Chapter 10 Colloids and Colloidal Stability

10.1.   The importance of Colloids and Colloidal Phenomena

TABLE 10.1. Illustrative Examples of Practical Applications of Colloids and Colloidal Phenomena

Application	Principles Involved
Pharmaceuticals, cosmetics, inks, paints, foods, lubrication, food products, dyestuffs, foams, agriculture chemicals	Formation and stabilization of colloids for end-use products
Photographic products, ceramics, paper coatings, magnetic media, catalysts, chromatographic adsorbents, membrane and latex film, electrophotographic toners	Formation of colloids for use in subsequent manufacturing processes
Wettings of powders, enhanced petroleum recovery detergency, mineral ore flotation, purification by adsorption, electrolytic coatings, industrial crystallization, chemical waste control, electrophotography, lithography	Direct application of colloidal phenomena to processing
Pumping of slurries, coating technology, caking, powder flow, filtration	Handling properties of colloids, rheology, sintering
Water purification, sewage disposal, disperal of aerosols, pollution control, fining of wines and systems beers, radioactive waste disposal, breaking of unwanted emulsions and foams	Destruction of unwanted colloidal phenomena

10.2 Colloids: A Working Definition

Definition:

One phase is dispersed in a second, but in units which are much larger than the molecular unit, or in which the molecular size at the dispersed material is significantly greater than that of the solvent (a polymer solution)

■   Two aspects of a colloidal system must be considered
   ● Colloid structure - how the components of the system are mixed.
   ● Colloid size - what the dimensions are of the dispersed units.

10.2.1 Colloid structure

Two phases are involved in a colloidal system

    (1) Dispersed phase - solid, liquid, gas

    (2) Continuous phase or dispersion medium --- solid, liquid, gas

General types of colloidal system:

    Aerosol : solid or liquid disperses in gas

    Emulsion : liquid in liquid

    Form : gas disperses in liquid (or solid)

    Association colloid : aggregates of molecules of hundreds to thousands units, often found in biological systems (cell membrane, micelle, vesicles).

    Lyophilic colloid : the solute molecules are much larger than those of solvent.

    Network colloid : consists of two inter-penetrating networks, and hard to specify which is dispersed and which is continuous phase. (porous glass, opal glass, gels)
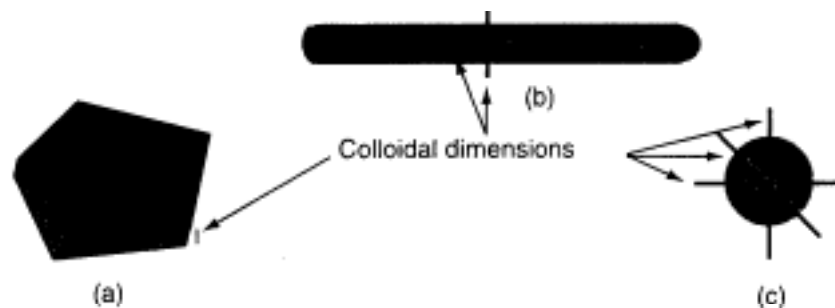
■ *Practical examples of colloidal system*

TABLE 10.2. Examples of Commonly Encountered Colloidal Systems

System	Type	Dispersed Phase	Continuous Phase
Fog, mist	Liquid aerosol	Liquid	Gas
Smoke	Solid aerosol	Solid	Gas
Shave cream	Foam	Gas	Liquid
Styrofoam	Solid foam	Gas	Solid
Milk	Emulsion	Liquid (fat)	Liquid (water)
Butter	Emulsion	Liquid (water)	Solid (fat)
Paint	Dispersion	Solid	Liquid
Opal	Dispersion	Solid	Solid
Jello	Gel	Macromolecules	Liquid
Liquid soaps and detergents	Micellar solution	Micelles of detergent molecules	Liquid

10.2.2 Colloid Size

■ The size of dispersed phase falls in the range of 1~1000nm. However, many systems with dimensions beyond that range (emulsions, paints, aerosols)

■ Other colloidal systems, such as **fibers**, **clays**, and **thin films**, may "*quality*" as colloids because one or two dimensions fall into the designated range, and the properties adhere to the "rules" of colloidal behavior. (Fig. 10.1)

■ The most useful definition: if it looks like a colloid and acts like a colloid, it is a colloid.

FIGURE 10.1. A colloid is basically defined by its dimensions. While one may set a size limit of, for example, 0.01 mm as an arbitrary upper limit to what may be called a colloid, the reality is that many systems with larger dimensions are considered "classic" colloids (e.g., clays) because at least one dimension falls into the limiting size range. To be considered a colloid, then, a system may have one dimension in the range as in a flat plate (*a*), two dimensions as in a cylinder (*b*), or three dimensions as in a drop or particle (*c*).

10.2.3 Some Points of Nomenclature

■ **Additional terms related to colloids:**

Coagulum: an aggregate of colloidal particles having a relatively **tight**, **dense structure**, normally formed **irreversibly**.

Coagulation: the process of forming coagulum.

Creaming: the separation of coagulum or flocs from the continuous phase, where the aggregate is less dense than that phase.

Floc: an aggregate of colloidal particles that have **a rather loose**, **open structure** (related to coagulum) may be **reversible** to the dispersed state with minimal energy input.

Flocculation: the process of forming flocs.

Monodisperse: particles in the colloidal system have approximately same size.

Polydisperse: a broad range of particle sizes.

Sedimentation: as in creaming except that the aggregates are denser than the liquid and settle to the bottom.

10.3 Mechanisms of Colloid Formation

A colloid can be prepared via two approaches:

■ **Comminution or Dispersion**:

By breaking down large piece to the size required.

■ **Condensation** :

By aggregation a molecular dispersion to the size range of a colloid.

10.3.1 Comminution or Dispersion Methods

■ Works should be applied in the comminution process, and the *theoretical work* require is

W = (specific surface free energy, σ) × (total new surface area produced)

● Higher-surface-energy materials require more work input.

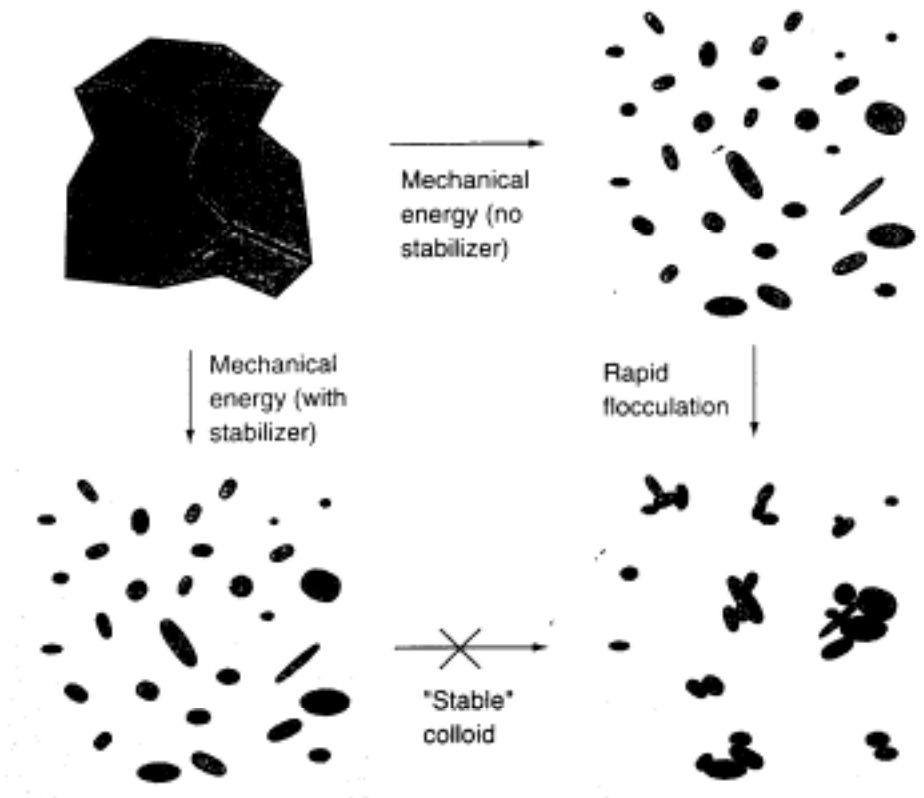■ The natural tendency of subdivided particles

→ Reduce the total surface area by aggregation processes.--- A serious technological problem need to be overcome.

● The attractive interaction between particles can be reduced by an intervening medium (a liquid). Its positive functions are :

(1) Reduce the surface energy of the system by adsorption on the new surface;

(2) Reduce the van der Walls attraction between the particles (averaging its Hamaker constant)

- Once the comminution process is halted, the dispersed particles may begin to flocculate or coagulate (Fig.10.2)

FIGURE 10.2. In the preparation of colloids by comminution, it is usually necessary to include a surfactant or polymeric stabilizer to inhibit the rapid flocculation of the newly formed particles.

- Solution for the problem :
  Addition of new components (*surfactant, polymer, small particle, …*) that adsorb at the solid-liquid interface and provide an electrostatic or steric barrier. --- termed as **dispersing aids** or **agents**.

- Comminution of liquid phase => emulsification
  example: suspension or dispersion polymerization.

- Process involves the formation of liquid aerosol:
  Spraying the liquid precursor into an atmosphere containing a reagent that induces the reaction.
  example : titanium (IV) ethoxide into water vapor => TiO_2

10.3.2 Condensation Methods

■ Commonly employed for the fabrication of dispersion and aerosols, and less commonly in the production of emulsions.
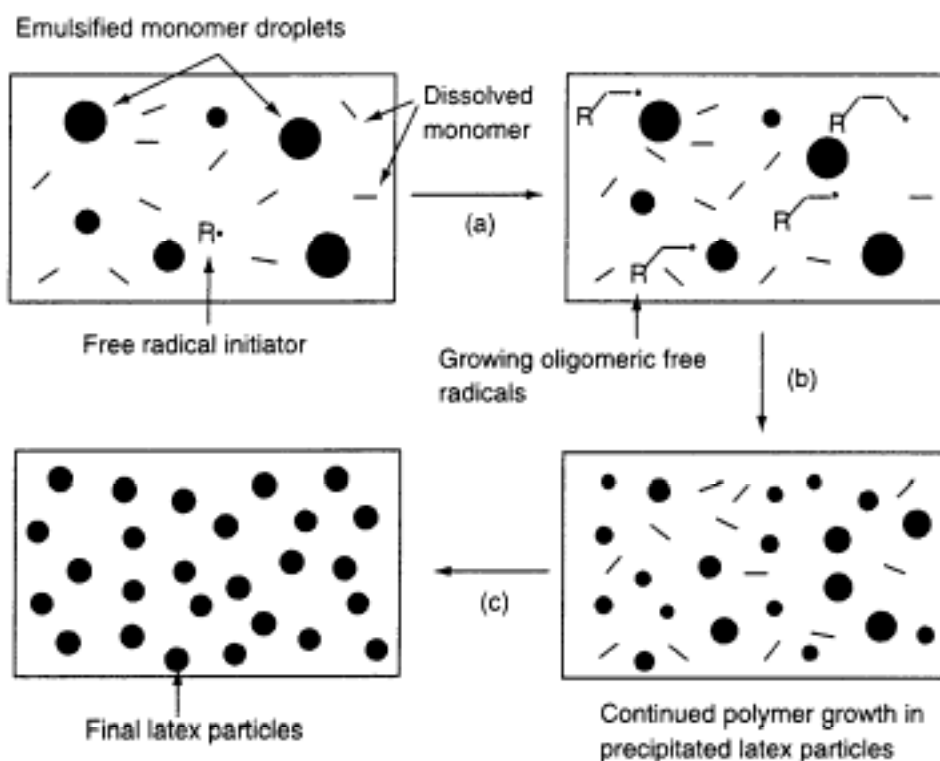
● Typical example: fog formation; silver halide dispersion, crystallization processes, etc.

■ Emulsion Polymerization

  Monomers stay in: emulsified droplets, dissolved in water.

  Initiator: solved in water phase.

● Particle formation and growth occur initially in the water phase, and continues in precipitated particles. (Fig.10.3)

FIGURE 10.3. In the process of emulsion polymerization, the incipient latex particle begins as a free-radical-initiated dimer or oligomer in solution (*a*). As polymerization proceeds, the growing chain precipitates and continues to grow, fed by new monomer taken from the reservoir of emulsified material (*b*). Polymerization continues until all available monomer is consumed (*c*).

10.4 The "Roots" of Colloidal Behavior

■ As the bulk phase is subdivided into finer and finer particles, the relative *ratio of surface to bulk* molecules increases, and the specific surface properties becomes more significant.

■ For a cubic structure with edge length d, density ρ:

● Specific surface area $= \dfrac{surface\ area}{mass} = \dfrac{6d^2}{d^3\rho} = \dfrac{6}{d\rho}$

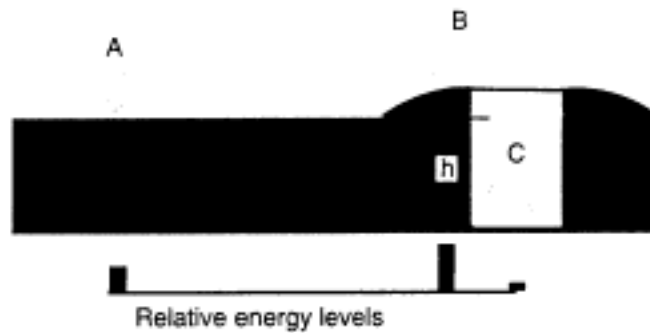● If the molecular dimension is χ, fraction of molecules at the surface

$$= \dfrac{molecules\ at\ surface}{molecules\ in\ bulk} = \dfrac{6(d/x)^2}{(d/x)^3} = 6(\dfrac{x}{d})$$

●

d	χ	fraction of molecules at surface
1 cm	0.4 nm	0.000025%
1000 nm	0.4 nm	0.25%
10 nm	0.4 nm	25%

■ It is difficult to determine exactly where the distinction between colloids and a molecularly dispersed system.

10.5 Ground Rules for Colloidal Stability

■ From the **thermodynamic** point of view, any system tends to approach the condition of *minimum total free energy*.
However, nothing was said about "*how fast such a transformation will occur*", and "*whether the system will approach another metastable configuration*".

■ Example illustrates the metastable, and stable state (Fig 10.4, golf game)

FIGURE 10.4. In colloids, as in golf, the system (the player) is seeking a minimum in energy (point C). While thermodynamics may be the ultimate controlling factor (the difference in height, h), inherently unstable systems (points A and B) may appear stable (to the golfers dismay) as a result of kinetic or other factors that prevent the system from readily reaching its final goal.

The difference of energy between position A (metastable) and position C (stable) is,

$$\Delta G_g = mg\Delta h \tag{10.1}$$

- Without sufficient energy to overcome the barrier (activation energy), the system will remain in the metastable state.

■ In terms of colloids: the energy considerations indicate that colloids should be unstable and will revert to a state of complete phase separation.
However, Nature has designed things in such a way that we can impose barriers of various types between metastable and stable states so that useful colloidal systems can exist for enough time.

10.5.1 A Problem of Semantics

■ Three terms relates to the state of colloid; "**stable**", "**unstable**", "**metastable**".
- "metastable" is inconvenient to be used since its meaning can be somewhat ambiguons.
- If a colloids remains in a metastable state, it is often described as "stable".
- "Unstable" means a colloid begins to lose its colloidal properties.

- The designations of "stable" and "unstable" colloids depend on the application in question.

    "two days" or "two years"

- The kinetic (rather than energetic) definition of stability will be employed in its most general sense.

- All colloids are in reality **<u>metastable</u>** systems.

10.5.2 Mechanisms of Stabilization

- Colloids → a metastable state
  - If imposes an energy barrier high enough → transition from the metastable to the stable is difficult.
  - Lower energy barrier → allow the system to approach the stable state.

- In colloids, the energy of phase transition is supplied by random collision between particles --- by **Brownian motion.**
  - The average translational energy to a particle due to the Brownian motion → **(3/2)kT**

      at room temp. (298K), energy of a particle is about 5×10^{-21} J (10^{-20} J in a collision)
  - Considering the energy distribution of particles, the actual energy of a collision may be smaller or larger.

- If energy barrier is **nkT**

    n   10   a stable colloid is obtained

    n   1   instability may be induced

- The mechanisms for lowing the barrier energy :
  - Changes in temperature
  - Changes in solvent properties
  - Pressure change
  - Change in electrolyte content

10.5.3. A Review of Basic Intermolecular Forces

■ The attractive force (van der Waals force) between two molecules is given by:

$$F_{att} = -Ar^{-7} \qquad (10.2)$$

   r: the distance between two spherical molecules,
   $A = (3/4)h\nu\alpha^2$,
      α: electronic polarizability
      ν: characteristic frequency identified with the first ionization
         potential of the atom (in UV region)

for two different interacting units,

$$A_{12} = \frac{3}{2}h\left(\frac{\upsilon_1\upsilon_2}{\upsilon_1 + \upsilon_2}\right)\alpha_1\alpha_2 \qquad (10.6)$$

■ The work required to separate two molecules from a distance, d, to infinity :

$$\Delta W = -\int_r^\infty F_{att}dr = A\int_r^\infty (r^{-7})dr = 6Ar^{-6} = A'd^{-6} \qquad (10.3)$$

the free energy of attraction at distance r will be

$$G_{att} = -\ W = -A'r^{-6} \qquad (10.4)$$

(curve 1 in Fig. 10.5)

FIGURE 10.5. A "typical" interaction energy curve for two interacting units (curve 3) is the sum of the attractive potential (curve 1) and the repulsive contribution (curve 2).

- As the electron clouds of the two molecules begin to interact, the interaction becomes repulsive (Born repulsion) :

$$F_{rep} = B\, l^{-ar}, \text{ and} \tag{4.33}$$

$$G_{rep} = \frac{B}{a}\, l^{-ar} \tag{4.34}$$

Eq. (4.34) is commonly approximated by

$$G_{rep} = B'd^{-12} \tag{10.7}$$

(Fig. 10.5, curve 2)

- The total free energy will be the sum of attractive and repulsive terms :

$$G = G_{rep} + G_{att} = \frac{B'}{d^{12}} - \frac{A}{d^6} \tag{10.8}$$

- Known as **Lennard-Jones *6-12 potential*** (curve 3 in Fig. 10.5)

10.5.4. Fundamental Interparticle Forces

- *From intermolecule to interparticle*:
  consider the system involving two hard, flat, nonpolar, effectively infinite surfaces separated by a distance (H) in a vacuum.

$$G_{att} = -\frac{A_H}{12\pi H^2} \tag{10.9 or 4.43}$$

A_H : Hamaker constant
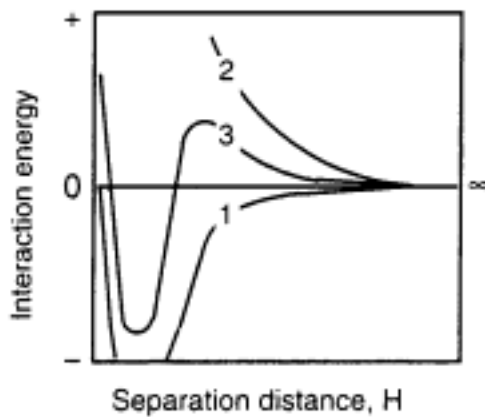
$$A_H = 3/4 h v \alpha^2 \pi^2 n^2 = A\pi^2 n^2 \tag{10.10}$$

n : number of atoms (or molecules) in a unit volume.

- for two identical spheres of radius, a, where H/a<<1, a similar type of approximate Eq. is :

$$\Delta G_{att} = (-\frac{A_H a}{12H})[1 + \frac{\frac{3}{4}H}{a} + higher\ terms] \tag{10.11}$$

it is always safe to neglect the higher terms.

■ Comparision of Eqs. (10.4) and (10.10) -----------
   the free energy of attraction between two surfaces falls off much
   more slowly than that between individual molecules.
   (the extended range of bulk interactions plays an important role)

■ When both attractive and repulsive terms are taken into account for
   particles, the interaction energy (ΔG) resembles that shown in Fig.
   10.5, curve 3

● The primary maximum,
   G_{max}, is the key element
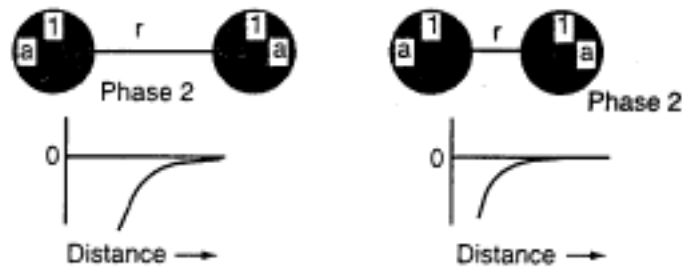   in determining the colloidal
   stability.

■ For the preceding discussion, the particles (or atoms) are positioned in
   a vacuum or inert environment.
   In real colloidal system, the effects of an intervening medium must be
   taken into consideration.

10.5.5. Attractive Interactions in Nonvacuum Media

How will the relevant equations be modified by the presence of the
   intervening medium.

■ Due to the presence of the third component (fluid medium), the
   surfaces interacting between units will experience a reduced mutual
   attraction.

■ A *composite* **Hamaker constant** is used to modify the relevant
   equations.

● Considering two particles (material 1) dispersed in medium2.

FIGURE 10.6. For two particles of phase 1 interacting in a medium of phase 2, as the nature of phase 2 more closely resembles that of phase 1, the attractive van der Waals interactions between the two particles is reduced, as is the distance over which they act. If the Hamaker constant of phase 2 becomes equal to that of phase 1, the system will be thermodynamically stable.

The effective Hamaker constant, (A^{eff}_H) is

$$A^{eff}_H = [A_{H(10)}^{1/2} - A_{H(20)}^{1/2}]^2 \qquad (10.12)$$

$A_{H(10)}$: Hamaker constant for component 1 in vacuum

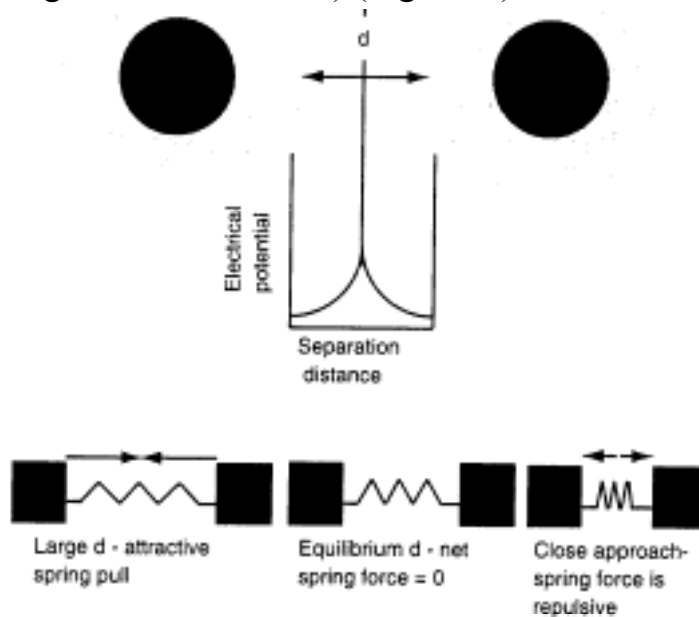$A_{H(20)}$: Hamaker constant for component 2 in vacuum

● As $A_{H(10)}$ and $A_{H(20)}$ become closer in value, A^{eff}_H becomes smaller and ends toward zero.

➔ free energy of attraction tends toward zero.

➔ the attraction force decreases.

➔ repulsive terms necessary to maintain a stable colloid (G_{max}) is also decreased.

10.6 Source of Colloidal Stability

■ Two practical mechanisms for stabilizing lyophobic colloid:

(1) electrostatic repulsion between electrical double layers;

(2) steric on entropic stabilization

10.6.1 Charged Surfaces and the Electrical Double Layer (EDL)

■ A system is stable so long as the individual particles maintain their identities.

● Two primary criteria which must be considered in the discussion of colloid stability:

(1) frequency of particle collisions

(2) effectiveness of the collisions

■ The EDL can be viewed as a spring located between the two particles. The repelling force will depend on the force constant of the spring (i.e., the magnitude of the EDL) (Fig. 10.7).

FIGURE 10.7. The interactions between two colloidal particles with electrical double layers can be visualized as two blocks connected by a spring. At large distances of separation the spring is stretched and applies a net force pulling the blocks together (attractive van der Waals interactions). At close approach, the spring is compressed producing a net repulsive force pushing the blocks apart (electrostatic repulsion). At some intermediate distance, the forces will be in equilibrium.

● The interaction of EDLs represents an energy barrier in the total interaction curve.

■ As two particles approach, there will be two (at least) types of interaction:

(1) the repulsive interaction, G_{rep};

(2) van der Waals attractive interactions, G_{att};

● The total interaction energy:

$$G_{total} = G_{att} + G_{rep} \qquad (10.13)$$

● A simple equation to express the repulsive interaction between particles with EDLs is derived by Reerink and Overbeek:

$$G_{rep} = \frac{Bek^2T^2a\gamma^2}{Z^2}\exp(-\kappa H) \qquad (10.14)$$

H: distance between spheres of radius a,
B: $3.39 \times 10^{39} A^{-2}\gamma^{-2}$,   Z: charge of the counterion

$$\gamma = \frac{\exp(Ze\psi_s/2kT)-1}{\exp(Ze\psi_s/2kT)+1} \qquad (10.15)$$

Ψs: the electrical potential at the Stern layer.

● The total interaction, G_{total} is

$$G_{total} = G_{rep} + G_{att}$$

$$= [(\frac{Bek^2T^2a\gamma^2}{Z^2})\exp(-\kappa H)] + [\frac{-A_H}{12\pi H^2}] \qquad (10.16)$$

The curves illustrating the individual and summed interaction are shown in Fig. 10.5 (page 12).

● The key element in determining the height of energy barrier imposed by the electrical double layer is the concentration and valence of electrolyte.

➢ increase in electrolyte concentration, reduces the repulsive interaction, reduces the energy barrier, the system is less stable.

- A good approximation to the point the system will begin to undergo rapid coagulation → $G_{total} = 0$ and $d\ G_{total}/dH = 0$
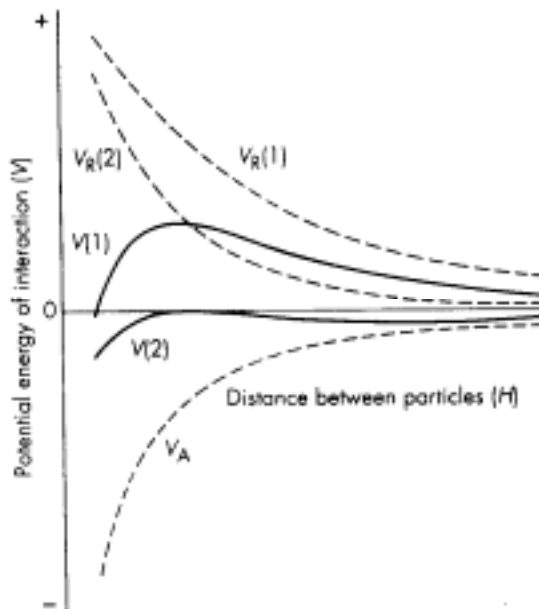
10.6.2 Some Complicating Factors

- Eq. (10.16)-------
  repulsive potential energy function → exponential function of H
  attractive potential energy function → inverse square of H
  - at small and large distance → attractive potential dominates
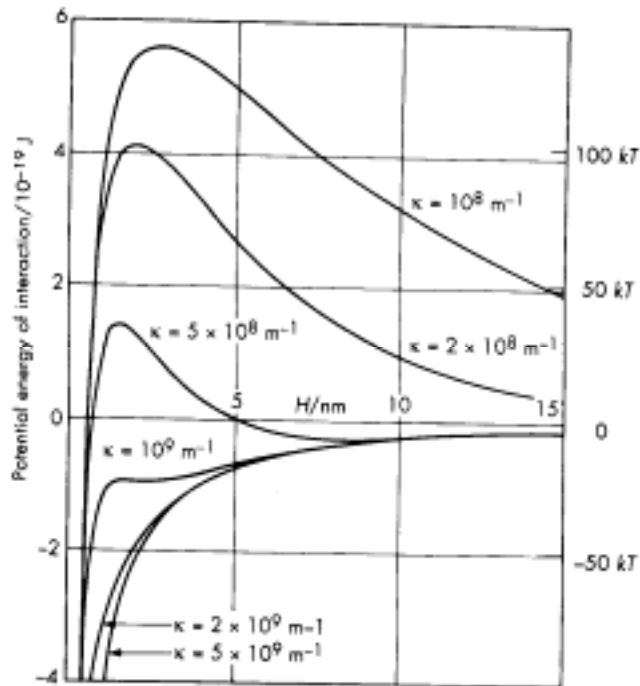 - at intermediate distances → EDL repulsive potential dominates

✧ total interaction energy curve, V(1) and V(2), obtained by the summation of an attraction curve, V_A, with different repulsion curves, $V_R(1)$ and $V_R(2)$

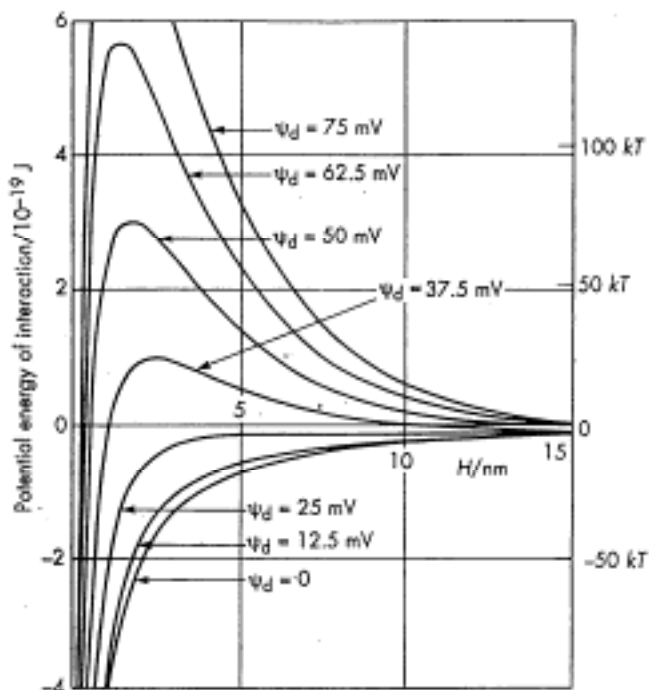- In summary:
  - total potential maximum > thermal energy of particles (10KT)
    → the system is stable
  - the height of barrier is determined by:
    (1) surface potential at the stern layer, Ψs,
    (2) thickness of the double layer, $1/\kappa$

- ♦ **The influence of electrolyte concentration**, **κ**, on the total potential energy of interaction of two spherical particles: $a=10^{-7}$m; $T=298$ K; $z=1$; $A_{11}=2 \times 10^{-19}$J; $A_{33}=0.4 \times 10^{-19}$J; $\varepsilon/\varepsilon_0 = 78.5$; $\psi_d = 50$mV $\sim 2kT/e$.

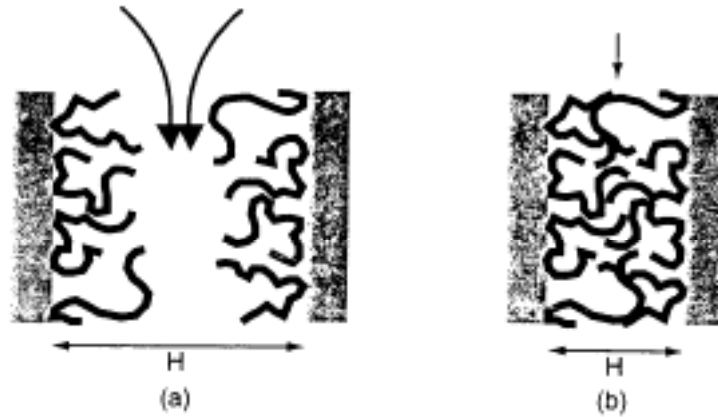

- ♦ **The influence of Stern potential, ψ_d,** on the total potential energy of interaction of two spherical particles: $a=10^{-7}$m; $T=298$ K; $z=1$; $A_{11}=2 \times 10^{-19}$J; $A_{33}=0.4 \times 10^{-19}$J; $\varepsilon/\varepsilon_0 = 78.5$; $\kappa = 3 \times 10^{8}$ m^{-1}

10.7 Steric or Entropic Stabilization

■ A stabilizing mechanism which is much less studied and understood.

■ The mechanism involves the presence of a lyophilic colloid (   ) which adsorbs onto the particle surface and provides steric or entropic stabilization.

● The added lyophilic colloid acts as the "protective colloids".

■ Steric "protective agents":
● need not carry an electrical charge.
● relatively high molecular weight. (especially macromolecules)
● has one portion of its molecule exhibits relatively low solubility in the dispersion medium (so, a high tendency to adsorb onto the particle surface)

10.7.1 The Mechanism of Steric Stabilization

■ When two colloidal particles approach each other, the adsorbed layers begin to interpenetrate. Such interpenetrations have two effects:

(1) Osmotic effect due to increase in local concentration of the adsorbed species. → solvent molecules move into the area and pushes them apart (Fig 10.8.a).
(2) Entropic or volume restriction effect: the interacting species lose certain degrees of freedom → decrease in entropy which is unfavorable (Fig 10.8.b)

■ In order to regain the lost entropy, the particles must move apart, which solvent moves in to resolvate the units. ------- the result is an energy barrier retarding the approach of particles.

FIGURE 10.8. As two surfaces having adsorbed polymer approach, two phenomena occur that produce a net repulsive force between the surfaces. (*a*) At relatively close approach, but before actual interpenetration of the layers, the local concentration of polymer chains (between particles) increases above the "normal" equilibrium value giving rise to an osmotic pressure effect; solvent molecules move into the area between the surfaces and pushes them apart. (*b*) At distances where layer interpenetration occurs, the polymer chains begin to lose degrees of freedom (an entropy decrease) and thermodynamic factors introduce a second repulsive term.

■ The net energy of interaction will be:
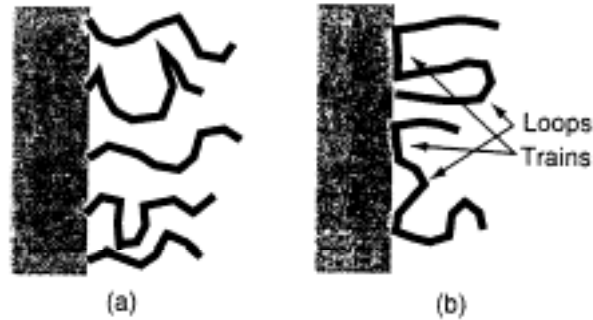
$$G_{total} = \quad G_{steric} + \quad G_{att}$$

■ The anchoring methods of polymeric protective agents to the particles:

(1) single-point attachment (Fig 10.9a)

a free-swinging "tail" projecting into the solution, so the distance of the protective layer will be greater.

(2) two or more points attachment (Fig 10.9b)

The polymer chains will form various loops and tails. When interpenetration occurs, such attachment will lead to stronger entropic effect.
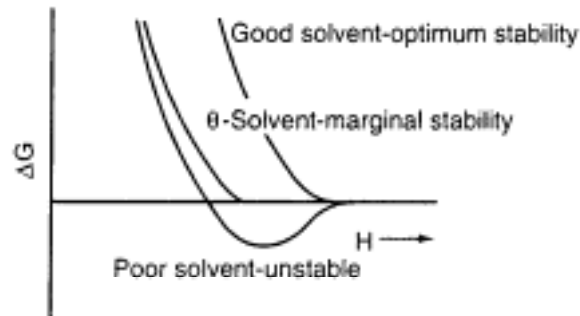
FIGURE 10.9. A polymer may be adsorbed at one end of the chain to produce "tails" (*a*) or in "loops" and "tails" as in (*b*). The situation in (*a*) has some advantage in terms of producing a thicker adsorbed layer for a given polymer chain length, but (*b*) will usually produce a stronger adsorption and a higher chain density.

■ One can not say which configuration is better than the other. In most practical systems, both configurations will be involved.

10.7.2 Solvent Effect in Steric Stabilization

■ If the solvent becomes a better solvent for the monomer units <u>acting as anchors</u>, the chains may be more weakly adsorbed. → decrease stability.

■ If the solvent is changed from a "good" to a "poor" solvent for the <u>loops and tails</u>, the thickness of the protective layer will be reduced (polymer chains collapse on the particle surface). → reduced stability.

■ The solubility of polymer in a given solvent is a function of temperature.

● In a "good" solvent, polymer chains extend in open and random-coil configuration, given optimum protective layer thickness.

● **The θ point**: the temperature at which the solvent changes from "good" to "poor" properties.

● **Critical flocculation temperature**: the temperature at which the colloidal stability changes from good to bad.

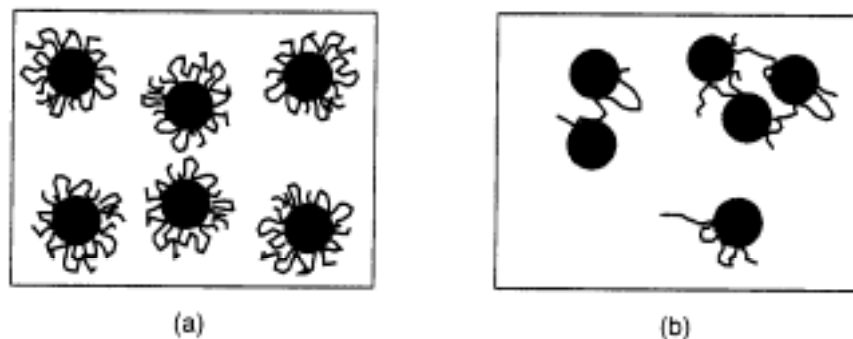● The interaction potential affected by the quality of solvent - Fig 10.10

FIGURE 10.10. Because steric stabilization depends to a great extent on the thickness of the adsorbed polymer layer, the quality of the solvent for the adsorbed polymer is important. Curve 1 represents the steric repulsion curve in a "good" solvent (but not so good as to desorb the stabilizing polymer). Curve 2 represents a situation in which the solvent is borderline (a so-called θ solvent). Curve 3 is the general curve for a "poor" solvent that produces little or no stability.

10.7.3 Effects of Polymer Molecular Weight

■ In general, a *higher-molecular weight* material can be expected to provide *better protection* against flocculation. (longer chains imply longer loops and tails, and thicker protective layer)

● However, a very high molecular weight may lead to sensitization and <u>bridging flocculation</u> -----

Reason: when there is more than one attachment point, it is possible that various attaching points will encounter two (or more) different particles and ties them together. (Fig 10.11)

(a)   (b)

FIGURE 10.11. In sterically stabilized systems, a given adsorbed polymer molecule will be associated with one particle (a). In systems containing a low polymer concentration and/or very high-molecular-weight polymer, molecules can become adsorbed to two or more particles leading to "bridging" flocculation (b).

- Can be used to the flocculation of particulate matter that are difficult to remove otherwise.---- promote the separation and filtration.

10.7.4 Depletion Flocculation

- For a polymer that is not adsorbed or poorly adsorbed on the particles. (Fig 10.12)

FIGURE 10.12. In a sterically stabilized system containing low-molecular-weight or weakly adsorbed polymer (*a*), as two particles approach, the loosely bound polymer may desorb, leaving "bare" spots on the approaching surfaces, leading to an enhanced flocculation tendency (*b*). That process is referred to as "depletion flocculation."

- As two particles approach, such polymer molecules are squeezed out of the area of closest approach, leaving "bare" surfaces.

- There may arise an additional attractive force caused by osmotic balance. ----- As polymer is forced out, the concentration of polymer between particles is less than in the bulk. Osmosis then forces solvent to flow from between the particles out into the solution.

10.8 Coagulation Kinetics

10.8.1 Kinetics of Particle Collisions: Fast Coagulation

- If no barrier to particle approach (said to be noninteracting), the coagulation process is equivalent to a reaction with zero activation energy. The rate of coagulation will be controlled by diffusion kinetics.
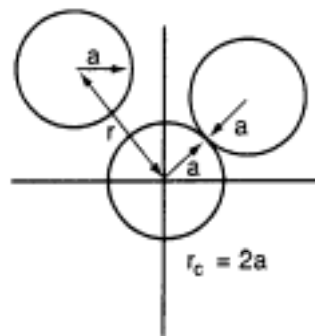
- the Fick's first law of diffusion

$$J = 4\pi r^2 D \frac{dn}{dr}$$

(10.18)

J: number of collisions per unit time between particles and reference particles (Fig 10.13)

a: radius of the central particle

D: diffusion coefficient

FIGURE 10.13. In a colloidal system, the rate of particle flocculation will depend on the rate of particle collision. That rate, in turn, will depend on the diffusion coefficients of the respective particles and their effective particle diameters (or collision cross sections).

- The collision diameter of particles $r_c = 2a$ (for monodisperse particles)
- At time $t = 0$

  particle concentration $n = n_0$, as $r \rightarrow \infty$

  $n = 0$, as $r = r_c$

  from Eq.(10.18), the number of collisions per unit time between the central stationary and a second particle, (J at r_c)

$$J = 4\pi D r_c n_0$$

(10.19)

the diffusion coefficient D is given by:

$$D = \frac{kT}{6\pi\eta a}$$

(10.20)

  η: viscosity of the dispersion medium

- If the central particle is considered to be moveable,

$$D = D_1 + D_2 \text{ (particles of different radii)}$$
$$D = 2D \text{ (particles of identical radii)}$$

- The rate of disappearance of primary particles:

$$\frac{dn}{dt} = -8\pi r_c D n^2 \tag{10.21}$$

n: concentration of primary particles

- The time for the reduction of the particle number by one half, (half-life, $t_{1/2}$)

$$t_{1/2} = (8\pi r_c D n_0)^{-1} \tag{10.22}$$

Substitute Eq (10.20) into (10.22), and for water at 25

$$t_{\frac{1}{2}} = \frac{3}{4kTn_0} = \frac{2 \times 10^{11}}{n_0} \text{ (seconds)}$$

- For a dilute dispersion containing 10^{12} particles per cm^3.
  $t_{1/2}$ 0.2 – 1 sec. (shorter than are normally encountered in practice for noninteracting dispersions)
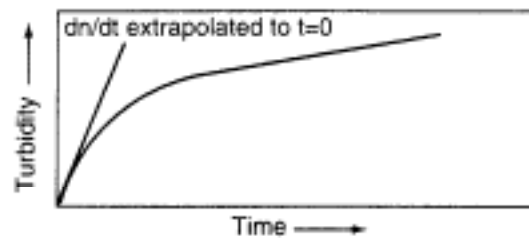
- *The primary reason for the discrepancy*:

When two particles approach to a distance of molecular dimensions, the "microscopic" viscosity of solvent increases, so the diffusion is slowed. The effective diffusion coefficient, D_{eff}, under this hydrodynamic effect was simplized as:

$$D_{eff} = D \frac{6s^2 - 20s + 16}{6s^2 - 11s} \tag{20.23}$$

Where   s = r/a

- The theory presented above considers only collisions between single primary particles. When all particles (dimmers, trimers, ……) are taken into consideration, n is the number of all particles present, but it's complicated to define r_c, D, ….

  - The relevant experiments are normally interpreted for the early stapes of the coagulation process only. (t → 0 in Fig 10.14)

FIGURE 10.14. Experimentally, the rate of particle flocculation can be determined by measuring the change in turbidity of the system as a function of time and extrapolating back to zero time. A typical turbidity curve would have the form shown.

10.8.2 Slow coagulation

- Some energy barrier to particle contact exists.

- Analogous to a bimolecular reaction in which there is a substantial activation energy.

- Can be described kinetically by:

$$\frac{dn}{dt} = -8\pi r_c D n^2 \exp(\frac{-\Delta G_{max}}{kT}) \tag{10.24}$$

G_{max} : activation energy (energy barrier of coagulation)

- Stability ration (W) is defined as the ratio of *coagulation rate* without energy barrier (Eq 10.21) to that with (Eq 10.24) energy barrier:

$$W = \exp(\frac{\Delta G_{max}}{kT}) \tag{10.25}$$

  - error in Eq (10.25) occurs due to the difference between colloidal diffusion and molecular diffusion.

- Distance for the formation of aggregative or molecular activated complexes:

  Particles: 10 -100 nm ;   *molecules*: 0.1 -1.0 nm

- The interactions between particles tends to extend over distances much greater than those involves in formation the complexes.

  Results: mutual diffusion rate is reduced, and collision frequency will drop

- A more accurate expression for W, taking into consideration the interaction potential:

$$W = r_c \int_{r=2a}^{r=\infty} (\frac{1}{r^2}) \exp[\frac{G(r)}{kT}] dr \qquad (10.26)$$

  G(r): interaction potential as a function of separated distance *r*.

- For a changed particles experiencing electrostatic repulsion:

$$W = (\frac{1}{\kappa r_c}) \exp \frac{G_{max}}{kT} \qquad (10.27)$$

  κ : thickness of electrical double layer

$$\text{Eq (10.27)} \rightarrow \quad \ln W = -\ln \kappa r_c + \frac{G_{max}}{kT} \qquad (10.28)$$

- G_{max} is a roughly linear function of electrolyte concentration, C_0. (ln W v.s. ln C_0 $\rightarrow$ linear)

10. 8. 3 Critical Coagulation Concentration

■ For charge-stabilized colloidal system
  Critical Coagulation Concentration (CCC):
    The concentration of electrolyte necessary to bring the system into the regime of rapid coagulation (W=1)

- By using of Eq. (10.28), extrapolation of curve of (lnW) v. s. (ln C_0) to lnW=0
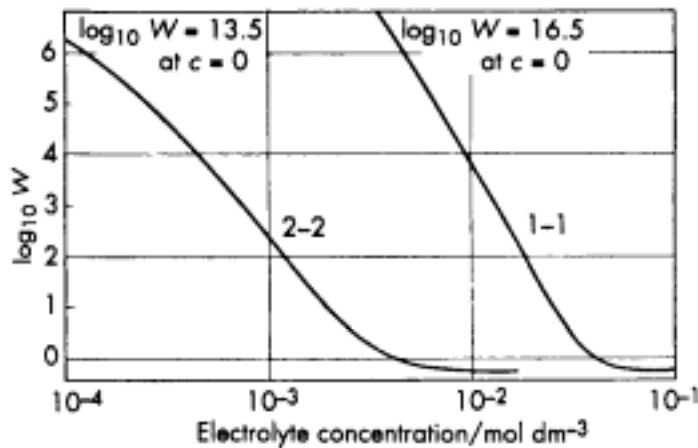
Figure 8.7 Theoretical dependence of stability ratio on electrolyte concentration calculated from equation (8.2) for $a = 10^{-8}$ m, $A = 2 \times 10^{-19}$ J and $\psi_d = 76.8$ mV $= 3kT/e$. At high electrolyte concentrations $W < 1$ owing to coagulation being accelerated by van der Waals attractive forces (reduced flow rate in the narrow inter-particle gap has not been allowed for) (*By courtesy of Elsevier Publishing Company*)

- Schultze and Hardy indication:

  The primary factor controlling the effect of an electrolyte on a colloid of opposite charge was the <u>valance of counterion</u>. (the valence of ions of the same charge as the colloid was of minor importance)

- CCC varies as the inverse sixth power of the valence (Z),

$$\text{CCC } \alpha \text{ } Z^{-6}$$

- However, for the same valence, the ion properties vary slightly with their ionic radius, hydration radius, …..

- The effectiveness for coagulating negatively charged colloids:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$
$$Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$$

10. 8. 4 The Deryagin-Landau-Verwey-Overbeek (DLVO) Theory

■ Consider only two contributing factors:

    (1) the attractive van der Waals terms;

    (2) the repulsive double-layer term.

■ The excess charge density (ρ_e) at a point in the electrical double of potential (ψ): (from eq. 5.6)

$$\left[C^+ - C^-\right]Z = \rho_e = ZCo\left[\exp\left(\frac{-ze\psi}{kT}\right) - \exp\left(\frac{+ze\psi}{kT}\right)\right] \qquad (10.29)$$

Z: valence of electrolyte (1 to 1)

Co: bulk concentration

■ The relation of ρ_e to ψ (Poisson's Eq.):

$$\frac{\delta^2\psi}{\delta\chi^2} = -\frac{\rho_e}{\varepsilon} \qquad (10.\,30)$$

ε: permitivity of the media

■ Combination of Eq. (10.29) and Eq. (10.30)
→ Poisson-Boltzmann Eq.

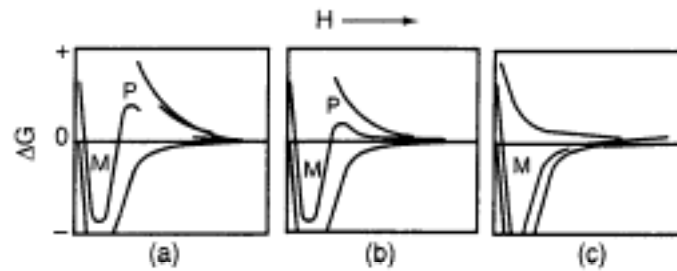$$\psi = \left(\frac{4kT}{ze}\right)\exp(-\kappa\chi) \qquad (10.31)$$

: thickness of the EDL

● The potential (ψ) falls off exponentially with distance (χ)

■ The form of EDL overlap potential as a function of distance of separation, H, of two parallel surface:

$$\Delta G_{elec} = \left(\frac{64CokT}{\kappa}\right)\exp(-\kappa H) \qquad (10.32)$$

● κ is dependent on the ion concentration, and the primary concentration effect comes from the exponential term.

■ The total potential-energy (attractive van der Waals and repulsive electrostatic potentials):

$$\Delta G_T = \left[\left(\frac{64CokT}{\kappa}\right)\exp(-\kappa H)\right] - \frac{A_H}{(12\pi H^2)} \qquad (10.33)$$

● a series of curves of Eq. (10.33) were shown in Fig. 10.15.

FIGURE 10.15. In an electrostatically stabilized colloid, the concentration of electrolyte will greatly affect the stability of the system: (*a*) with low electrolyte concentration, a relatively high energy barrier will impart stability; (*b*) as electrolyte is added, the stabilizing barrier will be reduced, but reasonable stability may be maintained (depending on the valency of the added electrolyte); (*c*) at a critical electrolyte concentration the energy barrier will effectively disappear and rapid flocculation will occur.

- The maximum in the curves represent the barriers to coagulation imposed by the electrical double layer.
- As the electrolyte concentration increases, the height of the barrier decreases.
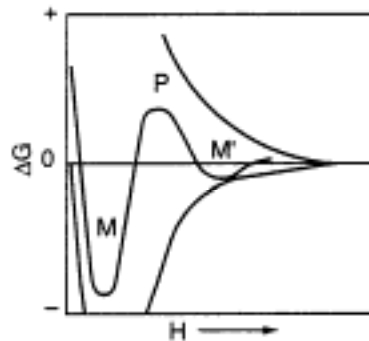- The rapid coagulation (the CCC) will be met when $\Delta G_T = 0$ and $d\Delta G_T / dH = 0$

$$Co(CCC)\alpha \frac{1}{(A_H{}^2 Z^6)} \qquad (10.34)$$

✧ $Co(Z = 1): Co(Z = 2): Co(Z = 3) = 1 : 0.016 : 0.00014$

✧ A_H increase → CCC values decreases

As characteristics of medium and dispersed phase become more similar → A_H decreases → more stable

10. 8. 5 Reversible flocculation of a colloid
— existence of secondary minimum energy

FIGURE 10.16. In many colloidal systems, the interaction energy curve will have a small minimum, the secondary minimum, M', that allows the particles to undergo a lose, reversible flocculation. In some systems of relatively large, monodisperse particles, the secondary minimum may lead to an optical phenomenon called "opalescence" in which a very regular structure is developed (similar to a crystal structure) that produces beautiful and interesting patterns with incident light.

- Secondary minimum flocculation is found to be caused from the entropy effects.

- The flocs formed are held together rather weakly and tend to be unstable. For

    $r < 100$ nm $\rightarrow$ Brownian motion can prevent flocculation,

    $r \gg 100$nm $\rightarrow$ apparent phase separation, gentle stirring will regenerate the original homogeneous dispersion.