecules

Universal Gas Law Development

K = Nk_B where:

- N: Number of molecules
- k_B: Boltzmann constant = 1.38×10^{-23} J K^{-1}

Avogadro's Hypothesis: Equal volumes of gases at same T and P contain equal number of molecules

- **Avogadro Number**: N_A = 6.02×10^{23} molecules in 22.4 L at STP

Perfect Gas Equation

$PV = \mu RT$ ...(12.3)

- μ: Number of moles
- $R = N_A k_B$: Universal gas constant = 8.314 J mol^{-1} K^{-1}

Alternative Forms

$PV = k_B NT$ (using number of molecules) **$PV = nk_B T$** (using number density n) **$P = (\rho RT)/M_0$** (using mass density ρ)

Individual Gas Laws

1. Boyle's Law (Constant Temperature)

PV = constant

- Pressure inversely proportional to volume
- **Condition**: Fixed temperature and mass

2. Charles' Law (Constant Pressure)

$V \propto T$

- Volume directly proportional to absolute temperature
- **Condition**: Fixed pressure and mass

3. Dalton's Law of Partial Pressures

$P_{total} = P_1 + P_2 + P_3 + \ldots$

- Total pressure = sum of partial pressures
- **Partial Pressure**: Pressure gas would exert if alone in container

Real Gas Behavior

- **Deviations**: Occur at high pressure, low temperature
- **Ideal Behavior**: Approached at low pressure, high temperature
- **Reason**: Molecular interactions become negligible

12.4 KINETIC THEORY OF AN IDEAL GAS

Basic Assumptions

1. **Large number** of molecules ($\sim 10^{23}$)
2. **Random motion** following Newton's first law
3. **Negligible interactions** except during collisions
4. **Elastic collisions** (kinetic energy conserved)
5. **Point masses** (molecular size negligible)

12.4.1 Pressure of Ideal Gas - Derivation

Setup

- Gas in cube of side l
- Molecule with velocity (v_x, v_y, v_z)
- Collision with wall parallel to yz-plane

Collision Analysis

Before collision: velocity (v_x, v_y, v_z) **After collision**: velocity ($-v_x$, v_y, v_z) **Momentum change**: $\Delta p = -2mv_x$ **Momentum imparted to wall**: $+2mv_x$

Force Calculation

Molecules hitting wall in time Δt: ½nAv_x Δt

- n: number density (molecules per unit volume)
- A: wall area = l^2
- Factor ½: Only half molecules moving toward wall

Total momentum transfer: Q = $(2mv_x)(½nAv_x \Delta t) = nmAv_x^2 \Delta t$

Force on wall: F = Q/Δt = $nmAv_x^2$

Pressure: P = F/A = nmv_x^2

Final Result

For all molecules: P = $nm\langle v_x^2 \rangle$

Using isotropy: $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = (1/3)\langle v^2 \rangle$

Final pressure equation: $\mathbf{P = (1/3)nm\langle v^2 \rangle}$ ...(12.14)

12.4.2 Kinetic Interpretation of Temperature

Energy Relations

From pressure: PV = $(2/3)N \times ½m\langle v^2 \rangle = (2/3)E$

Where E: Total translational kinetic energy = $N \times ½m\langle v^2 \rangle$

Temperature Connection

Combining with ideal gas law: PV = $Nk_B T$

Result: E = $(3/2)k_B NT$

Average kinetic energy per molecule: $\mathbf{½m\langle v^2 \rangle = (3/2)k_B T}$ ...(12.19)

Key Insights

1. **Temperature** is measure of average kinetic energy
2. **Independent** of gas type, pressure, or volume
3. **Only depends** on absolute temperature
4. **Universal relationship** through Boltzmann constant

Root Mean Square Speed

Definition: $v_{rms} = \sqrt{\langle v^2 \rangle}$

Formula: $v_{rms} = \sqrt{(3k_B T/m)} = \sqrt{(3RT/M)}$

Example (N_2 at 300 K): $v_{rms} \approx 516$ m/s

Important Relationships

- **Lighter molecules**: Higher rms speed at same temperature
- **Speed order**: Similar to speed of sound in air
- **Gas mixtures**: Equal average kinetic energies in equilibrium

12.5 LAW OF EQUIPARTITION OF ENERGY

Degrees of Freedom

Definition: Number of independent coordinates needed to specify molecular motion

Types of Motion

1. **Translational**: Motion of center of mass
   - 1D: 1 degree of freedom
   - 2D: 2 degrees of freedom

- 3D: 3 degrees of freedom

2. **Rotational**: Motion about center of mass
   - **Monatomic**: 0 degrees (point mass)
   - **Diatomic**: 2 degrees (two rotation axes)
   - **Polyatomic**: 3 degrees
3. **Vibrational**: Oscillatory motion
   - Each mode contributes 2 degrees (kinetic + potential energy)

Maxwell's Equipartition Theorem

Statement: In thermal equilibrium at temperature T, energy is equally distributed among all energy modes, with each mode having average energy ½k_B T.

Energy Contributions

- **Each translational degree**: ½k_B T
- **Each rotational degree**: ½k_B T
- **Each vibrational mode**: 2 × ½k_B T = k_B T

Molecular Energy Analysis

Monatomic Gas (e.g., He, Ar)

- **Degrees of freedom**: 3 translational
- **Average energy per molecule**: (3/2)k_B T
- **Total energy per mole**: U = (3/2)RT

Diatomic Gas (e.g., N_2, O_2)

Rigid Rotator Model:

- **Degrees of freedom**: 3 translational + 2 rotational = 5
- **Average energy per molecule**: (5/2)k_B T
- **Total energy per mole**: U = (5/2)RT

With Vibration:

- **Additional degrees**: 1 vibrational mode = 2 degrees
- **Total degrees**: 7
- **Total energy per mole**: U = (7/2)RT

Polyatomic Gas

- **Translational**: 3 degrees
- **Rotational**: 3 degrees
- **Vibrational**: f modes (2f degrees)
- **Total energy per mole**: U = (3 + f)RT

12.6 SPECIFIC HEAT CAPACITY

12.6.1 Monatomic Gases

Derivation

Internal energy: U = (3/2)RT (per mole)

Molar specific heat at constant volume: $C_v = dU/dT = (3/2)R = 12.5\ J\ mol^{-1}\ K^{-1}$

For ideal gas: $C_p - C_v = R$

Molar specific heat at constant pressure: $C_p = C_v + R = (5/2)R = 20.8\ J\ mol^{-1}\ K^{-1}$

Heat capacity ratio: $\gamma = C_p/C_v = 5/3 = 1.67$

12.6.2 Diatomic Gases

Rigid Diatomic

Internal energy: $U = (5/2)RT$

Specific heats:

- $C_v = (5/2)R = 20.8\ J\ mol^{-1}\ K^{-1}$
- $C_p = (7/2)R = 29.1\ J\ mol^{-1}\ K^{-1}$
- $\gamma = 7/5 = 1.40$

Non-rigid Diatomic (with vibration)

Internal energy: $U = (7/2)RT$

Specific heats:

- $C_v = (7/2)R$
- $C_p = (9/2)R$
- $\gamma = 9/7 \approx 1.29$

12.6.3 Polyatomic Gases

General formulas:

- $C_v = (3 + f)R$
- $C_p = (4 + f)R$
- $\gamma = (4 + f)/(3 + f)$

Where f = number of vibrational modes

Summary Table - Theoretical Predictions

Gas Type	Degrees of Freedom	C_v (J mol^{-1} K^{-1})	C_p (J mol^{-1} K^{-1})	γ
Monatomic	3	12.5	20.8	1.67
Diatomic (rigid)	5	20.8	29.1	1.40
Diatomic (vibrating)	7	29.1	37.4	1.29
Triatomic (rigid)	6	24.9	33.2	1.33

12.6.4 Specific Heat of Solids

Classical Theory

Model: N atoms, each oscillating in 3D **Energy per atom**: 3k_B T (3 oscillators × k_B T each) **Total energy per mole**: U = 3RT

Dulong-Petit Law: C = 3R ≈ 25 J mol^{-1} K^{-1}

Agreement: Good for most solids at room temperature **Exceptions**: Light elements (C, Be, B) due to quantum effects

12.7 MEAN FREE PATH

Physical Concept

Observation: Despite high molecular speeds (~500 m/s), gas diffusion is slow **Reason**: Frequent collisions between molecules

Theoretical Derivation

Setup

- Spherical molecules of diameter d

- Focus on one molecule with speed $\langle v \rangle$
- Number density n (molecules per unit volume)

Collision Analysis

Volume swept in time Δt: $\pi d^2 \langle v \rangle \Delta t$ **Number of collisions in Δt**: $n\pi d^2 \langle v \rangle \Delta t$ **Time between collisions**: $\tau = 1/(n\pi d^2 \langle v \rangle)$

Mean Free Path

Definition: $l = \langle v \rangle \tau$

Simple derivation: $l = 1/(n\pi d^2)$ ...(12.39)

More accurate (accounting for relative motion): $\mathbf{l = 1/(\sqrt{2}\, n\pi d^2)}$ ...(12.40)

Numerical Example

For air at STP:

- $\langle v \rangle \approx 485$ m/s
- $n \approx 2.7 \times 10^{25}$ m^{-3}
- $d \approx 2 \times 10^{-10}$ m

Results:

- $\tau \approx 6.1 \times 10^{-10}$ s
- $l \approx 2.9 \times 10^{-7}$ m $\approx 1500d$

Key Features

1. **Inverse dependence** on density and molecular size
2. **Much larger** than molecular size (~1500 times)

3. **Explains** gaseous behavior and diffusion rates
4. **In vacuum**: Can be as large as container dimensions

SUMMARY - KEY EQUATIONS

Gas Laws

1. **Ideal Gas Law**: $PV = \mu RT = Nk_B T$
2. **Pressure from Kinetic Theory**: $P = (1/3)nm\langle v^2 \rangle$
3. **Temperature-Energy Relation**: $\frac{1}{2}m\langle v^2 \rangle = (3/2)k_B T$
4. **RMS Speed**: $v_{rms} = \sqrt{(3k_B T/m)}$

Equipartition of Energy

1. **Energy per degree of freedom**: $\frac{1}{2}k_B T$
2. **Total energy**: $U = (f/2)k_B NT = (f/2)RT$
3. **Specific heats**: $C_v = (f/2)R$, $C_p = (f/2 + 1)R$

Mean Free Path

1. **Mean free path**: $l = 1/(\sqrt{2}\, n\pi d^2)$
2. **Collision time**: $\tau = l/\langle v \rangle$
3. **Collision frequency**: $\nu = \langle v \rangle / l$

IMPORTANT CONSTANTS

Constant	Symbol	Value	Units
Universal Gas Constant	R	8.314	$J\ mol^{-1}\ K^{-1}$
Boltzmann Constant	k_B	1.38×10^{-23}	$J\ K^{-1}$
Avogadro Number	N_A	6.02×10^{23}	mol^{-1}

Constant	Symbol	Value	Units
Atomic Size	-	$\sim 10^{-10}$	m
STP Molar Volume	-	22.4	L

JEE/NEET SPECIFIC POINTS

High-Yield Topics

1. **Kinetic interpretation of temperature**
2. **RMS speed calculations and comparisons**
3. **Degrees of freedom and specific heat predictions**
4. **Mean free path concept and calculations**
5. **Gas law applications and molecular properties**

Common Question Types

1. RMS Speed Problems

- Comparing speeds of different gases at same temperature
- Temperature dependence of molecular speeds
- Effusion and diffusion rate calculations

2. Specific Heat Calculations

- Predicting C_v, C_p, and γ for different gas types
- Energy required for temperature changes
- Equipartition theorem applications

3. Mean Free Path

- Calculating collision frequency and time
- Dependence on pressure, temperature, and molecular size
- Applications to gas transport properties

4. Molecular Energy

- Average kinetic energy calculations
- Energy distribution in different modes
- Relationship between macroscopic and microscopic properties

Memory Aids

Gas Law Constants

"Really Big Kids Always Talk More"

- $R = 8.314\ J\ mol^{-1}\ K^{-1}$
- $k_B = 1.38 \times 10^{-23}\ J\ K^{-1}$
- $N_A = 6.02 \times 10^{23}\ mol^{-1}$

Specific Heat Ratios

- **Monatomic**: $\gamma = 5/3 = 1.67$
- **Diatomic**: $\gamma = 7/5 = 1.40$
- **Triatomic**: $\gamma = 4/3 = 1.33$

Degrees of Freedom

"3 Translate, 2 Rotate, 2 Vibrate per mode"

- Translational: Always 3

- Rotational: 0 (mono), 2 (diatomic), 3 (polyatomic)
- Vibrational: 2 per mode

Practice Problems

1. RMS Speed Comparison

Two gases A and B at same temperature have molecular masses in ratio 1:4. Find ratio of their RMS speeds. **Answer**: $v_A : v_B = 2:1$

2. Specific Heat Prediction

Calculate C_v for rigid diatomic gas. **Answer**: $C_v = (5/2)R = 20.8\ J\ mol^{-1}\ K^{-1}$

3. Mean Free Path

If pressure doubles at constant temperature, how does mean free path change? **Answer**: Becomes half ($l \propto 1/P$)

Advanced Applications

1. **Maxwell-Boltzmann distribution**
2. **Transport phenomena** (viscosity, thermal conduction)
3. **Real gas effects** at high density
4. **Quantum corrections** at low temperature

EXAM SPRINT - Master kinetic theory through understanding molecular motion, energy equipartition, and transport properties. Focus on quantitative problem-solving and conceptual connections between microscopic and macroscopic properties.