2. Particle Motion

- Gravitational settling
- Brown motion (diffusive-type process)

The transport of particles within fluids is very strongly influenced by their size and mass. For larger particles, transport mechanisms depend on mass and predominate over diffusive motion.

2.1 Drag on Particle

$$F_{G} = \rho_{p} \cdot g \cdot V_{p}$$

$$F_{B} = \rho_{f} \cdot g \cdot V_{p}$$

$$F_{D} = C_{D} \cdot A_{p} \cdot \rho_{f} \cdot \frac{v^{2}}{2}$$



where F_G = gravitational force;

- F_B = buoyancy force;
- $F_D = drag force;$
- ρ_p = density of a particle;
- ρ_f = density of a fluid;
- g = acceleration due to gravity;



 V_{p} = volume of the particle;

 $C_D = drag \ coefficient;$

 A_p = cross sectional area of the particle; and

v = speed of the particle relative to the fluid.

The drag force on a spherical particle (F_D) is computed by the following expression,

$$\mathbf{F}_{\mathrm{D}} = \mathbf{C}_{\mathrm{D}} \cdot \left(\frac{\pi}{4} \cdot \mathbf{d}_{\mathrm{p}}^{2}\right) \cdot \left(\frac{1}{2} \cdot \boldsymbol{\rho}_{\mathrm{f}} \cdot \mathbf{v}^{2}\right)$$

where d_p = particle diameter.



Figure 4.B.1 Drag coefficient as a function of particle Reynolds number for smooth, spherical, nonaccelerating particles in a uniform fluid flow. The experimental data are from Lapple and Shepherd (1940). The correlation equations are described in the text.

$$R = \frac{d_{p} \cdot v}{v} = \frac{d_{p} \cdot \rho_{f} \cdot v}{\mu}$$

$$C_{D} = \frac{24}{R} (R < 0.3)$$

$$C_{D} = \frac{24}{R} \cdot (1 + 0.14 \cdot R^{0.7}) (0.3 < R < 1,000)$$

$$C_{D} = 0.445 (1,000 < R < 350,000)$$



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where v = kinematic viscosity; and

 μ = dynamic viscosity

$$F_{\rm D} = 3 \cdot \pi \cdot \mu \cdot d_{\rm p} \cdot v \quad (\mathsf{R} < 0.3)$$

$$F_{\rm D} = 0.173 \cdot \rho_{\rm f} \cdot d_{\rm p}^{-2} \cdot v^{2} \quad (1,000 < \mathsf{R} < 350,000)$$

One important correction is made in considering the drag force on small particle ($d_p < 1\mu m$) in air because the air is made up of molecules rather than a continuously smooth fluid. The drag force on very small particles in air is computed by introducing the Cunningham slip correction factor, C_c ,

$$F_{\rm D} = \frac{1}{C_{\rm c}} \cdot \left(3 \cdot \pi \cdot \mu \cdot d_{\rm p} \cdot v \right) = f \cdot v \quad (\mathsf{R} < 0.3)$$

where f = friction coefficient

2.2 Gravitational Settling

Terminal Settling Velocity (or Terminal Rising Velocity)

$$\begin{split} & \mathsf{F}_{\mathsf{G}} = \mathsf{F}_{\mathsf{B}} + \mathsf{F}_{\mathsf{D}} \\ & \mathsf{F}_{\mathsf{G}} = \mathsf{m} \cdot \mathsf{g} = \rho_{\mathsf{p}} \cdot \frac{\pi}{6} \cdot \mathsf{d}_{\mathsf{p}}^{-3} \cdot \mathsf{g} \\ & \mathsf{F}_{\mathsf{B}} = \rho_{\mathsf{f}} \cdot \frac{\pi}{6} \cdot \mathsf{d}_{\mathsf{p}}^{-3} \cdot \mathsf{g} \\ & \mathsf{F}_{\mathsf{D}} = \mathsf{C}_{\mathsf{D}} \cdot \left(\frac{\pi}{4} \cdot \mathsf{d}_{\mathsf{p}}^{-2}\right) \cdot \left(\frac{1}{2} \cdot \rho_{\mathsf{f}} \cdot \mathsf{v}^{2}\right) = \mathsf{C}_{\mathsf{D}} \cdot \frac{\pi}{4} \cdot \mathsf{d}^{2} \cdot \rho_{\mathsf{f}} \cdot \frac{v^{2}}{2} \\ & \therefore \mathsf{v} = \sqrt{\frac{4 \cdot \mathsf{g} \cdot \mathsf{d}_{\mathsf{p}}}{3 \cdot \mathsf{C}_{\mathsf{D}}} \cdot \left(\frac{\rho_{\mathsf{p}} - \rho_{\mathsf{f}}}{\rho_{\mathsf{f}}}\right)} \end{split}$$

If the density of the settling particle is less than that of the fluid, the terminal rising



velocity is,

The particle flux caused by gravitational settling is analogous to the contaminant flux caused by advection as follows:

J_g = C·v

The vector form of this relationship is,

$$\vec{\mathbf{J}}_{g}(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \mathbf{C}(\mathbf{x}, \mathbf{y}, \mathbf{z}) \cdot \vec{\mathbf{v}}$$

Drag Force on Nonspherical Particle

Shape	X
Cube	1.08
Cylinder $(L/D = 4$, axis normal to flow)	1.32
Aggregates of spheres	
Chain of 2	1.12
Chain of 3	1.27
Chain of 4	1.32
Compact aggregate of 3	1.15
Compact aggregate of 4	1.17
Bituminous coal	1.05 - 1.11
Quartz	1.36
Sand	1.57
Talc	2.04

 Table 2.2. Shape Factors for Nonspherical Particles

Source: Hinds, Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, © 1982, p. 48. Reprinted by permission of John Wiley & Sons, Inc.



2.3 Brownian Diffusion

A transport mechanism caused by the random motion of fluid molecules, so called "Brownian motion" is molecular diffusion. An analogous phenomenon applies to particles suspended in a fluid.

The Brownian diffusivity of particles **in air** is determined by an equation known as the Stokes-Einstein relation,

$$D = \frac{k \cdot T}{f}$$

where k = Boltzmann's constant (1.38 x 10⁻¹⁶ erg/K);

T = temperature (K); and

$$f = friction \ coefficient. \ f = \frac{1}{C_c} \cdot \left(3 \cdot \pi \cdot \mu \cdot d_p \right)$$



Figure 4.B.6 Brownian diffusivity for particles in air and water; T = 20 °C, P = 1 atm.





Figure 4.B.7 Distance traveled in 10 s by particles in air or water because of gravitational settling and Brownian diffusion. Particle settling velocities were determined from Stokes's law (Table 4.B.1) with T = 293 K and P = 1 atm. Diffusion distances were estimated from expression 4.A.7, using the Stokes-Einstein relation to compute diffusivity (equation 4.B.18). Particle density is 2.5 g cm⁻³.



2.4 Double Layer and Colloidal Stability

What is "Colloids"?

- aggregates of atoms, molecules, or mixed materials
- considered larger than individual atoms or molecules
- enough small to possess properties greatly different from coarse particles dispersion behavior
- normally range in size from about 1 nm to 100 nm



Figure 3.6. Negatively charged particle surrounded by diffuse layers of counterions and coions.

Concentration Curve

For the conterions, the concentration curve is a decaying exponential type. Similarity to gravity (e.g., atmosphere distribution on the earth)

$$\frac{\mathbf{P}}{\mathbf{P}_0} = \exp\left(-\frac{\mathbf{g}\cdot\mathbf{m}_a\cdot\mathbf{z}}{\mathbf{R}\cdot\mathbf{T}}\right)$$



where P_0 = gas pressure at the surface m_a = molar mass of the gas

At the enough far from the particle, $\sum_{i=1}^{i} [counterions]_i = \sum_{i=1}^{j} [coions]_i$ because of the

"law of principle of solution electroneutrality". However, it is not true near the charged particle.

 \int counterion concetration curve - \int coion concetration curve = surface excess of the particle charge

Fundamental equation for electrical potential to charge in the diffuse ion distribution

 \rightarrow Poisson equation

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho}{\epsilon \cdot \epsilon_0}$$

where ψ = electro field potential (V, volts);

 ρ = charge density (coulomb/cm³);

 ε_0 = permittivity in a vaccum (= 8.854x10⁻¹² C/V·m or 8.854x10⁻¹² C²/J·m)

 ϵ = relative permittivity of the medium (dimensionless) (e.g., 78.5 for water at 25°C).

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\rho}{\varepsilon \cdot \varepsilon_0}$$

On the other hand,

$$\rho = \sum_{i} (z_i \cdot e \cdot n_i)$$

and



$$\frac{\mathbf{n}_{i}}{\mathbf{n}_{i,0}} = \exp\left(-\frac{\mathbf{z}_{i} \cdot \mathbf{e} \cdot \boldsymbol{\psi}}{\mathbf{k} \cdot \mathbf{T}}\right)$$

where z_i = valence of the ith-type ion;

 n_i = number of the ith-type ion per cubic concentration (#/cm³);

 $n_{i,0}$ = number of the ith-type ion per cubic concentration at an infinite distance (#/cm³);

e = electron charge (= 4.80×10^{-10} esu or 1.602×10^{-19} C);

then,

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\varepsilon \cdot \varepsilon_0} \cdot \sum_{i} \left\{ z_i \cdot e \cdot n_{i,o} \cdot exp\left(-\frac{z_i \cdot e \cdot \psi}{k \cdot T}\right) \right\}$$

Since $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$

If the electro filed potential, ψ is low, $\left|\frac{z_i \cdot e \cdot \psi}{k \cdot T}\right| << 1$ and

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\varepsilon \cdot \varepsilon_0} \cdot \sum_{i} \left\{ z_i \cdot e \cdot n_{i,o} - \frac{z_i^2 \cdot e^2 \cdot n_{i,o} \cdot \psi}{k \cdot T} \right\}$$

Since $\sum_{i} (z_i \cdot e \cdot n_{i,o}) = 0$ for the condition of solution electroneutrality

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{e^2 \cdot \psi}{\varepsilon \cdot \varepsilon_0 \cdot k \cdot T} \cdot \sum_i (z_i^2 \cdot n_{i,o})$$

B.C $\psi = \psi_0$ at $x = 0$
 $\frac{d\psi}{dx} = 0$ at $x = \infty$

The solution is,

 $\psi = \psi_0 \cdot \exp(-\kappa \cdot x)$

 $\label{eq:kinetic} \text{where} \quad \kappa^2 = \frac{e^2 \cdot \sum_i \Bigl({z_i}^2 \cdot n_{i,o} \Bigr)}{\mathcal{E} \cdot \mathcal{E}_o \cdot k \cdot T}$



$$n_{i,o}\left(\frac{\#}{cm^{3}}\right) = \frac{6.02 \times 10^{23} \#}{mol} \cdot \frac{L}{10^{3} cm^{3}} \cdot M_{i,o}\left(\frac{mol}{L}\right)$$
$$\sum_{i} \left(z_{i}^{2} \cdot n_{i,o}\right) = \frac{2 \times 6.02 \times 10^{23} \#}{10^{3} cm^{3}} \cdot \frac{1}{2} \sum_{i} \left(z_{i}^{2} \cdot M_{i,o}\right) = \frac{2 \times 6.02 \times 10^{23} \#}{10^{3} cm^{3}} \cdot I$$

where $M_{I,0}$ = molar concentration of the ith-type ion at an infinite distance (moles/L). I = ionic strength of the solution.

Then,

$$\kappa^{2} = \frac{2 \times (1.602 \times 10^{-19} \text{C})^{2} \times (6.02 \times 10^{23})}{78.5 \times \left(8.854 \times 10^{-12} \frac{\text{C}^{2}}{\text{J} \cdot \text{m}}\right) \times \left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}\right) \times 298 \text{K} \times 10^{3} \text{cm}^{3} \times \left(\frac{\text{m}}{10^{2} \text{cm}}\right)^{3}} \cdot \text{I}$$

 $\kappa = 3.29 \times 10^{9} \times \text{I}^{1/2} (1/\text{m})$

 $1/\kappa$ has dimension of [L].

 $1/\kappa$ = Double layer thickness

The assumption of low potential can be released in an analysis known as the Gouy-Chapman theory. The final results are (Hienmenz, 1977)

$$\frac{\exp\left(\frac{\mathbf{z}\cdot\mathbf{e}\cdot\boldsymbol{\psi}}{2\cdot\mathbf{k}\cdot\mathbf{T}}\right)-1}{\exp\left(\frac{\mathbf{z}\cdot\mathbf{e}\cdot\boldsymbol{\psi}}{2\cdot\mathbf{k}\cdot\mathbf{T}}\right)+1} = \frac{\exp\left(\frac{\mathbf{z}\cdot\mathbf{e}\cdot\boldsymbol{\psi}_{0}}{2\cdot\mathbf{k}\cdot\mathbf{T}}\right)-1}{\exp\left(\frac{\mathbf{z}\cdot\mathbf{e}\cdot\boldsymbol{\psi}_{0}}{2\cdot\mathbf{k}\cdot\mathbf{T}}\right)+1} \cdot \exp\left(-\kappa\cdot\mathbf{x}\right)$$

or

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$$\gamma = \gamma_0 \cdot \exp(-\kappa \cdot x)$$



where
$$\gamma = \frac{\exp\left(\frac{z \cdot e \cdot \psi}{2 \cdot k \cdot T}\right) - 1}{\exp\left(\frac{z \cdot e \cdot \psi}{2 \cdot k \cdot T}\right) + 1}$$

The two relationships are only for symmetrical electrolytes (i.e., magnitude of the valences of cations and anions are identical, e.g., 1:1 NaCl, 2:2 MgSO₄, etc.)

For the surface charge density, σ_p (C/m², or surface excess)

$$\sigma_p = \int_0^\infty \rho \, dx$$

٦2

since

$$\frac{d^{2}\psi}{\partial x^{2}} = -\frac{\rho}{\varepsilon \cdot \varepsilon_{0}}$$

$$\sigma_{p} = -\varepsilon \cdot \varepsilon_{0} \int_{0}^{\infty} \frac{d^{2}\psi}{dx^{2}} dx = -\varepsilon \cdot \varepsilon_{0} \frac{d\psi}{dx} \Big|_{0}^{\infty} = -\varepsilon \cdot \varepsilon_{0} \cdot \frac{d\psi}{dx} \Big|_{x=0}$$

$$\frac{d\psi}{dx} \Big|_{x=0} = -\kappa \cdot \psi_{0}$$

$$\therefore \sigma_{p} = \varepsilon \cdot \varepsilon_{0} \cdot \kappa \cdot \psi_{0}$$

The surface charge density (σ_p) is simply related to (1) and (2)

Approximation of $1/\kappa$ of a clay particle in water is as follows:

$$\frac{1}{\kappa} = \left(\frac{\mathbf{D} \cdot \mathbf{k} \cdot \mathbf{T}}{8 \cdot \pi \cdot \mathbf{n}_0 \cdot \mathbf{e}^2 \cdot \mathbf{v}^2}\right)^{1/2}$$

where D = dielectric constant of the solvent, e.g., water=80, ethylalcohol=24.3); v = counterion (i.e., cation) valence.

Overlapping Double Layers and Interparticle Repulsion

Under the assumption of flat surface of a particle for symmetrical electrolytes (Hiemenz, 1977)

$$F_{R} \simeq 64 \cdot n_{0} \cdot k \cdot T \cdot \gamma_{0}^{2} \cdot exp(-l \cdot \kappa)$$



where F_R = repulsion force;

I = separation distance;

$$\gamma_0 = \frac{\exp\left(\frac{\mathbf{z} \cdot \mathbf{e} \cdot \boldsymbol{\psi}_0}{2 \cdot \mathbf{k} \cdot \mathbf{T}}\right) - 1}{\exp\left(\frac{\mathbf{z} \cdot \mathbf{e} \cdot \boldsymbol{\psi}_0}{2 \cdot \mathbf{k} \cdot \mathbf{T}}\right) + 1}$$

1



Figure 3.7. Overlap of two-plane double layers.

Van der Waals Force and the DLVO Theory

Van der Waals force:

DLVO (Derjaguin, Landau, Vervey, and Overbeek)

$$\phi_{\rm A} = -\frac{\rm A}{12 \cdot \pi} \cdot l^{-2}$$

where ϕ_A = attractive energy



Waste Management & Resource Recirculation Lab. http://waste.snu.ac.kr/ A = Hamaker constant

$$= \left(\frac{\rho \cdot \mathbf{L}_{\mathrm{A}} \cdot \boldsymbol{\pi}}{\mathbf{m}_{\mathrm{a}}}\right)^{2} \cdot \boldsymbol{\beta}$$

where ρ = particle density;

 L_A = Avogadro's number;

m_a = molar mass of the particle material;

 β = composite Van der Waals parameter.



 There is an energy barrier (i.e., the peak in positive net interaction energy) to particle contact.



(Problem 1) Calculate the double-layer thickness around colloids in 10^{-3} M and 10^{-2} M solution of sodium chloride at 25° C using the Debye-Huckel approximation. How does the ionic strength of a solution affect the thickness of double-layer in the solution qualitatively? Also make a plot of the change of ψ/ψ_0 versus distance from the particle surface.

