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## Colloids, A Fascinating Subject: Introductory Lecture

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### Summary

Colloid science may be considered to start with the study of *pseudo-solutions* in water of sulphur, silver chloride, Prussian blue (SELMI, 1845), of colloidal gold (FARADAY, 1857) and with the coining of the term "colloid" by GRAHAM in 1861. Colloids are present as dispersed systems, characterized by slow diffusion and slow (often negligible) sedimentation under normal gravity, which set the size of the colloidal particles in the range of about 1 nm to 1  $\mu\text{m}$ .

Some colloid systems such as polymer solutions and soap solutions, containing *micelles*, form spontaneously. They are thermodynamically stable, and are called *lyophilic colloids*. Others, which contain particles, insoluble in the solvent (e.g. AgCl, S, Au, oil in water), must be prepared in a roundabout way. These are called *lyophobic colloids*. In their preparation the presence of *peptizing* or *stabilizing* substances is essential. Since van der Waals forces always tend to lead to agglomeration (flocculation) of the particles, stability (i.e. a long shelf life) of such colloids requires that the particles repel one another, either by carrying a net electrostatic charge or by being coated with a sufficiently thick adsorbed layer of large molecules compatible with the solvent.

Potential energy curves are very useful for the display of the various types of interaction between colloidal particles.

Colloidal dispersions have interesting optical properties, such as TYNDALL light scattering, turbidity and birefringence. They often show remarkable non-Newtonian rheological behaviour.

In the many practical applications in paints, inks, emulsions, pharmaceutical, agricultural and cosmetic preparations, photographic films, foams, etc. the stability and the rheological properties are of the utmost importance.

Colloidal aspects are numerous in biology, biopolymers, biological membranes and cells in general.

## 1 Introduction

Colloid Science finds its origin in the discovery of solutions of certain insoluble substances. SELMI<sup>1</sup> described in 1845 *pseudosolutions* in water of silver chloride, sulphur and Prussian blue. He included them in the same class as solutions of albumin and starch. All these solutions are clear or slightly turbid. SELMI considered them to contain particles which are larger than the usual molecules. MICHAEL FARADAY<sup>2</sup>, towards the end of his life, made fairly extensive studies of the colloidal gold sol and to the present day the very fine gold sols (particles of about 3 nm radius) prepared by reduction of a gold chloride solution with phosphorus are called *Faraday sols*. GRAHAM<sup>3</sup> who coined the term "colloid" (= glue like) in 1861 emphasized the low rate of diffusion and the lack of crystallinity of all these colloidal systems and from this slow diffusion drew the correct conclusion that colloid particles are fairly large (say larger than 1 nm). On the other hand the fact that these same colloidal solutions do not sediment (or only very slowly) under normal gravity proves that the particles cannot be very large (say not larger than 1  $\mu\text{m}$ ).

Colloidal suspensions ( $\equiv$  sols) have found numerous fundamental applications, as in PERRIN's studies<sup>4</sup> of Avogadro's constant, where colloidal particles acted as very large, individually visible molecules, or, very recently, in VRIJ's use of concentrated colloidal suspensions as models for the liquid state<sup>5</sup>. The rate of rapid coagulation of colloids, in which each Brownian encounter between two particles results in permanent contact, was clarified in 1916 by the beautiful theoretical work by VON SMOLUCHOWSKI<sup>6</sup>. This rate of coagulation is essentially identical to the rate of diffusion - controlled bimolecular reactions between small molecules<sup>7</sup>. A small but necessary refinement to the theory, which takes into account that the last approach between two particles or molecules is slowed down, because it is difficult to squeeze out the last layers of liquid from between the particles, was recently formulated by several authors (DERYAGIN and MULLER<sup>8</sup>, SPIELMAN<sup>9</sup>, HONIG, ROEBERSEN and WIERSEMA<sup>10</sup>, DEUTCH and FELDERHOF<sup>11</sup>) and nicely confirmed by experiments on the coagulation of latex particles (LICHTENBELT et al.<sup>12</sup>). Phase transitions (HACHISU<sup>13</sup>) between concentrated liquid-like colloidal dispersions and crystalline arrangements of the particles have been observed and they follow from the statistical thermodynamics of such systems<sup>14</sup>.

Other applications of colloids are eminently practical. Emulsions (dispersions of liquid particles in a liquid, such as oil in water or water in oil) are used very widely. Milk, mayonnaise, crude oil containing water at the well head, and many cosmetic and pharmaceutical preparations belong in this category. Latices of various polymers are

prepared in quantities of millions of tons per year in a process called emulsion polymerization, in which one starts with an emulsion of the monomer in water.

Suspensions (dispersions of solid in liquid) are found in the kitchen in the form of various soups and sauces. Many paints, inks, and lacquers are fine suspensions of the pigments in oil or water or even in an emulsion. Clay particles are of colloidal size. It is hardly possible to exaggerate their importance in agriculture, in ceramics and even in delta formation.

Fogs and smokes are colloidal dispersions in gases. They are called *aerosols*.

Soap bubbles, foams and biological membranes show colloidal properties, since the thickness of the lamellae ranges from 4 nm to over 1  $\mu$ m.

Colloidal systems have interesting optical properties, colour, turbidity, birefringence. Some of these properties are peculiar because the wavelength of visible light lies in the colloidal size range. Many colloidal particles carry an electric charge due to surface dissociation or to the adsorption of ions. This electric charge happens to be very important in stabilizing colloidal dispersions, in characterizing the particles and in several applications.

Colloids, especially concentrated colloids, have remarkable mechanical properties. Think of gelatin solutions, which flow freely above 40°C, but become rigid (form a *gel*) at room temperature. A good paint must flow easily when applied, but then must rigidify soon in order to prevent it from flowing off vertical surfaces. Wet clay must not change its shape in normal gravity, but yield easily to the sculptor's thumb.

I hope that this introduction has shown that the study of colloids is worthwhile to increase our understanding of nature and to allow us to control it more efficiently and that it has what your appetite to taste more of this field of neglected dimensions. Cf. W.O. OSTWALD's book, *Die Welt der vernachlässigten Dimensionen*<sup>15</sup>.

## 2. Types of colloids and their preparation

The simplest type of colloid is formed by solutions of *macromolecules* (polymers), including biopolymers such as proteins, nucleic acids and polysaccharides. These systems belong to colloid science since the sizes of macromolecules fall in the colloidal size range. The older generation of colloid scientists (FREUNDLICH,<sup>16</sup> KRUYT and BUNGENBERG DE JONG<sup>17</sup>) considered them as an important part of their science, but more recently on account of the great technical importance especially of man-made polymers, polymer science has developed as a science on its own with its own

textbooks (e.g. FLORY<sup>18</sup>) and periodicals.

However, colloid science is not complete without the inclusion of polymers, not only because techniques such as light scattering, sedimentation, and electrophoresis are applied to polymers just as to many other colloids, but also because of the many other links. There are polymer colloids (FITCH<sup>19</sup>), in which particles of colloid size made of polymers are dispersed in non-solvents for the polymer molecules. Furthermore polymers are frequently used to modify the properties of other colloids as we shall see in section 3 on steric stabilization.

The next class of colloids consists of solutions of soaps and other *amphipolar* substances. These molecules are characterized by a large non-polar part (hydrocarbon or fluorocarbon) and a water compatible polar part. The polar part may be anionic, as in  $C_{12}H_{25}OSO_3Na$ , or cationic, as in  $C_{16}H_{33}N(CH_3)_3Br$ , or non-ionic as in  $C_9H_{19}(C_6H_4)O(CH_2CH_2O)_8H$ . In water, above a certain concentration (the lower, the larger the non-polar part), aggregates of 20 or more molecules, which are called *micelles*, are formed. Therefore these colloids are called *association colloids*. The

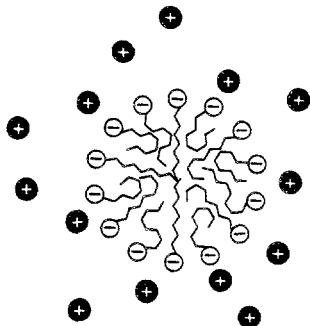


Figure 1. Schematic representation of a spherical or cylindrical micelle

lack of solubility of the hydrocarbon (fluorocarbon) part in water drives the non-polar groups together, but instead of then forming a separate phase the particle growth stops when the non-polar nucleus is sufficiently surrounded by polar groups, thus minimizing the water-hydrocarbon contact area. The same substances may form *inverse micelles* (polar parts inside) in non-polar solvents.

Micelles and inverse micelles may take up other molecules in their interior in a process called *solubilization*. This may even go so far as to result in the formation of fairly large droplets with a radius of say 10 nm. Such systems are called *microemulsions* and may be either of the water-in-oil or oil-in-water type. In recent years microemulsions have drawn a great deal of attention, since they are applied in tertiary oil

recovery on the basis of the extremely low interfacial tensions (to less than  $0.001 \text{ mN m}^{-1}$ ) exhibited by these systems

All the categories mentioned so far are thermodynamically stable colloids and are known as *lyophilic colloids* (*hydrophilic* if water is the dispersion medium).

Colloidal dispersions of insoluble substances, called *lyophobic* (*hydrophobic*) *colloids*, are not in thermodynamic equilibrium, but, if well prepared, they may have life times of many years. (Some of FARADAY's gold sols still exist). Lyophobic colloids are prepared either by *dispersion methods* (= grinding, milling, etc. until the particles are small enough) or - more subtly - by *condensation methods*. In a condensation method the insoluble material is precipitated from a solution of small molecules or ions under circumstances in which a high rate of nucleation of the new phase is combined with a relatively slow rate of growth of these nuclei. The process may sometimes be carried out in such a way that all the nuclei are formed in a very short time early in the process, whereas the growth to larger particles occurs over a longer time without further nucleation. Under these circumstances all particles grow at the same rate which leads to *monodisperse* (= *isodisperse*) systems. The method goes back to ZSIGMONDY'S<sup>20</sup> gold sols, but it was applied to many other cases (sulphur sols, aerosols) and interpreted more fully by LA MER and coworkers<sup>21</sup>. Figure 2, based on LA MER's work<sup>22</sup> shows that, if the material for the particles is supplied continuously (e.g. by slow formation of sulphur from acidified thiosulphate) and if the nucleation concentration is sufficiently far above the saturation concentration, a short burst of nucleation may rapidly lower the concentration below the supersaturation needed for nucleation, after which all further material will only cause growth of the existing particles, without any new ones being formed.

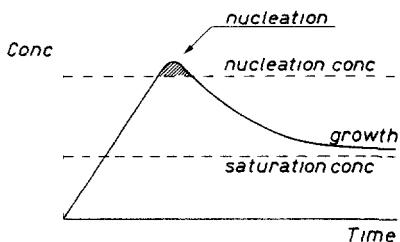


Figure 2. Showing schematically how a nucleation period and a growth period may be separated, thus leading to a monodisperse sol

Whether prepared by dispersion or by condensation lyophobic colloids only have a long life if suitable *peptizing* or *stabilizing substances* are present. Such substances are needed to prevent the particles from making actual contact and sticking together during their frequent Brownian encounters. The vivid Brownian motion of colloidal particles forms a fascinating sight, when observed in a dark field microscope (an *ultramicroscope*) and has been described as a tableau of "thousands of dancing gnats". Figure 3 shows the central part of the field of view in SIEDENTOPF and ZSIGMONDY's ultramicroscope<sup>23</sup>, in which the beam of a strong light source is concentrated by a microscope objective perpendicular to the line of sight of the microscope through which the phenomenon is observed.

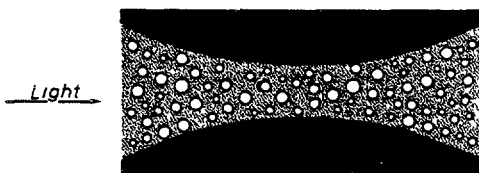


Figure 3 Central part of the field of view in SIEDENTOPF and ZSIGMONDY's ultramicroscope

We now give a few examples of the preparation of lyophobic colloids. Oil-in-water (O/W) and water-in-oil (W/O) *emulsions* are prepared by shaking, stirring, or sonication of a mixture of oil and water. The resulting emulsion is only stable if some soap, or some other stabilizer, is present to prevent the newly formed oil-water interfaces from coalescing. The type of stabilizer determines whether an O/W or W/O emulsion is formed.

*Silver halide sols* are formed by mixing solutions of silver nitrate and alkali halide. They require an excess of  $\text{Ag}^+$  or  $\text{Hal}^-$  ions for their stability.

The *arsenic sulphide sol* is prepared by pouring a saturated solution of  $\text{As}_2\text{O}_3$  into a solution of  $\text{H}_2\text{S}$  in water which is kept saturated by bubbling  $\text{H}_2\text{S}$  through it. The excess  $\text{H}_2\text{S}$  (sulphide ions) is the stabilizer.

*Ferric hydroxide* and *ferric oxide sols* are formed by the hydrolysis of ferric chloride solutions either by heating or by increasing the pH. Depending upon the conditions  $\text{Fe}^{3+}$  or  $\text{OH}^-$  ions are stabilizing ions.

*Gold sols* are formed by reducing dilute gold ( $\text{Au}^{\text{III}}$ ) chloride solutions with a great variety of reducing agents, such as formaldehyde, hydrazine, hydrogen peroxide, sodium citrate. The stabilizer is excess chloride or a gold chloride or gold citrate complex ion.

*Polymer latices* are usually prepared by free radical polymerization of vinyl and/or butadiene monomers in an emulsion or solution containing soap or soap-like substances, which act as stabilizers for the polymer particles (radius e.g. 100 nm) formed.

From these examples it may appear that the stabilizing substances provide ions that are adsorbed onto the particles, thus charging them, so that they repel one another. There are, however, other very general stabilizing substances, such as gums and gelatin which are non-specific *protective agents* for dispersions in water and which may protect even without being electrically charged.

This brings us to suspensions in oil and in other *non-aqueous media*, which are usually prepared by grinding in the presence of suitable, oil-soluble and adsorbable protective agents. Examples are paints and inks, doped engine oils in which the dopant, a protective agent, keeps carbon particles resulting from incomplete combustion in suspension, thus preventing them from causing abrasion.

Since many colloids contain contaminating substances that have remained from the preparation stage, it is desirable and sometimes essential to remove these substances. This can be accomplished by *dialysis*, i.e. by bringing the colloid in contact with pure, frequently renewed, solvent via a membrane with pores, small enough to retain the colloid particles, but large enough to let small molecules or ions pass through. The dialysis can often be accelerated by applying an electric field across the membrane. Figure 4 shows GRAHAM's original dialyzer<sup>24</sup>, an inverted bottomless beaker closed at one side by a parchment (later cellophane or collodion) membrane. Figure 5 shows a modern five chamber electro-dialyzer<sup>25</sup>.

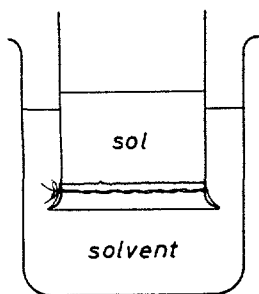


Figure 4. Dialyzer as used by GRAHAM.

In a very simple, but effective method of dialysis the sol is enclosed in a length of regenerated cellulose or nitrocellulose tubing ("artificial

sausage skin"), which is allowed to float around in the frequently renewed solvent

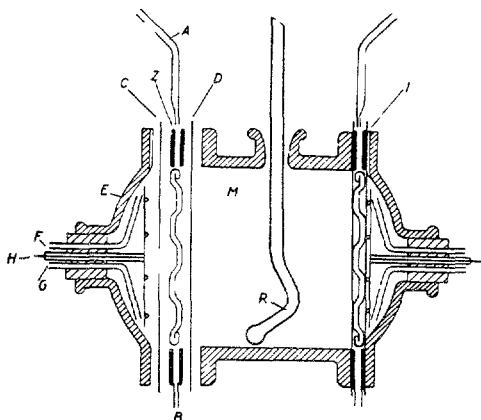


Figure 5. Electro-dialyzer with five chambers.

A, F = supply of distilled water, B = drain of rinsing chamber, C, D = membranes, E = electrode chamber, G = drain of electrode compartments, H = electrode, I = groove for escape of gas, M = middle chamber, containing sol, R = stirrer.

### 3. Stability of lyophobic colloids

Colloid particles always attract one another by *van der Waals forces* (*dispersion forces*), even across a condensed medium, although the medium weakens the force. Due to the near additivity of the forces between pairs of molecules, the attractive force has a fairly long range. Between two spherical particles of radius  $a$  at a distance  $R$  between the centers and a distance  $H = R - 2a$  between the surfaces, the energy of attraction is still of the order of  $kT$  ( $k$  = the Boltzmann constant,  $T$  = the absolute temperature) when  $H \approx 0.1a$ .

HAMAKER derived the following expression for the energy of attraction between two equal spherical particles<sup>26</sup>.

$$\Delta_{att} = -\frac{A}{6} \left[ \frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln \frac{R^2 - 4a^2}{R^2} \right] \quad (1)$$

where the *Hamaker constant*,  $A$ , depends strongly on the nature of the particles and the medium, but is usually in the range of  $10^{-21}$  -  $10^{-19}$  J, or  $A \sim 0.25 kT$  to  $25 kT$  at room temperature.



For small distances eq (1) can be approximated by

$$\Delta V_{att} \approx - \frac{Aa}{12H} \tag{2}$$

or more precisely<sup>27</sup>

$$\Delta V_{att} \approx - \frac{A}{12} \left[ \frac{L}{H} + 2 \ln \frac{q}{L} \right] \tag{3}$$

where  $L = a + 3H/4$ .

Given the intensity and the range of the van der Waals attraction, a sol can only be stable if the particles also repel one another with a force of sufficient strength and sufficiently long range.

Two types of repulsion are known and relatively well understood, an electrostatic and a steric repulsion. The *electrostatic repulsion* is based on the charge of the particles, obtained by surface dissociation or by preferential adsorption of ions of one type. It is, however, not a simple Coulomb repulsion, since, to conserve electroneutrality, the particle charge is surrounded by a more or less diffuse ion atmosphere, which forms an *electric double layer* with the surface charge. The double layer is represented in figure 6. It may be divided into a molecular

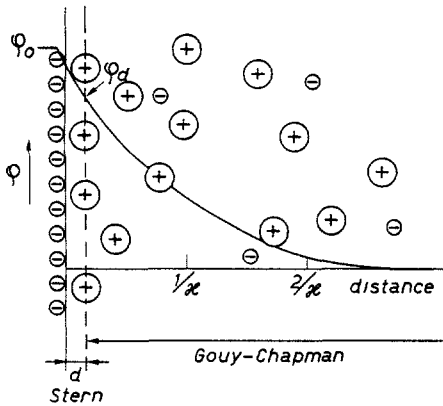


Figure 6. Schematic representation of the distribution of the ions and the decay of the electric potential  $\phi$  in a double layer.

condenser or STERN layer<sup>28</sup> and a diffuse or GOUY-CHAPMAN layer<sup>29</sup>. At large distances,  $x$ , from the surface the potential decays as  $\exp(-\kappa x)$ , at short distances somewhat more steeply.  $\kappa$  is the inverse DEBYE-HUCKEL length<sup>30</sup>. It is given by

$$\kappa = \left[ \frac{2 \sum c_1 z_1^2}{\epsilon_r \epsilon_0 R T} \right]^{1/2} \quad (4)$$

in which  $c_1$  and  $z_1$  are the concentration and charge number resp of the ions of type 1,  $\epsilon_r$  the dielectric constant of the solution,  $\epsilon_0$  the permittivity of the vacuum,  $R$  the gas constant and  $F$  the Faraday constant

The energy of repulsion between two particles carrying double layers decays approximately as  $\exp(-\kappa H)$  and can be written<sup>31 \*</sup>

$$\Delta V_{\text{rep}} \approx + 2\pi \epsilon_r \epsilon_0 a \left( \frac{4RT}{zI} \gamma \right)^2 \exp(-\kappa H) \quad (5)$$

where  $\gamma = \tanh(zI \phi_d / 4RT)$ ,  $z$  is the charge number of the counter ions and  $\phi_d$  the potential at the plane of the Stern-ions (dissolved counter ions in closest approach to the surface, see fig 6).

Because the attraction decays as an inverse power of the distance (as  $H^{-1}$  for spherical particles at short distances, and as  $H^{-6}$  at large distances) but the repulsion decays exponentially with  $H$ , the attraction prevails both at short and at large distances, but at intermediate distances ( $H \approx \kappa^{-1}$ ) the repulsion may win and an energy barrier is formed which keeps the particles apart and thus stabilizes the sol. Increasing the concentration and/or the charge number of the electrolyte in the solution *compresses the double layer* ( $\kappa \approx z \sqrt{c}$ ), shortens the range of the repulsion, tends to decrease  $\phi_d$ , and thus eventually eliminates the energy barrier. This is most strikingly illustrated by a table (Table 1) of electrolyte concentrations (*critical coagulation concentrations*) at which a sol loses its stability and coagulates (= flocculates). The disproportionately large influence of the charge number of the counterions (= ions charged oppositely to the particle charge) and the small influence of the specific nature of the ions is typical for hydrophobic sols and is known as the *rule of Schulze<sup>35</sup> and Hardy<sup>36</sup>*.

When a d.c. electric field is applied to a sol with charged particles, the particles move with a velocity proportional to the applied field strength and in a first approximation proportional to the potential of the

\* This equation is an approximation in several respects. It assumes that  $\phi_d$  is independent of  $H$ , whereas  $|\phi_d|$  in general will increase with decreasing  $H$ . Moreover even at  $\phi_d = \text{constant}$  the repulsion would increase more steeply than  $\exp(-\kappa H)$  for small values of  $H$ . However eq.(5) is a good approximation at large  $\kappa H$  and it predicts the effects correctly in a semi-quantitative sense at smaller  $\kappa H$ .

Table 1

Critical coagulation concentrations (c.c.c) in millimol/l.

As <sub>2</sub> S <sub>3</sub> - sol, negatively charged <sup>32</sup>						
	c.c.c.		c.c.c		c c c.	
LiCl	58	MgCl <sub>2</sub>	0.72	AlCl <sub>3</sub>	0.093	
NaCl	51	CaCl <sub>2</sub>	0.65	$\frac{1}{2}$ Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.096	
KNO <sub>3</sub>	50	ZnCl <sub>2</sub>	0.69	Ce(NO <sub>3</sub> ) <sub>3</sub>	0.080	
Au - sol, negatively charged <sup>33</sup>						
	c.c.c.		c c.c.		c c c.	
NaCl	24	CaCl <sub>2</sub>	0.41	$\frac{1}{2}$ Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.009	
KNO <sub>3</sub>	25	BaCl <sub>2</sub>	0.35	Ce(NO <sub>3</sub> ) <sub>3</sub>	0.003	
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	23					
Fe <sub>2</sub> O <sub>3</sub> - sol, positively charged <sup>34</sup>						
	c.c.c		c c c.			
NaCl	9.25	K <sub>2</sub> SO <sub>4</sub>	0.205			
KCl	9.0	MgSO <sub>4</sub>	0.22			
KBr	12.5	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.195			

mobile part of the double layer, the so-called zeta ( $\zeta$ ) potential. The  $\zeta$  - potential is usually close to the Stern - potential,  $\phi_d$ . This motion is called *electrophoresis*. It is one of the *electrokinetic phenomena*. They all have their origin in the double layer and manifest themselves when either an electric field or a flow field is applied parallel to the interface. Electrophoresis is often a valuable source of information on the sign and the value of the charge and the potential of the double layer

We now consider the other type of repulsion, *steric repulsion*. It is obtained when the particle surface is covered (by adsorption or chemical reaction) by bulky molecules, usually long chain molecules, thus giving the particles a "hairy" surface. If these hairs are compatible with (= soluble in) the medium, they repel one another and they cause a steep repulsion between the particles, with a range of the order of the size of the randomly coiled hairs. As sketched in figure 7 the repulsion is due to two effects, an *osmotic effect* caused by the high concentration of chain elements in the region of overlap, and a *volume restriction effect* due to the loss of possible conformations in the narrow space between the two surfaces<sup>37,38</sup>.

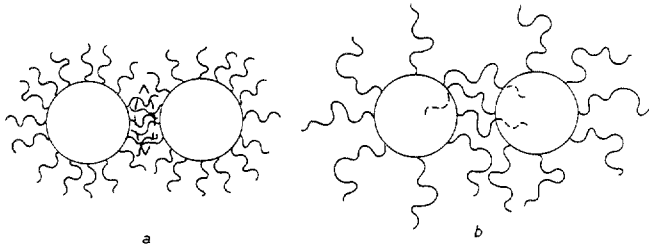


Figure 7. Illustrating two aspects of steric repulsion *a*. Osmotic effect due to high concentration of chain elements in the region of overlap *b* Volume restriction effect due to loss of possible conformations of the "hairs"

Steric repulsion is particularly important for stabilization in non-aqueous, non-polar media. It can be influenced by changing the length and nature of the hairs, by influencing the adsorption energy, and by changing the properties of the solvent. In worse than  $\theta$  conditions the hairs collapse and steric repulsion is not effective. Substances causing steric stabilization are either of the *anchor and chain* type or *homopolymers*. The anchor is easily adsorbed, the chain soluble in the medium (soaps are examples, so are suitable block copolymers). With the homopolymers a fraction of the chain elements is adsorbed (as *trains*), most of the elements are in the solvent as *loops* and *tails*. Protective agents mentioned earlier act by steric repulsion, even in water.

In the last few years renewed interest<sup>39</sup> has arisen in the so called *structural forces*. These are due to the modification of the solvent structure near interfaces as a result of packing restrictions. As far as can be judged now, these forces in themselves probably do not lead to a repulsion of a sufficiently long range for stability, but they may have a comparatively large effect at small separations between the particles where they have an oscillating character and they may play an essential role in *redeposition* (= redispersion of a coagulated suspension or emulsion)

#### 4. Potential energy curves

Potential energy curves, in which the change in free energy ( $\Delta V$ ) is plotted against the distance ( $H$ ) between the particle surfaces, form a powerful instrument for surveying the interplay between different forces

Figure 8 shows a set of such curves for the repulsion, the attraction and the combination of the two in the case of electrostatic stabilization. If the particles are caught in the very deep minimum (the *primary minimum*) at small separations ( $\Delta V_{total} \rightarrow -\infty$  as  $d \rightarrow 0$ ) it is very difficult

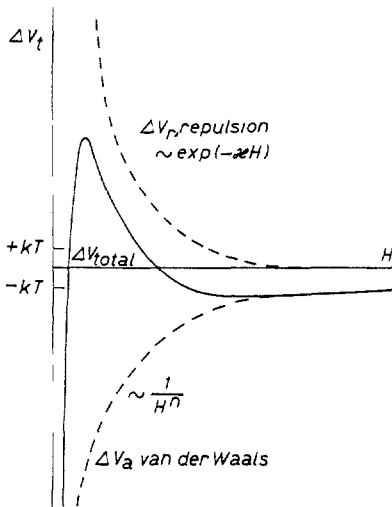


Figure 8 Electrostatic repulsion, van der Waals attraction and the combination  $\Delta V_{total} = \Delta V_r + \Delta V_a$ .

or impossible to separate them. The shallow minimum at large  $H$  (the *secondary minimum*), which may be only a fraction of  $kT$  deep, acts as a temporary trap, from which the particles can be removed easily by mechanical means, change of composition of the medium, or even simply by Brownian motion. If the maximum in the curve is more than 15 or 20  $kT$ , effective collisions leading to permanent contact in the primary minimum become so rare that the suspension is stable. The effect of changes in the parameters of the system (electrolyte composition, Hamaker constant) on the potential energy curves can be followed easily and then conclusions can be drawn on the behaviour of the actual system.

Figure 9 shows the corresponding curves for steric stabilization. The repulsion is very steep, the primary minimum often unattainable

Figure 10 is an example of the possible form of the free energy curve for structural forces. The wavelength of the oscillations corresponds to the distance between the molecules in the solvent in the neighbourhood of an interface. Depending on how difficult or easy it is to remove the last layer of molecules between two interfaces the structural force may be repulsive or attractive at very small separations. The subject is in rapid

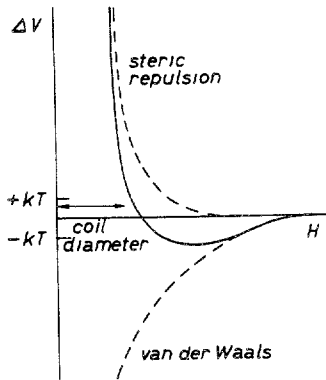


Figure 9 Schematic representation of the free energy as a function of  $H$  in the case of steric stabilization

development, both theoretically and experimentally, but has not quite advanced to the point for application to the stability of real examples, say that of silica particles in water

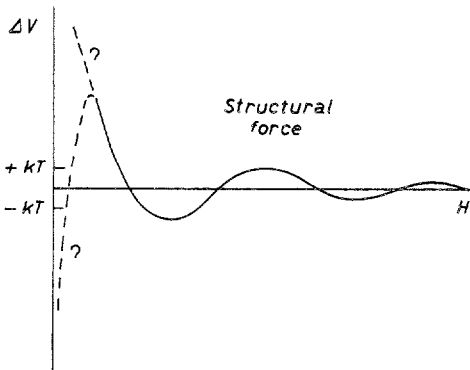


Figure 10 Schematic representation of the free energy curve for structural forces

##### 5. Properties of colloids and some applications

Most colloid suspensions, emulsions and aerosols are *turbid*. They scatter light (TYNDALL light<sup>40</sup>) in all directions. For small particles the scattered intensity is proportional to the square of the volume of the particles. The scattering per unit volume of the suspension is thus proportional to its mass concentration times the volume (or mass, or mole-

cular weight) of the particles. For larger particles, where particle size and wavelength of light are of comparable dimensions, the total intensity and the angular dependence of the scattered light become very complicated (MIE theory<sup>41</sup>). The turbidity of colloids is applied in a variety of ways. It is used for the determination of the molecular weight and, if large enough, the size of the particles. Fibers such as nylon or polyester are made opaque by the incorporation of finely divided  $TiO_2$ . The back scatter of the head lamp is known to everyone who has driven a car at night in a fog. Aerosols are used for military camouflage purposes, but also for the protection of orchards against frost damage by excessive radiation to the clear night sky.

The availability of lasers has made it possible to determine the diffusion coefficient of colloidal particles by analyzing the shift in wavelength of the scattered light caused by the Doppler effect or by photon correlation spectroscopy<sup>42</sup>.

Colloids are often deeply coloured (red gold sol, deep yellow  $As_2S_3$  sol, red  $V_2O_5$  sol) if the colloid material absorbs visible light. Paints and inks in which the pigment particles are finely dispersed are an obvious application of this effect.

As mentioned before colloids show *electrophoresis* in an electric field. In such a field the double layer is polarized as shown in figure 11, but not permanently stripped off the particle. This polarization

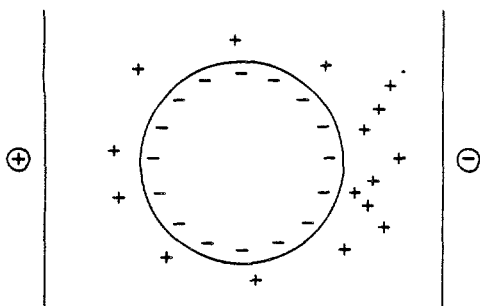


Figure 11. Showing how the double layer around a particle is polarized in an electric field.

affects the electrophoretic mobility of the particle. The dipoles formed cause an increase (in some cases a very large increase) in the dielectric constant of the system. If the particles are rod-like or plate-like the polarization tends to orient the particle parallel to the lines of force

(see figure 12) thus causing electric birefringence (Kerr-effect<sup>4,3</sup>)

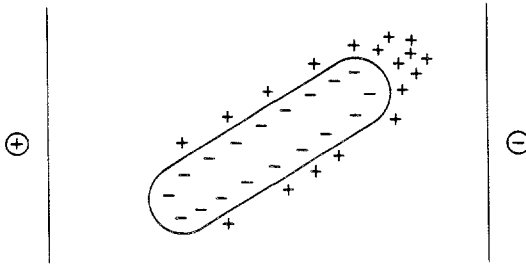


Figure 12 The electric polarization of an anisodimensional particle leads to orientation parallel to the field and thus to electric birefringence (Kerr effect)

Electrophoresis finds analytical and preparative applications in sorting out the complicated mixtures of proteins and other substances in biochemistry. In *electrodeposition* paint suspensions are deposited by electrophoresis onto metal substrates. The process is used on a large scale in painting car platework.

Suspensions of *ferromagnetic* particles become birefringent by orientation of the particles in a magnetic field (Cotton-Mouton effect). Concentrated suspensions of this nature may flow freely in zero field but become rigid in a strong magnetic field.

Correct preparation and handling of suspensions of magnetic particles is essential for the preparation of sound tapes and videotapes.

Concentrated colloid systems have remarkable *rheological properties*. Stable suspensions and emulsions behave as Newtonian liquids in weak shearing fields, but under strong shear the particles cannot move fast enough past one another and the system rigidifies (shear thickening or *dilatancy*). If one walks on a wet sandy beach one sees a ring of dry sand around each footstep caused by dilatancy of the wet sand.

Stable systems settle eventually to a very *dense sediment* since the particles can roll over each other until the closest packing is reached. This may happen in a can of paint which is too well stabilized. If the system is unstable, even when it is only "weakly flocculated", the sediment volume is large and it may even fill the whole suspension, thus causing the formation of a *gel* as illustrated in figure 13. If such a weakly



flocculated suspension is stirred or shaken it may become fluid because

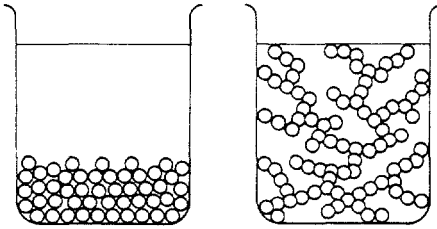


Figure 13. A stable suspension forms a dense sediment, a flocculated suspension has a large sediment volume and may even form a gel

a sufficient number of bonds between particles is broken. After being left undisturbed for some time it returns to the gel state. This is called *thixotropy*<sup>44</sup> or *reversible sol-gel transformation*, a property essential for a good paint, for the drilling muds used in oil well drilling, and in many pastes.

Soap bubbles and foam lamellae would break very quickly, if they were not stabilized by the adsorption of the amphipolar soap or soap-like molecules at their surfaces. Figure 14 illustrates for an ionized soap how the overlap of the two double layers is similar to that between electrically stabilized colloidal particles and how this may prevent the ultimate thinning and breaking of the lamella.

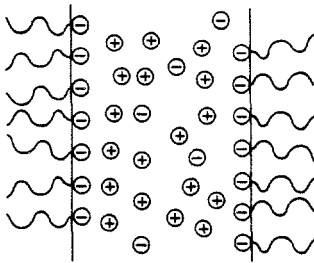


Figure 14. Cross section through a soap film stabilized by the adsorption of soap ions at its surfaces and by the overlap of double layers.

Foams are sometimes a nuisance and must be destroyed or their formation prevented as in distillations or in washing machines. They also find many useful applications as in *froth flotation*, a process by which yearly millions of tons of minerals are separated from gangue and from one another, in beer, whipped cream and many other applications in foods, also in fire fighting foams.

Foams and soap films bring us close to at least one application of colloids in biology. All *biological cells* are surrounded by a membrane and similar membranes occur copiously inside the cell. The essential structure of those membranes is that of a soap film turned inside out. The amphipolar molecules in this case are lecithins and other phospholipids. Figure 15 gives a schematic picture of such a membrane. As can be seen it forms an oily layer between two water layers, thus separating the inside and outside of the cell with respect to all water soluble molecules. If such molecules have to pass the membrane, special mechanisms are locally built into the membrane.

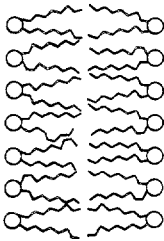


Figure 15 Biological membrane built from phospholipids with two hydrocarbon chains and a polar part which is zwitterionic (phosphate and ammonium) in lecithin

Other colloidal aspects in biology are the biopolymers (proteins, nucleic acids, polysaccharides), cell adhesion, rheology of blood, the emulsion aspect of milk etc.

## 6 Conclusion

The description of colloid systems as dispersions of particles with interparticle forces of various origins forms a good framework for the understanding of many properties of these systems. Thermodynamics and statistical thermodynamics are important both for the understanding of lyophilic colloidal solutions as a whole and for the detailed treatment of interparticle forces in lyophobic systems. A number of aspects have been treated incompletely or not at all in this introductory lecture. They will be treated more fully in later lectures in this symposium.

Colloids find a great many applications, some based on the small size and the large number of the particles, some on the huge interfacial area with its capacity for heterogeneous reactions, others again on their optical, electrical or mechanical properties. Not a few of these applications are found in fundamental research.

Colloids are fascinating to look at, fascinating to understand, fascinating in their applications.

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