In the last lecture, we have talked about Einstein's work on the Brownian motion.
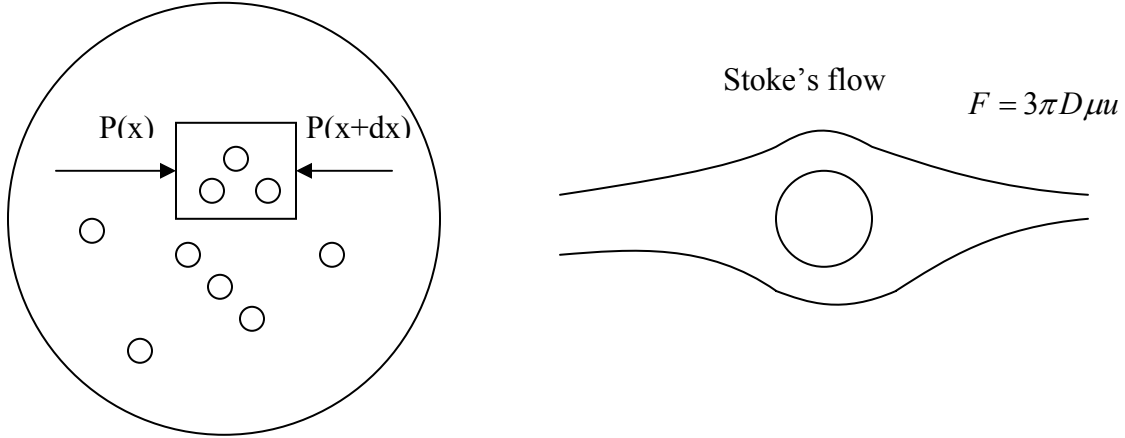
Stoke's flow

$$F = 3\pi D\mu u$$

In the left figure above, pressure difference exists in the fluid. For one particle, the osmotic pressure is determined by

$$P = \frac{1}{V} N k_B T = n k_B T .$$

Also, we can use the solution of Stoke's flow around a sphere to estimate the drag force. The value is $F = 3\pi D\mu u$. For area A_c, the forced balance over the control volume gives

$$A_c \left(P(x) - P(x+dx) \right) = FdN ,$$

$$-A_c dx \cdot \frac{dP}{dx} - 3\pi D\mu u dN = 0 ,$$

$$-\frac{dP}{dx} - 3\pi D\mu u n = 0 ,$$

$$-k_B T \frac{dn}{dx} - 3\pi D\mu u n = 0 ,$$

in which the product un indicates flux. We have

$$J_p = -\frac{k_B T}{3\pi D\mu} \frac{dn}{dx} = -a \frac{dn}{dx} ,$$

where a=$\dfrac{k_B T}{3\pi D\mu}$ is the diffusivity and can be obtained by the diffusion experiment of

some materials. In a time t, the diffusing radius is $\Delta r = \sqrt{6at}$. We can calculate the

constant a and substitute back into a=$\dfrac{k_B T}{3\pi D\mu}$, thus D can be obtained. The relationship

between thermal diffusivity and viscosity is an example of the more general fluctuation-dissipation theory as viscosity is a measure of dissipative process and diffusivity is a measure of random walk (fluctuation) process. The relationship between thermal

diffusivity and viscosity is also called Einstein relation. In chapter 6, there is a similar Einstein relation between electron diffusivity and mobility. But Einstein really worked on the Brownian motion.

Note: The osmotic pressure can be observed by putting a semi-permeable membrane such that only the base molecules in the solution penetrate the membrane, building up a concentration gradient on the two sides of the membranes.

In addition to the above approach, Einstein also established another method to determine the diameter of the solute particles. He proposed to measure the viscosity of the solvent and of the solution, μ, and $\mu_{b, \lambda}$, respectively, and derived, again assuming dilute solute particles, the following relationship between the viscosities

$$\frac{\mu}{\mu_o} = 1 + 2.5\varphi \ ,$$

where φ is the volumetric concentration of the solute molecules.

The Einstein relation can also be derived from the stochastic approach developed by Langevin to treat Brownian motion of particles much larger than that of the surrounding medium. The key idea of the Langevin equation is to consider that the motion of a Brownian particle is subject to a friction force that is linearly proportional to its velocity, as in Stokes law, and a random driving force (or "noise"), R(t), imparted by the random motion of the molecules in the bath. In the absence of an external force, the Langevin equation that governs the instantaneous velocity of the Brownian particle can be written as,

$$m\frac{d\mathbf{u}}{dt} = -m\eta\mathbf{u} + \mathbf{R}(t),$$

where η is the friction coefficient, and for Brownian particles in a fluid the Stokes law gives $F = 3\pi D\mu u$, so that the random driving force R(t) has the following characteristics:

$\langle \mathbf{R}(t) \rangle = 0$ (average of random driving force is zero)

$\langle \mathbf{R}(t) \bullet \mathbf{u}(t) \rangle = 0$ (random driving force is not correlated to the velocity)

$\langle \mathbf{R}(t+s) \bullet \mathbf{R}(s) \rangle = 2\pi R_o \delta(t)$.

9.2 Force and potentials
For liquids, potential interaction contributes significant to transport. In previous lectures, we have discussed force $\overrightarrow{F} = -\nabla\Phi$. For the interaction of two charged particles as the following left figure, the Coulomb potential is $\Phi = \frac{Q_1 Q_2}{4\pi\varepsilon r}$, in which $\varepsilon = \varepsilon_{vacuum}\varepsilon_r$.
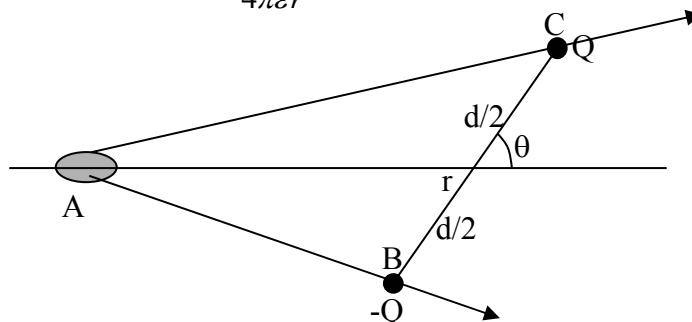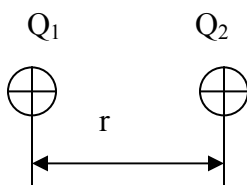
You can build up all potentials from the Coulomb potential. Now let us consider the interaction of a charge and a dipole as shown in the right figure above case. We have

$$\phi = -\frac{Qq}{4\pi\varepsilon_o}\left[\frac{1}{AB} - \frac{1}{AC}\right],$$

where

$$AB = \left[\left(r - \frac{d}{2}\cos\theta\right)^2 + \left(\frac{d}{2}\sin\theta\right)^2\right]^{1/2},$$

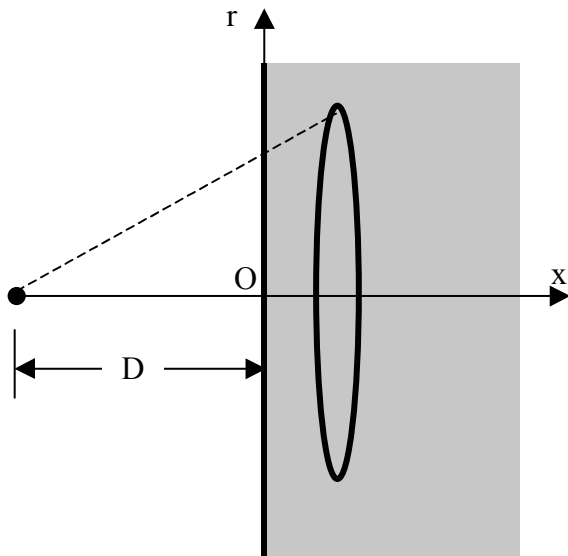$$AC = \left[\left(r + \frac{d}{2}\cos\theta\right)^2 + \left(\frac{d}{2}\sin\theta\right)^2\right]^{1/2}.$$

Under the approximation r>>d, we obtain

$$\phi(r,\theta) = -\frac{q\beta\cos\theta}{4\pi\varepsilon_o r^2},$$

where β=Qd is the dipole moment.

Note: (1) The superimposed two fields yield $\Phi \sim r^{-2}$ instead of $\Phi \sim r^{-1}$. (2) If we have two dipoles, the potential becomes $\Phi = -Cr^{-6}$.

The van der Waals potential between one atom and a surface

Based on the elementary potential interactions discussed in the previous section, the force interaction between particles and surfaces can be obtained by summing up the interactions between the atoms or molecules involved, as demonstrated in the above

figure. For two opposite surfaces, the Van der Waals force is $-\dfrac{A}{12\pi D^2}$. The **Hamaker constant**, after Hamaker (1937)
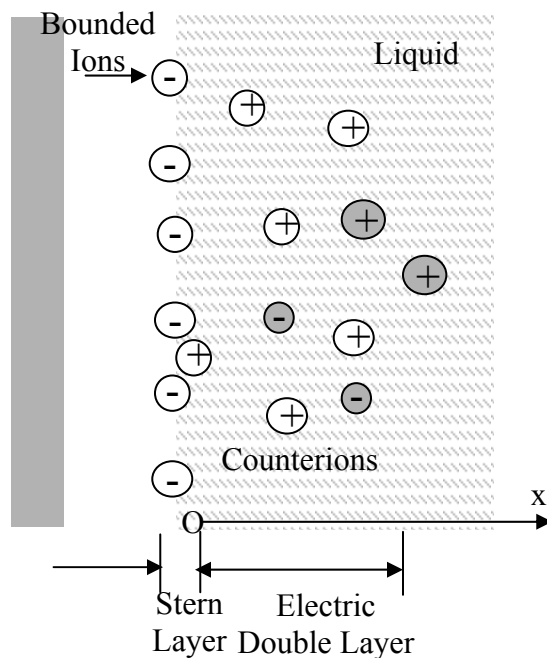
$$A = \pi^2 C n_1 n_2,$$

where n_1 and n_2 are the number density of molecules of the two interacting media.
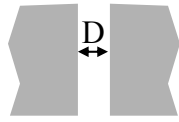
$$\Phi = -\frac{A}{12\pi D^2}$$

Note: In $\vec{F} = -\nabla\Phi$, a positive A leads to positive $\vec{F}$ (attractive force); otherwise it is repulsive force.

9.2.3 Electric double layer potential

(Solid surface should not be separated from the negative ions.)

Surfaces immersed in liquids are usually charged due to the ionization or dissociation of surface groups or due to the adsorption of ions from the solution onto a previously uncharged surface. The charges accumulated at the surface are balanced by an equal but oppositely charged region of counterions. Some of these counterions are also bounded to the surface, forming a so-called **Stern or Helmholtz layer**, which is usually very thin (a few Angstroms). The remaining counterions distribute near the surfaces but are free to move, forming a diffuse **electric double layer**. This electric double layer is of fundamental importance for a wide range of technologies such as batteries, fuel cells, colloids, and in biochemistry and biotechnology.

Note: You may compare this case to a p-n junction with the built-in potential.
We first determine the magnitude of the potential developed on the solid-liquid interface. This potential can be easily measured using the solid as an electrode. The ion density on the solid-surface obeys the Botlzmann distribution,

$$c_s = c_{zp} e^{-Ze\psi_s / \kappa_B T} ,$$

where Z is the number of charges per ions and e is the unit charge (–e for an electron), ψ_s is the electrostatic potential of the solid surface, and c_{zp} is the ion density at zero surface electrostatic potential. The above equation is also called the Nerst equation.

The Maxwell equation determines the displacement $\vec{D}$ as

$$\nabla \cdot \vec{D} = \rho_{net} , \quad \vec{D} = \varepsilon \vec{E} = \varepsilon \left(-\nabla \Psi \right).$$

Thus we obtain the **Poisson-Boltzmann equation**

$$-\varepsilon_0 \varepsilon_r \frac{d^2 \Psi}{dx^2} = \rho_{net} = \sum_i Z_i e n_{oi} \exp\left(-\frac{Z_i e \psi}{\kappa_B T} \right).$$

Finally we obtain the **Debye length**,

$$\frac{1}{\delta} = \sqrt{\sum_i \frac{Z_i^2 e^2 n_{oi}}{\varepsilon_o \varepsilon_r \kappa_B T}} .$$

Note: $\varepsilon_r \uparrow, \delta \uparrow$.

Now we consider the force balance inside the liquid. Because the liquid is stationary, the electrostatic force on liquid must balance the pressure force. The pressure inside the electric double layer is higher than that inside the bulk liquid at the equilibrium state. Furthermore, the electric double layer creates an attraction force between the ions on the solid surface and the counterions in the liquid. This attraction electrostatic force is balanced by the positive pressure in the liquid. When two solid surfaces are brought close to each other, a repulsive force develops between the two surfaces because the electrostatic force no longer balances the positive pressure inside the liquid.
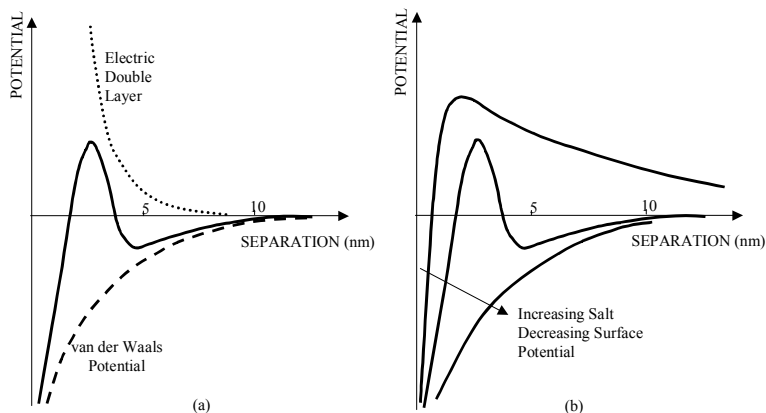

Now consider particles in a solution. Two main potentials interactions exist. One is the van der Waals (usually attractive) and the other is double layer interaction (repulsive). In

the above figure (a), a superposition of the double layer potential (repulsive electro potential) and van der Waals potential (attractive) is shown. Under varying salt concentration, different combinations can be obtained (figure (b)). A colloid forms when there exists a minimum in potential so that particles are separated at a distance.

The repulse forces between surfaces also created another interesting phenomenon, the disjoining pressure. The following figure shows an example where the disjoining pressure plays an important role. At the base of liquid surface intersection the wall, the liquid layer climb up the wall due to surface tension. The vapor and the solid wall are two parallel surfaces. The medium in between is liquid. When the interaction force between wall and vapor is repulsive (due to a negative Hammaker constant or electric double layer), a positive pressure in the liquid layer develops, superimposed on normal compressive pressure. The thinner is the film, the more positive is the pressure. Which means that a lifting force (due to larger compression pressure) at the base will push liquid up the wall, till it is balanced by the gravitational force.
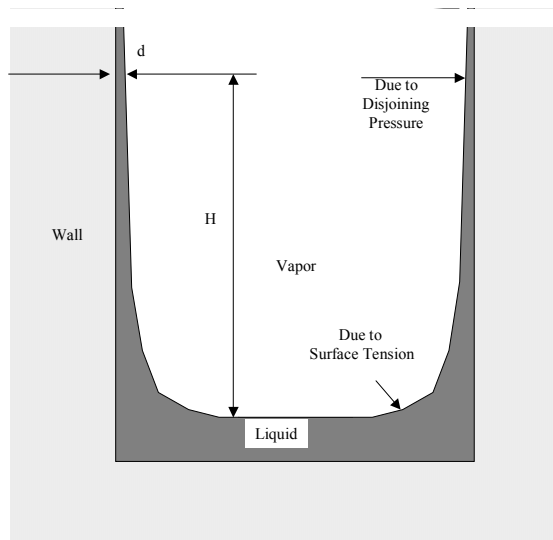
The appreciation of importance of potential and force interactions also allows one to do some quick orders of magnitude analysis. Can liquid slip on a wall. My conclusion, based on a simple orders of magnitude analysis, as given in an example in the book, says not in practical cases. You can analyze this problem by considering how much bonding force an atom experiences from the wall, and compare that to the shear stress generated in practical situations.
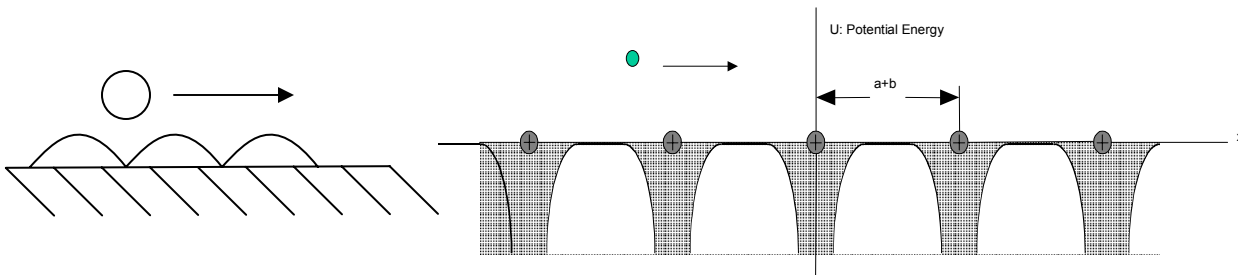
Electric double layer is the basis of many microfluidc technologies. Because the solid and the liquids are charged, an external field can create their motion. There are two cases, one is the particle in a liquid moves (called electrophoretic motion). This is the basis in DNA separation. In the following left figure, charged DNA molecules can be separated by the electric field. In the second case, the solid walls are stationary. The ions will move under an external electric field (called electrokinetic flow). The moving ions will also cause the fluid to move, and form a plug flow (flat profile). This is used for pumping purpose.
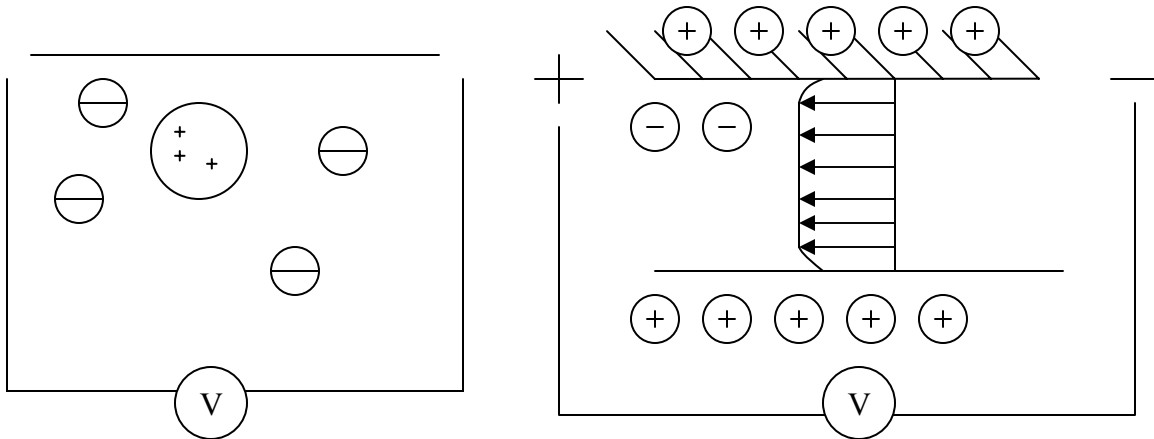
Surface tension
The idea of surface tension can be understand in terms of the energy stored in the surface. When we stretch the rod till it breaks, the work input is stored in the two new surfaces, i.e., $\gamma_1 = \frac{1}{2} W_{11}$.
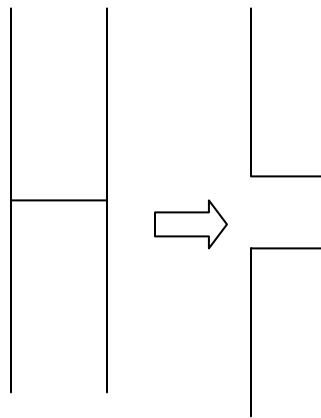
Now consider the separation of two immiscible liquids in contact into two stand-alone parts at the interface. After separation, the interfacial energy on each surface is γ_1 and γ_2. The energy difference between the surface energy after the separation and the interfacial tension γ_{12} before the separation is called the work of adhesion,
$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}.$$
The work of adhesion can be approximately estimated from the work of cohesion,

$$W_{12} = \sqrt{W_{11d}W_{22d}} = 2\sqrt{\gamma_{1d}\gamma_{2d}} .$$
Thus
$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_{1d}\gamma_{2d}} .$$

Surface tension is very important for microsystems. There are two basic equations for analyzing surface tension. One is the **Laplace equation**
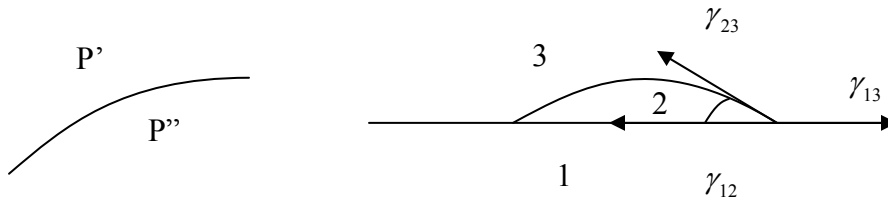$$p'' - p' = \frac{2\gamma}{r} ,$$
if the two radii of curvature in two orthogonal directions are both r. The equation says there is a pressure difference between inside and outside a particle due to surface tension.

The other is for the interaction of three surfaces. For the following right case, the **Young equation** gives
$$\gamma_{13} = \gamma_{23} \cos\theta + \gamma_{12} .$$
The forces are shown in the figure.

Size can affect the phase change processes. One can easily appreciate this from the Laplace equation. Since pressures inside and outside a particle (droplet, bubble, solid particle) are different, and they are further related to other thermodynamic properties, it is reasonable to anticipate that certain thermodynamic properties will be influenced by the size (saturation temperature, pressure, enthalpy, surface tension). Due to the surface tension, an isolated nanoparticle usually has lower melting points compared with bulk materials. The equilibrium vapor pressure increases as the liquid droplet radius decreases. For a given vapor pressure, smaller droplets tend to evaporate.