# STUDY MATERIAL AND NUMERICAL PROBLEMS: DIFFUSION, VISCOSITY, AND SURFACE TENSION

## I. DIFFUSION AND FICK'S LAW

**Diffusion** is the net movement of anything generally from a region of higher concentration to a region of lower concentration. It is a consequence of the random motion of particles (Brownian motion).

### Fick's First Law of Diffusion

States that the diffusion flux of a chemical species is proportional to the concentration gradient of that species. Mathematically:

$$J = -D \nabla C$$

Where:

- $J$ is the diffusion flux (amount of substance passing through a unit area per unit time).
- $D$ is the diffusion coefficient (a measure of how quickly a substance diffuses). Units: $m^2/s$.
- $\nabla C$ is the concentration gradient (change in concentration per unit distance).
- The negative sign indicates diffusion occurs from high concentration to low concentration.

### Fick's Second Law of Diffusion

Describes how the concentration changes over time due to diffusion. It is a partial differential equation:

$$\partial C/\partial t = D \nabla^2 C$$

This law is analogous to the heat equation and is crucial for predicting concentration profiles over time.

## Flux

Flux (J) quantifies the rate of flow of a substance per unit area. For one-dimensional diffusion, $J = -D\ (dC/dx)$.

## Driving Force and Phenomenological Coefficients

The driving force for diffusion is the **concentration gradient** (or chemical potential gradient in a more general thermodynamic sense). Phenomenological coefficients (like D) relate this driving force to the resulting flux. In the general form of linear irreversible thermodynamics, flux (J) is related to generalized forces (X) by a coefficient (L):

$$J = L\ X$$

For diffusion, $J$ is the mass flux and $X$ is the concentration gradient ($\nabla C$), with $L = -D$.

## Examples of Transport Properties

Transport properties describe the rate at which mass, momentum, or energy is transported through a system due to concentration gradients, velocity gradients, or temperature gradients, respectively.

- **Diffusion Coefficient (D)**: Relates to mass transport (diffusion).
- **Viscosity (η)**: Relates to momentum transport (viscous flow).
- **Thermal Conductivity (k)**: Relates to energy transport (heat conduction).

## Numerical Problems: Diffusion

1. A chemical spills into a river. The concentration gradient of the chemical 1 meter away from the spill is 5 $kg/m^4$. If the diffusion coefficient of the chemical in water is $1 \times 10^{-9}$ $m^2/s$, what is the diffusion flux? Assume one-dimensional diffusion.
   **Solution:**
   $J = -D\ (dC/dx) = -(1 \times 10^{-9}\ m^2/s) * (5\ kg/m^4) = -5 \times 10^{-9}\ kg/(m^2 \cdot s)$
   The negative sign indicates flow in the direction of decreasing concentration. The magnitude of the flux is $5 \times 10^{-9}$ $kg/(m^2 \cdot s)$.

2. Estimate the time it would take for a molecule to diffuse across a cell membrane (50 nm thick) if its diffusion coefficient is $1 \times 10^{-12}$ $m^2/s$. (Hint: Use $t \approx x^2/D$ for random walk diffusion).
   **Solution:**
   $t \approx (50 \times 10^{-9}\ m)^2 / (1 \times 10^{-12}\ m^2/s) = (2500 \times 10^{-18}\ m^2) / (1 \times 10^{-12}\ m^2/s) = 2.5 \times 10^{-6}\ s = 2.5\ \mu s$

## II. VISCOSITY

**Viscosity** is a measure of a fluid's resistance to flow. It quantifies the internal friction of a fluid.

### General Features of Fluid Flow

- **Streamline Flow (Laminar Flow)**: Fluid particles move in smooth layers (laminae) that slide past one another. There is no mixing between layers. Flow is orderly.
- **Turbulent Flow**: Characterized by chaotic, irregular fluid motion, with eddies and swirls. Significant mixing occurs. Occurs at higher velocities and/or with larger dimensions.

### Newton's Equation and Viscosity Coefficient

For Newtonian fluids, the shear stress ($\tau$) is directly proportional to the shear rate (velocity gradient). Newton's law of viscosity states:

$$\tau = \eta\ (du/dy)$$

Where:

- $\tau$ is the shear stress (force per unit area). Units: Pa ($N/m^2$).
- $\eta$ (eta) is the **coefficient of viscosity**. Units: Pa·s or Poise (P). 1 Pa·s = 10 Poise.
- $du/dy$ is the velocity gradient (shear rate).

## Poiseuille's Equation

Describes the pressure drop ($\Delta P$) along a cylindrical pipe of length (L) and radius (r) for laminar flow of a Newtonian fluid with viscosity ($\eta$) and flow rate (Q).

**Concept of Derivation:** It balances the pressure driving the flow against the viscous forces resisting it. Assumes steady, laminar, incompressible flow in a horizontal pipe.

$$Q = (\pi r^4 \Delta P) / (8 \eta L)$$

This can be rearranged to find viscosity:

$$\eta = (\pi r^4 \Delta P) / (8 Q L)$$

## Determination of Viscosity

1. **Falling Sphere Method (Stokes' Law)**:
   A sphere of radius $r$ and density $\rho_s$ falling through a fluid of density $\rho_f$ and viscosity $\eta$ reaches a terminal velocity ($v_t$) when the gravitational force is balanced by the buoyant force and the viscous drag force (Stokes' Law: $F_{drag} = 6\pi\eta r v$).
   At terminal velocity: $(4/3)\pi r^3(\rho_s - \rho_f)g = 6\pi\eta r v_t$.
   This allows calculation of $\eta$ if $v_t$ is measured.
2. **Ostwald Viscometer**:
   This is a capillary viscometer. It measures the time it takes for a fixed volume of liquid to flow through a narrow capillary tube under its own weight or a small applied pressure. The time is proportional to the viscosity. For two liquids (1 and 2) flowing through the same viscometer:
   $\eta_1/\eta_2 = (\rho_1 t_1) / (\rho_2 t_2)$

## Temperature Variation of Viscosity

- **Liquids**: Viscosity generally **decreases** significantly with increasing temperature. Increased thermal energy overcomes intermolecular attractive forces, allowing molecules to move more freely.
- **Gases**: Viscosity generally **increases** with increasing temperature. Higher temperatures mean faster-moving molecules, leading to more frequent momentum transfer between layers, thus higher resistance to shear.

Relation between Viscosity Coefficient of a Gas and Mean Free Path

For gases, viscosity is related to the average speed of molecules and their mean free path (λ, the average distance between collisions):

$$\eta \approx (1/3) * \rho * \bar{V} * \lambda$$

Where ρ is the density and $\bar{V}$ is the average molecular speed. As temperature increases, $\bar{V}$ increases, and λ also tends to increase slightly, leading to an overall increase in viscosity.

Numerical Problems: Viscosity

1. Water (viscosity 0.001 Pa·s, density 1000 kg/m$^3$) flows through a pipe of radius 0.01 m and length 10 m. If the pressure drop is 1000 Pa, what is the flow rate? Use Poiseuille's equation.
   **Solution:**
   $Q = (\pi * (0.01\ m)^4 * 1000\ Pa) / (8 * 0.001\ Pa\cdot s * 10\ m) = (\pi * 10^{-8}\ m^4 * 10^3) / (8 * 10^{-3}) = (\pi * 10^{-5}) / (8 * 10^{-3}) \approx 3.93 \times 10^{-3}\ m^3/s$

2. A steel ball bearing (density 7800 kg/m$^3$, radius 2 mm) falls through oil (density 900 kg/m$^3$, viscosity 0.5 Pa·s). What is its terminal velocity? (g = 9.8 m/s$^2$)
   **Solution:**
   $(4/3)\pi r^3(\rho_s - \rho_f)g = 6\pi\eta r v_t$
   $v_t = [2r^2(\rho_s - \rho_f)g] / (9\eta)$
   $v_t = [2 * (2 \times 10^{-3}\ m)^2 * (7800 - 900\ kg/m^3) * 9.8\ m/s^2] / (9 * 0.5\ Pa\cdot s)$
   $v_t = [2 * 4 \times 10^{-6}\ m^2 * 6900\ kg/m^3 * 9.8\ m/s^2] / 4.5\ Pa\cdot s$
   $v_t \approx (5.41 \times 10^{-1}\ m/s) \approx 0.541\ m/s$

3. Using an Ostwald viscometer, water (density 1000 kg/m$^3$) takes 40 seconds to flow a certain volume, while an unknown liquid (density 800 kg/m$^3$) takes 60 seconds. If the viscosity of water is 0.001 Pa·s, what is the viscosity of the unknown liquid?
   **Solution:**
   $\eta_{liquid} / \eta_{water} = (\rho_{liquid} * t_{liquid}) / (\rho_{water} * t_{water})$
   $\eta_{liquid} = \eta_{water} * (\rho_{liquid} * t_{liquid}) / (\rho_{water} * t_{water})$
   $\eta_{liquid} = (0.001\ Pa\cdot s) * (800\ kg/m^3 * 60\ s) / (1000\ kg/m^3 *$

40 s)
$\eta_{liquid}$ = (0.001 Pa·s) * (48000) / (40000) = 0.001 * 1.2 = 0.0012 Pa·s

## III. SURFACE TENSION AND ENERGY

**Surface Tension (γ)**: The tendency of liquid surfaces to shrink into the minimum surface area possible. It is the force per unit length acting along the surface, or equivalently, the surface energy per unit area. Units: N/m or $J/m^2$.

**Surface Energy**: The excess energy which a surface has by comparison with the corresponding bulk phase. For liquids, it is directly related to surface tension: Surface Energy = γ.

### Excess Pressure

Due to surface tension, there is an excess pressure inside a curved liquid surface compared to the outside pressure. For a spherical droplet (one interface):

$$\Delta P = 2\gamma / r$$

For a soap bubble (two interfaces, air inside, air outside):

$$\Delta P = 4\gamma / r$$

Where $r$ is the radius of curvature.

### Capillary Rise

When a narrow tube (capillary) is placed in a liquid that wets the tube, the liquid rises inside the tube. The upward force due to surface tension balances the weight of the liquid column.

Force of surface tension = $2\pi r \gamma \cos(\theta)$ (where $r$ is capillary radius, $\theta$ is contact angle)

Weight of liquid column = $\pi r^2 h \rho g$

For a liquid that wets the tube (e.g., water on glass, $\theta=0$, $\cos(\theta)=1$):

$$2\pi r \gamma = \pi r^2 h \rho g$$

$h = (2\gamma) / (r \rho g)$

If the liquid does not wet the tube (e.g., mercury on glass), it will be depressed.

## Work of Cohesion and Adhesion

- **Cohesion**: The intermolecular attraction between like molecules (e.g., water molecules attracting each other).
- **Adhesion**: The intermolecular attraction between unlike molecules (e.g., water molecules attracting glass molecules).
- **Spreading of Liquid**: A liquid spreads on a surface if the adhesive forces between the liquid and the surface are greater than the cohesive forces within the liquid. The spreading coefficient (S) is given by $S = \gamma_{substrate} - \gamma_{liquid} - \gamma_{adhesion}$. If $S > 0$, spreading occurs.

## Vapour Pressure Over Curved Surface

The vapour pressure of a liquid is higher over a curved surface (especially convex) than over a flat surface. This is due to the surface tension trying to minimize the surface area, which requires work to expand the surface (creating more vapour molecules).

The Kelvin equation describes this:

$$\ln(P/P_0) = 2\gamma V_m / (rRT)$$

Where P is vapour pressure over curved surface, $P_0$ is vapour pressure over flat surface, $V_m$ is molar volume, R is gas constant, T is temperature, $r$ is radius of curvature.

## Temperature Dependence of Surface Tension

Surface tension **decreases** with increasing temperature. At the critical temperature, surface tension becomes zero.

Numerical Problems: Surface Tension

1. Calculate the excess pressure inside a spherical water droplet (radius 0.1 mm) compared to the outside air. (Surface tension of water $\gamma = 0.072$ N/m).
   **Solution:**
   $\Delta P = 2\gamma / r = (2 * 0.072 \text{ N/m}) / (0.1 \times 10^{-3} \text{ m}) = 0.144 \text{ N/m} / 10^{-4} \text{ m} = 1440 \text{ Pa}$

2. If a capillary tube of radius 0.5 mm is dipped into water, how high will the water rise? Assume the water wets the glass (contact angle $\theta=0$) and the surface tension is 0.072 N/m. (Density of water = 1000 kg/$m^3$, g = 9.8 m/$s^2$).
   **Solution:**
   $h = (2\gamma) / (r \rho g) = (2 * 0.072 \text{ N/m}) / (0.5 \times 10^{-3} \text{ m} * 1000 \text{ kg/m}^3 * 9.8 \text{ m/s}^2)$
   $h = 0.144 \text{ N/m} / (4.9 \text{ N/m}^2) \approx 0.0294 \text{ m} = 29.4 \text{ mm}$

3. Determine the surface tension of a liquid if it rises to a height of 1 cm in a capillary tube of radius 0.2 mm, given the liquid's density is 900 kg/$m^3$ and the contact angle is 0. (g = 9.8 m/$s^2$).
   **Solution:**
   $\gamma = (r h \rho g) / 2 = (0.2 \times 10^{-3} \text{ m} * 0.01 \text{ m} * 900 \text{ kg/m}^3 * 9.8 \text{ m/s}^2) / 2$
   $\gamma = (0.1764 \text{ N/m}) / 2 \approx 0.0882 \text{ N/m}$