Ch 12
Particle interactions in suspensions

Overview

For an initially stable sol composed of colloidal particles, the gelling agent, which is usually a pH modifier, an electrolyte, or a polymer, produces gellation by reducing repulsive interactions, so that attractive van der Waals forces can draw particles into contact.

Preparation of stable sols;

1. Match the index of refraction of particles to that of the medium to reduce van der Waals force

2. To use particles whose surfaces are charged, resulting in electrostatic stabilization (OH groups); addition of an acid or an acid former neutralizes chaged O- groups, producing gelation; addition of salt collapses electrostatic double layer so that particles can approach closely enough to be drawn into near contact by van der Waals forces

3. To graft or adsorb surfactant, hydrocarbon, or polymer chains, producing steric barrier to flocculation. Long polymers that strongly adsorb to the particle surfaces can also induce flocculation by bridging the gap between neighboring particles

Interparticle potentials

Effective interparticle potential W(D)

-> prediction of the critical conditions for flocculation and the rheological
    properties of the flocculated gel

<- hard-core steric interaction, van der Waals interaction, electrostatic
    interaction, other interactions

-> other interactions such as those from absorbed, grafted, or dissolved
    chains, or from thin layers of adsobed ions, along with their hydration
    shells

Interparticle potentials (DLVO)

Hard-core steric potential $\qquad W_{steric} = \begin{cases} \infty & D < 0 \\ 0 & D \geq 0 \end{cases}$

van der Waals potential $\quad W_{vdw} = -\dfrac{A_H}{12}\left\{ \dfrac{4a^2}{4aD + D^2} + \left(\dfrac{2a}{2a+D}\right)^2 + 2\ln\left[1 - \left(\dfrac{2a}{2a+D}\right)^2\right]\right\}$

A_H: Hamaker constant, a: particle radius, D: separation

For small separation $\quad W_{vdw} \approx -\dfrac{aA_H}{12D} \quad$ *for* $D << a$

Electrostatic potential $\quad W_e = 2\pi\varepsilon_0\varepsilon a\,\psi_s^2 \ln\left[1 + \exp(-\kappa D)\right]$

In the limit of constant surface charge $\quad W_e = 2\pi\varepsilon_0\varepsilon a\,\psi_s^2 \ln\left[\dfrac{1}{1 - \exp(-\kappa D)}\right]$

ε_o permittivity $\qquad\qquad \varepsilon$ dielectric constant

κ^{-1} Debye length

ψ_s Electrostatic potential at the particle surface
zeta potential

Interparticle potentials (non-DLVO)

If non-adsorbing polymer is present, exclusion by this polymer layer produces a potential

$$W_{depl} = \begin{cases} -\dfrac{4\pi}{3}(a+\Delta_d)^3\left[1-\dfrac{3(2a+D)}{4(a+\Delta_d)}+\dfrac{(2a+D)^3}{16(a+\Delta_d)^3}\right]\Pi, & 0 \le D < 3\Delta_d \\ 0, & D > 3\Delta_d \end{cases}$$

Δ_d depletion layer thickness

Π osmotic pressure

As particle separations shrink to a couple of nanometers or less, there are strong steric forces that prevents closer approach. In aqueous system, steric forces are generated by adsorbed ions and hydration layers

$$W_{hyd} = W_0 \exp(-D/2\Delta_{hyd})$$

Interparticle potentials
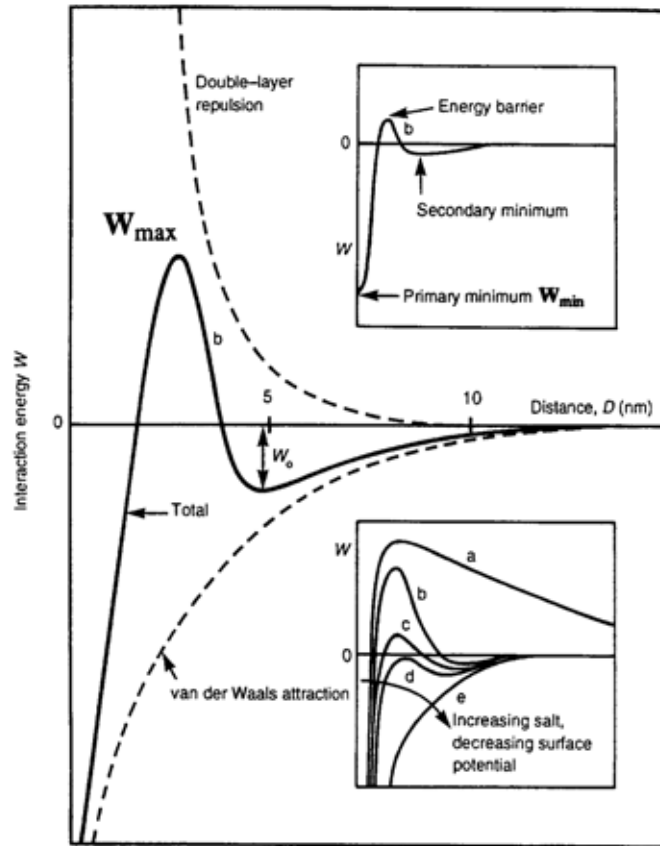
$$W = W_{steric} + W_{vdw} + W_e + W_{depl} + W_{hyd}$$

Figure 7.1 Schematic diagram of interaction potential versus separation distance D for van der Waals and electrostatic "double-layer" interactions. The lower inset shows the collapse of the repulsive barrier as the electrolyte concentration is increased or the surface potential is decreased. At a separation distance of zero, there is an infinitely steep hard-core repulsive (or positive) interaction. (From Israelachvili 1991, reprinted with permission from Academic Press.)

Primary minimum;
particles stick to other particles the depth of the well can be reduced by increasing the magnitude of the zeta potential

Electrostatic stabilization

As one increases the surface potential or the Debye length, the local maximum in W becomes increasingly positive.

When W_{max} exceeds many $k_B T$, particles that are initially separated from each other rarely acquire enough kinetic engergy to surmount the high repulsive potential barrier W_{max} and fall into the deep van der Waals primary minimum
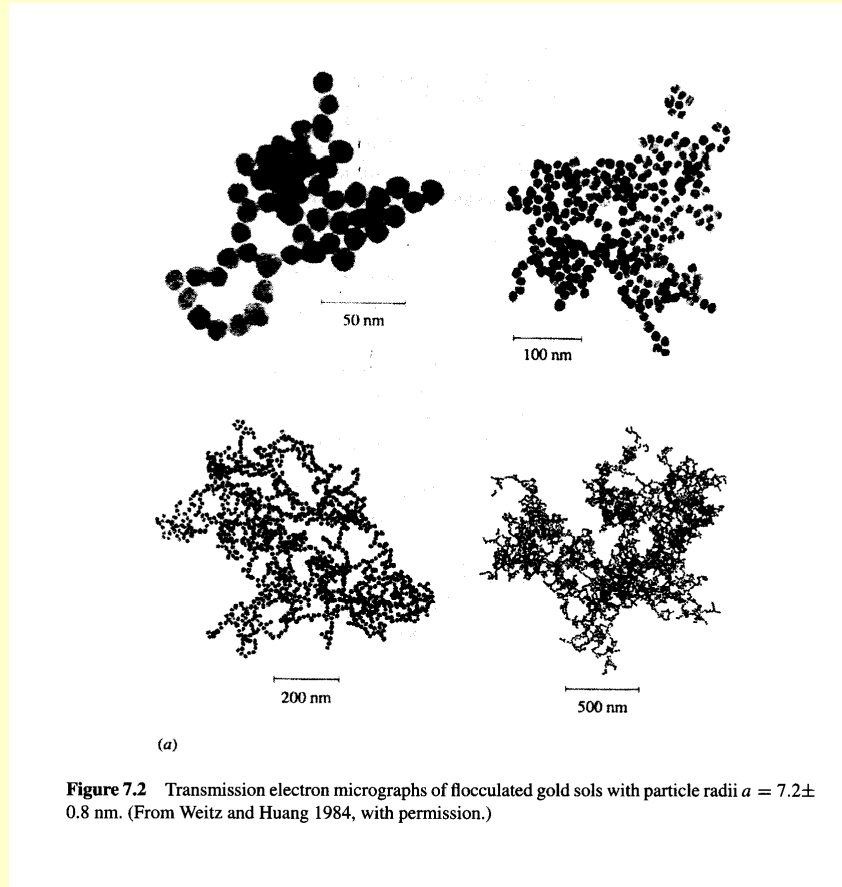
The time required for particles to diffuse into their attractive minima scales as

$$t_D \approx \frac{a^2}{D_0} \exp\left(\frac{W_{max}}{k_B T}\right) = \frac{6\pi\eta_s a^3}{k_B T} \exp\left(\frac{W_{max}}{k_B T}\right)$$

If even small 100nm particles in a low viscosity medium may take months or even years to aggregate if the potential barrier $W_{max} / k_B T \; > \; 25$

Flocculation and gelation

Flocculation of the stabilized sol can be deliberately induced, by adding electrolyte or by chaning the surface charge by altering the pH.

Figure 7.2 Transmission electron micrographs of flocculated gold sols with particle radii $a = 7.2 \pm 0.8$ nm. (From Weitz and Huang 1984, with permission.)

D_f: fractal dimension

Fractal: self-similar object which looks the same at different magnification

D_f=1.75; diffusion-limited aggregation fast flocculation

D_f=2~2.2; reaction-limited aggregation flocs penetrate to some extent after contacting, slow flocculation

Gelation and phase separation

For adhesive hard-sphere model,
   for weakly flocculated particles at low and modest volume fractions
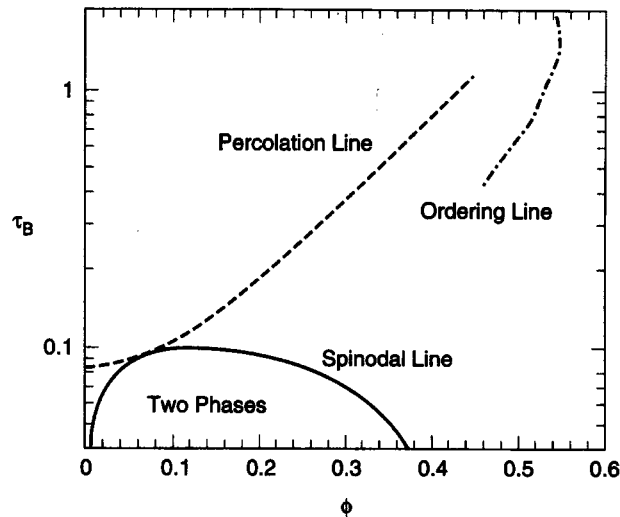

Figure 7.4 Phase diagram for adhesive hard spheres as a function of Baxter temperature τ_B. The solid line is the spinodal line for liquid–liquid phase separation (the dense liquid phase is probably metastable), the dot–dashed line is the "freezing" line for appearance of an ordered packing of spheres, and the dashed line is the percolation transition. (Adapted from Grant and Russel 1993, reprinted with permission from the American Physical Society.)

Baxter temperature;
   a rescaled temperature
   increases with T

$$\tau_B = \frac{2a + \Delta}{12\Delta} \exp\left(\frac{-\varepsilon}{k_B T}\right)$$

Gelation ~ percolation ~ phase separation

Gelation can occur without phase separatoin, if Baxter temperature is not too small, that is, if the gel is not too strongly flocculated