

Diffusion coefficient in liquids

Stokes-Einstein Law for Liquid

- Idealized slow movement of single rigid solute sphere through a continuum of solvent.
- Net velocity of the sphere proportional to force acting.
- For slow movement of sphere, Stokes law describes the force.
- Einstein proposed that **force in diffusion arises from the chemical potential gradient**.
- The analysis for diluted solution can be extended to concentrated solution.

Diffusion coefficient in gases

Chapman Enskog theory

Diffusion coefficient is function of temperature, pressure, molecular weight, collision diameter, Lennard Jones potential describing interaction of molecules.

Spreading of a spot in a resting fluid

- Very small spot of tracer at $t = 0$ is expressed using Dirac function that is zero everywhere except at the origin.
- The integral of the Dirac function is equal to one.
- Mass balance on a differential volume.
- Boundary conditions
- **Concentration = $f(z, t)$**

Mixing

Spreading of a front

- Same governing equation arising from a differential element.
- Initial and boundary conditions are different.

Pressure drop in non-circular channel based on Navier Stokes equation

Concentration distribution in two parallel streams.

Sequential Lamination

- Segregates the joined stream into two channels, and rejoins them in the next transformation stage.
- Also known as Split and Recombine (SAR) mixer.

Mixing ...contd.

Stretching function (linear and elongational)

- Repeated action by the flow generates a lamellar structure.
- Stretched and folded striations with thickness $s(t)$, characterized by a probability density function, whose mean decreases with time.
- Real stream in mixer composed of islands and chaotic regions. Islands translate, stretch, contract and undergo rotation as a whole. Stretching in island is linear.
- In chaotic regions, stretching is elongational.

Mixing ...contd.

Sequential Segmentation

Solvent and solute streams are broken up into segments along the axial direction by alternate switching of inlet flows.

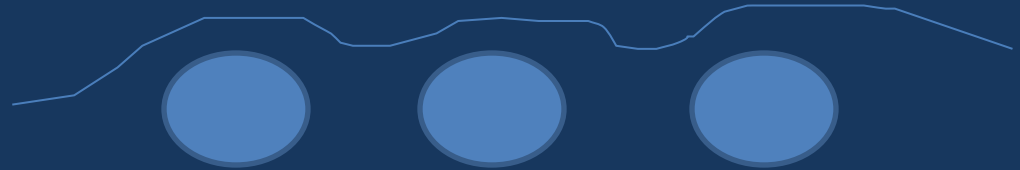
Difference between chaos promoted by advection and that by turbulence

At low Re number

- No wake or recirculation after the pillars
- Pillars induce shear and hence Taylor Aris dispersion

At high Re number

- Turbulence induced by pillars
- Very effective mixing
- Not used in microsystems



Herringbone Micromixer

- Series of herringbone shaped grooves placed in the channel
- The hollows force the fluid to flow obliquely with respect to the direction of principal flow.
- To satisfy mass-continuity, return flows develop, resulting in helically shaped trajectory of fluid.
- Pattern changes, say every five herringbones. Accordingly, the centre of fluid helices get displaced.

Mixing quality and mixing effectiveness

Taylor dispersion: Use in chromatography

- Dispersion (Flow + Brownian motion = rapid mixing)
- Example: smoke from plume, carried by wind velocity
- Difference between diffusion and dispersion
- Dispersion of tracer while flowing through a canal (circular or non-circular cross-section) that has small transverse dimension (capillary, microchannel).
- Mass transport in radial direction is by diffusion.
- Mass transport in axial direction is by convection.
- From the expression for the concentration profile, dispersion coefficient depends inversely on diffusivity

Taylor dispersioncontd.

- For zero diffusion, the pulse will continue to distort unabated → wide dispersion that depends on velocity.
- For rapid diffusion, the radial diffusion inhibits the dispersion induced by axial convection.
- The value of Dispersion coefficient for microsystems attain value of 0.1 to 100.

Solute transport in micro-scale chromatography

- To identify components in gas or liquid mixture.
- Accumulation of a component at the interface between two phases (e.g., solid-gas) due to attractive intermolecular forces.
- A pulse of mixed solutes is injected into one end of a tube with inner-wall coated with adsorbent (the stationary phase).
- Solutes are adsorbed to different degrees, and elute at different times.
- Conventional chromatography utilizes packed bed. Micro-scale chromatography uses adsorbent-coated inner walls of a channel, or a monolith coated with adsorbent.

Transport in microscale chromatography ..contd.

- The technique may be compromised by dispersion.
- Extended form of Taylor dispersion equation.
- Three components of E_z term.
- Second term arising from Taylor dispersion → making tube 10 times smaller can reduce this component of dispersion 100 times → small channels are ideal for chromatography.
- Third term arising from retardation in the adsorbent layer. If diffusion in the adsorbent is very fast or $\delta/R_0 \ll 1$, no effect of third term. The separation due to adsorption becomes dominant when $k' \gg 1$.

Transport in microscale chromatography...contd.

- Different solutes will have different retention time t_0
 - depending on the k' of corresponding solute.
- Objective is to make $E_z \rightarrow 0$, so that each solute elutes as sharp pulse. For broadened peak, the pulses overlap and identification is compromised.
- R_0 and v_0 should be decreased to achieve $E_z \rightarrow 0$, as long as pressure drop is not excessive.

Electrokinetics

- Interaction between solid surfaces, ionic solutions, and macroscopic electric field.
- Electrophoresis & Electroosmosis
- Both are manifestations of electrostatic component of the Lorentz force on ions and surface charges and Newton's second law of motion.
- Electrophoresis: Induced drift motion of colloidal particles or molecules, suspended in liquids due to an electric field.
- Electroosmosis: Motion of electrolyte liquid with respect to a fixed wall due to electric field, applied parallel to the surface.

Electric Double Layer

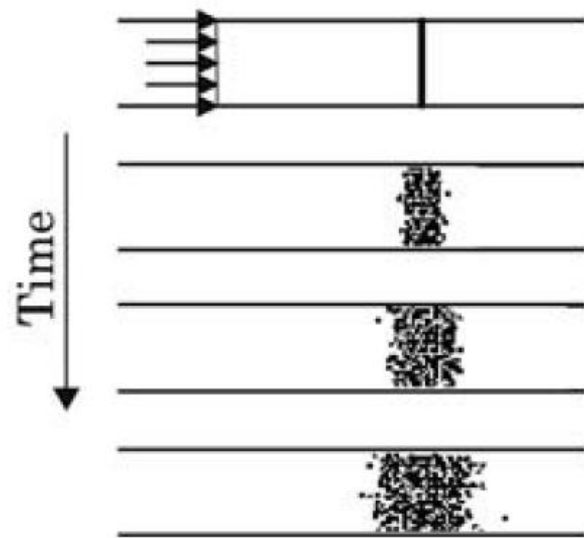
- Solid surface acquires surface charge when brought into contact with an electrolyte liquid due to
 - Differential adsorption of ions from electrolyte onto solid surface.
 - Differential solution of ions from the surface to the electrolyte.
 - Deprotonation /ionization of surface groups (e.g., surface silanol group of glass or silica: $\text{SiOH} \leftrightarrow \text{SiO}^- + \text{H}^+$)
- Deprotonation is most common.
- Net surface charge density at the liquid-solid interface is a function of local pH. Full deprotonation at $\text{pH} > 9$.

Electric Double Layercontd.

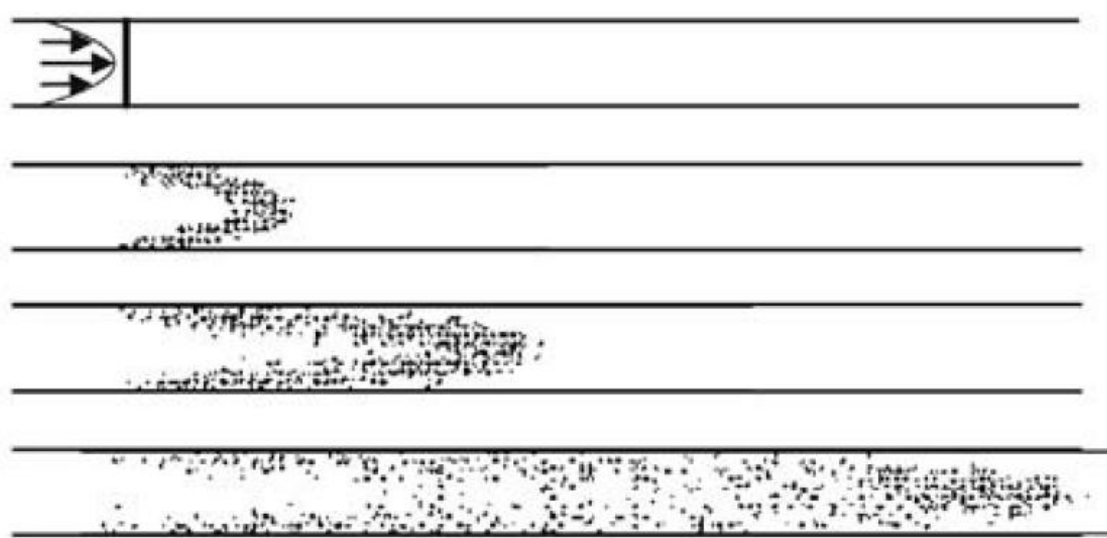
- Ions of opposite charge in the electrolyte are attracted and the like charges are repelled.
- The net excess of mobile ions near the interface with charge, opposite to that of the wall is referred as EDL.
- These excess charges can be used to impart a force on bulk fluid through ion-drag.
- Counter-ions reside in compact layer next to the wall (Stern layer) in adsorbed state.
- Counter ions also reside in more diffused layer next to the wall, where the ions are free to move.

Electric Double Layercontd.

- The potential at the shear plane (the boundary of the liquid flow problem) is called zeta potential.
- Debye length
- Debye Hückel limit
- Single flat plate and parallel plate geometry
- Velocity profile under electroosmotic flow



(a)



(b)

$$\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{g} - \nabla p + \mu \nabla^2 \mathbf{v}$$

