

Physics of Matter: A Summary

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From the ideal gas law, the following laws can be derived empirically:

Boyle's Law , for a fixed amount of gas at constant temperature, $p \propto V^{-1}$

Charles' Law , at a fixed pressure, $V \propto T$.

Gay-Lussac's Law , at a fixed volume, $p \propto T$

1.1 Brownian Motion

Brownian motion is the jiggling of small particles suspended in a fluid due to constant collisions with other particles, leading to a **random walk**.

1.1.1 Properties of random walks

As forward steps are just as likely as backward steps, the average displacement is 0:

$$\langle r_N \rangle = 0 \quad (2)$$

For a particle to take N steps of length λ , the average of the square of the displacement is:

$$\langle r_N^2 \rangle = N\lambda^2 \quad (3)$$

The above relation can be shown by considering the one-dimensional case:

$$\begin{aligned} \vec{r}_N &= \vec{r}_{N-1} \pm \vec{\lambda} \\ \langle r_N^2 \rangle &= \vec{r}_N \cdot \vec{r}_N \\ &= r_{N-1}^2 + 2 + 2\vec{\lambda} \cdot \vec{r}_{N-1} + \lambda^2 \\ &= N\lambda^2 \end{aligned}$$

Foreword

This is a summary sheet containing examinable materials for the course Physics of Matter taught by Dr Simon Titmuss and Dr Steward McWilliams.

1 Basic Concepts

The ideal gas equation is an equation of state:

$$pV = Nk_B T \quad (1)$$

1.2 Equipartition Theorem

Equipartition Theorem : If the energy of a classical system is the sum of n quadratic modes, and the system is in contact with a heat reservoir at

temperature T , then the mean energy of the system is:

$$\frac{1}{2}nk_B T \quad (4)$$

In three-dimension, each colloidal particle will have a mean kinetic energy:

$$\langle E_k \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T \quad (5)$$

The name equipartition suggests that the energy is partitioned equally between all the separate modes of the system.

1.3 Probability Distribution Functions

By taking the statistical approach to physics, PDF is something of great importance. For a discrete pdf, the mean of some variable x with probability P is given by:

$$\langle x \rangle = \sum_i x_i P_i \quad (6)$$

For a continuous pdf, $P(x)dx$ gives the probability of x lying in the range $x \rightarrow x + dx$. For a properly normalised pdf, we expect the integral of all possible values of x of $P(x)$ to be unity. The mean of x is given by:

$$\langle x \rangle = \int xP(x)dx \quad (7)$$

For a Gaussian distribution, $P(x)$ takes the form:

$$P(x) = C \exp\left(-\frac{x^2}{2a^2}\right) \quad (8)$$

1.4 Maxwell-Boltzmann Velocity Distribution

The velocity distribution function is the fraction of molecules with velocities between $v_x \rightarrow v_x + dv_x$, as $g(v_x)dv_x$ and is proportional to the Boltzmann factor associated with kinetic energy:

$$g(v_x) \propto \exp\left(-\frac{mv_x^2}{2k_B T}\right) \quad (9)$$

Normalising it gives:

$$g(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \quad (10)$$

The Maxwell-Boltzmann distribution function is given by:

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \quad (11)$$

1.5 Mean, Mode and RMS of the MB Distribution

The most probable speed for the Maxwell-Boltzmann distribution (mode) is given by:

$$v^* = \left(\frac{2k_B T}{m}\right)^{1/2} \quad (12)$$

The mean speed is given by:

$$\langle v \rangle = \int_0^\infty v f(v) dv = \left(\frac{8k_B T}{\pi m}\right)^{1/2} \quad (13)$$

And the RMS speed is given by:

$$\sqrt{\langle v^2 \rangle} = \sqrt{\int_0^\infty v^2 f(v) dv} = \sqrt{\frac{3k_B T}{m}} \quad (14)$$

2 Kinetic Theory of Ideal Gases

The basic assumptions that underpin the theory are:

- Large number of molecules
- The total volume occupied by the gas is much greater than the volume of the molecule
- Rapid motion and collisions take place with other molecules and walls
- Pressure is a manifestation of the collisions with the walls.

Three further assumption simplify this model even further, forming the **ideal gas law**:

- the volume of the molecules is negligible
- intermolecular forces are negligible
- all collisions are elastic

2.1 Pressure of an Ideal Gas

Given that pressure is a result of molecules colliding with the wall of a container. The pressure of a gas can be calculated by using momentum conservation. The rate of collisions between the wall of area A and molecules travelling with velocities $v \rightarrow v + dv$ and in directions $\theta \rightarrow \theta + d\theta$ is given by:

$$Anv dt \cos \theta \frac{1}{2} \sin \theta d\theta f(v) dv \quad (15)$$

where n is the number density.

The **molecular flux** Φ , is the number of collision per area per unit time, and its infinitesimal flux element $d\Phi$, gives the flux travelling with speed v and angle θ to the wall:

$$d\Phi = n(v \cos \theta) \frac{1}{2} \sin \theta d\theta f(v) dv \quad (16)$$

The above quantities, when combined and integrated over all possible values of θ and v , will give pressure:

$$dp = (2mv \cos \theta) d\Phi \quad (17)$$

$$dp = nm \sin \theta \cos^2(\theta) d\theta v^2 f(v) dv \quad (18)$$

$$p = nm \int_0^{\frac{\pi}{2}} -\cos^2(\theta) d(\cos \theta) \int_0^{\infty} v^2 f(v) dv \quad (19)$$

$$p = \frac{1}{3} nm \langle v^2 \rangle \quad (20)$$

2.2 Effusion

A gas is said to be effusing when its molecules escape through a small hole ($r \ll \lambda$). The rate of effusion is ΦA .

$$\Phi = \frac{1}{4} n \langle v \rangle \quad (21)$$

$$= \frac{1}{4} \left(\frac{P}{k_B T} \right) \left(\frac{8k_B T}{\pi m} \right)^{1/2} \quad (22)$$

Note that Φ depends on the square root of $\frac{1}{m}$, this is known as **Graham's Law**.

2.3 Collision Cross Section

A collision cross section σ is given by:

$$\sigma = \pi(a_1 + a_2)^2 + \pi d^2 \quad (23)$$

where a_1 and a_2 are the radii of two different particles, and d is the radii of a cylindrical path that is swept by the travelling particle. λ is given in terms of σ :

$$\lambda = \frac{1}{\sqrt{2} \sigma n} \quad (24)$$

$$= \frac{k_B T}{\sqrt{2} p \sigma} \quad (25)$$

3 Transport Properties of Gases

The three different transport properties of gases are as follows:

1. Diffusion, resulting from a concentration gradient.
2. Viscosity, resulting from a velocity gradient.
3. Thermal conductivity, resulting from a temperature gradient.

3.1 Diffusion

The diffusion equation is given by:

$$\Phi_z = -D \frac{\partial n^*}{\partial z} \quad (26)$$

which gives the molecular flux Φ_z along the z axis as a function of the partial derivative of the number of molecules with respect to position, multiplied by the **diffusivity constant**, D .

D is given by:

$$D = \frac{\lambda}{2} \langle v \rangle \quad (27)$$

3.2 Viscosity

The less able a fluid is at transporting momentum, the more viscous it is. Viscosity gives rise to a shear stress, τ .

$$\tau = \frac{F}{A} = \eta \frac{d\langle u_x \rangle}{dz} \quad (28)$$

where η is the viscosity.

$$\eta = \frac{1}{3} nm \lambda \langle v \rangle \quad (29)$$

It should be noted that η is independent of pressure and is proportional to $T^{1/2}$, which arose from $\langle v \rangle$ component. For gases, η increases as T increases, and decreases for most liquids.

3.3 Thermal Conductivity

Thermal conductivity is defined around κ :

$$\frac{dQ}{dt} = \kappa A \frac{dT}{dy} \quad (30)$$

where the thermal conductivity, κ is given by:

$$\kappa = \frac{1}{3} n C_{\text{molecule}} \lambda \langle v \rangle \quad (31)$$

3.4 Sound waves in Gases

The velocity of a longitudinal wave propagating through a medium via compression and rarefaction is given by:

$$v_B = \left(\frac{K}{\rho}\right)^{1/2} \quad (32)$$

where K is the **bulk modulus**:

$$K = -\frac{dp}{(dV/V)} \quad (33)$$

Assuming isothermal propagation, the modulus $K = p$.

4 Thermodynamics

Classical thermodynamics is based on four postulates:

- **Zeroth Law:** Two bodies A and B that are separately in thermal equilibrium with a third body C, will necessarily be in thermal equilibrium with each other.
- **First Law:** Energy is conserved, and that both heat and work are means of transferring energy to a system:

$$\Delta U = Q + W$$

- **Second Law:** $\Delta G = \Delta H - T\Delta S$
-

4.1 Gas Expansions

The work done in the compression/expansion of gases with a constant external pressure is given by :

$$dW = -p_{\text{ext}} dx = -p dV \quad (34)$$

$$W = -p_{\text{ext}} \int_{V_i}^{V_f} dV \quad (35)$$

Note that the gas does no work when expanding into vacuum.

A reversible change is one that can be reversed by an infinitesimal change in a certain variable. **Reversible isothermal expansion** is achieved by setting $p_{\text{ext}} = p_{\text{int}}$:

$$W = -\int_{V_i}^{V_f} p_{\text{int}} dV \quad (36)$$

where p is given by the ideal gas equation:

$$W = -n_m RT \int_{V_i}^{V_f} \frac{dV}{V} \quad (37)$$

$$= -n_m RT \ln\left(\frac{V_f}{V_i}\right) \quad (38)$$

4.2 Heat Capacity (I)

The heat capacity of an object is defined as:

$$C = \frac{dQ}{dT} \quad (39)$$

when considering the heat capacity of a gas, we need to specify is heat is being supplied in an isobaric condition or an isochoric condition.

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \quad (40)$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p \quad (41)$$

n.b. C_p is bigger than C_V due to the work that needs to be done against the atmosphere. By substituting in to the First Law, heat capacity at constant volume is given by:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (42)$$

The heat capacity at constant pressure is given by:

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p \quad (43)$$

For a monatomic ideal gas, the above equation simplifies to:

$$C_p = C_V + R \quad (44)$$

4.3 Heat capacities of diatomic gases

The initial consideration of equipartition yielded that every quadratic degree of freedom makes a contribution of $\frac{1}{2}k_B T$ to the internal energy. A diatomic gas will have, in addition to the translational kinetic energy, **rotational kinetic energy, potential energy due to bond stretching, and vibrational kinetic energy.** Totalling seven quadratic modes, hence a heat capacity of

$$C_V = \frac{7}{2}R = 29.1 \text{ J K}^{-1} \text{ mol}^{-1} \quad (45)$$

C_V can be generalised for bigger molecules:

$$C_V = \frac{3}{2}R + f_{\text{vib}}R + \frac{f_{\text{rot}}}{2}R \quad (46)$$

4.4 Coefficients of Expansivity

From the expression for C_p , the term $\left(\frac{\partial V}{\partial T}\right)_p$ is the isobaric thermal expansivity term. To estimate the change in volume given a change in temperature, the following equation may be used:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (47)$$

The isothermal compressibility is denoted with B and in an opposite sign, *i.e.* the change in volume given a change in pressure, while maintaining a constant temperature.

$$B = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (48)$$

4.5 Adiabatic Expansion

Adiabatic expansion occurs without the flow of heat and is reversible, thus the first law applies. By rearrangement, the following is true:

$$p V^\gamma = \text{constant} \quad (49)$$

$$\gamma = \frac{C_p}{C_V} \quad (50)$$