# INTERPARTICLE FORCES IN COLLOID SCIENCE

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## Abstract

The nature of the forces between polymolecular particles is the same as that of the forces between atoms, molecules and ions, but their dependence on the distance may be rather different. Colloid systems offer many opportunities for studying these forces. In this paper the following forces are dealt with in some detail: Van der Waals forces, electric double layer forces, and steric forces, connected with the presence of layers of large molecules on the particles. A few words are said about magnetic and about structural forces (due to modifications of the solvent structure near interfaces). Hydrodynamic forces, electrostatic forces in dry powders and the influence of the presence of a third phase are left to other lectures.

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## Introduction

Forces between particles are of the same nature as those between atoms, molecules and ions, but, since particles contain many molecules, the forces are larger and often have a longer range over which they are felt. A great deal of information about interparticle forces can be found in colloid science because these forces determine the behavior (e.g. rheology, phase separation) of colloidal suspensions, and moreover colloid particles are so small that interparticle forces are much more important than the pull of gravity.

The main forces in colloidal systems are Van der Waals forces and magnetic forces, which cause attraction, electrostatic and steric forces, which usually cause repulsion, but in some situations are attractive and structural forces, due to solvation about which our knowledge is yet limited. Furthermore hydrodynamic forces and forces, due to capillary bridges by a third phase play a role.

We shall open with a brief section about colloid science.

## Colloid science

Colloid science [1,2,3] deals with suspensions, emulsions and aerosols, and also with solutions of macromolecules (e.g. proteins, synthetic

polymers) and of micelle forming substances such as soaps. Traditionally dispersions are considered to be colloidal if the particle size is between 1 nm and 1 µm. At the lower end of the scale we find the transition to solutions of small molecules, at the upper end sedimentation in normal gravity starts to be important.

Polymeric and micellar solutions form spontaneously from the ingredients. They are known as *lyophilic colloids* and are thermodynamically stable. Colloidal dispersions of insoluble particles, the *lyophobic colloids* are not thermodynamically stable, but may nevertheless have a very long life. Gold sols (a sol is a colloidal dispersion) prepared by Michael Faraday [4] have been conserved for more than a century at the Royal Institution in London. Other examples of colloid systems are clay suspensions, photographic emulsions (a misnomer, since the term emulsion refers to dispersions of liquid drops in another liquid), mayonnaise, milk, latex and many others. Lyophobic colloid suspensions can be prepared of nearly everything that is insoluble enough to prevent coarsening by recrystallization (so-called Ostwald ripening).

The small colloidal particles have a relatively large interface and the properties of this interface are closely connected with interparticle forces. Any serious study of colloidal dispersions requires surface or interface science. It is no accident that two important colloid periodicals have "Colloid and Interface Science" in their titles.

Colloidal dispersions may be prepared by comminution (grinding, milling) of coarse material, or by forming the particle phase from a molecular solution or a gas, using a high rate of nucleation and a relatively slow rate of particle growth. The dispersion should contain suitable stabilizing agents to counteract the always present Van der Waals forces, which by themselves lead to agglomeration, coagulation and macroscopic phase separation. These stabilizing agents may give the particles an electric charge or surround them with a buffering layer of large molecules. Only when the repulsion between the particles is strong enough, they do not agglomerate and the dispersion is considered "stable in the colloidchemical sense".

Colloid forces have been studied by many methods. The conditions for colloid stability itself give a great deal of information [5], but the same forces also control the behavior of thin liquid films [6]. In thermodynamic [7] (osmotic pressure, light scattering) and rheological properties of concentrated suspensions interparticle forces show up and even experiments on the interaction of macroscopic surfaces [8] have been used to study these forces.

We shall now discuss these colloid forces one by one.

## Van der Waals forces

The generally observed loss of colloidal stability when the repulsive forces are taken away led Kallmann and Willstätter [9] to the suggestion that colloid particles always attract each other by Van der Waals forces. The Van der Waals energy, $V$, between a pair of atoms or molecules, 1 and 2, is inversely proportional to the sixth power of their distance, $r$.

$$V = -\frac{\lambda_{12}}{r^6} \tag{1}$$

where $\lambda_{12}$ is the London constant. The pair energies are *additive* in a first approximation and thus the energy of attraction, $V_{att}$, between two particles with volumes $V_1$ and $V_2$ is given by (see figure 1a):

$$V_{att} = -\int_{V_1}\int_{V_2} \frac{q_1 q_2 \lambda_{12}}{r^6}\, dV_1 dV_2 \tag{2}$$

where $q_1$ and $q_2$ are the numbers of molecules per unit volume in the particles 1 and 2 respectively.

Since $dV_1$ and $dV_2$ are proportional to the cube of the linear scale and $r^6$ to its sixth power, $V_{att}$ is independent of the scale. The attraction between two atoms is of the order of the thermal energy, $kT$, at room temperature when the distance between the atoms is of the order of their radius. Then, for colloidal particles (size 50 nm) the attraction energy is of the order of $kT$ at a distance between the surfaces of the order of 50 nm and for two marbles the energy is $kT$ at a distance of about 1 cm.

Equation (2) has been integrated for a number of cases [10,11]. For two parallel plates of the same material (two half spaces at a distance, $H$) the attraction energy per unit area is

$$V_{att}(\text{flat plates}) = -\frac{A}{12\pi H^2} \tag{3}$$

where the Hamaker constant [11]

$$A = \pi^2 q^2 \lambda \tag{4}$$

For two spheres (radius $a$, distance between the centers $R$) the energy is [12]

$$V_{att}(\text{two spheres}) = -\frac{A}{6}\left[\frac{2a^2}{R^2-4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2-4a^2}{R^2}\right] \tag{5}$$

If the distance, $H = R-2a$, between the surfaces is much smaller than $a$, equation (5) simplifies to [13]

$$V_{att}(\text{spheres at short distance}) \simeq -\frac{A}{12}\left(\frac{L}{H} + 2\ln\frac{H}{L}\right) \simeq -\frac{Aa}{12H} \tag{6}$$

with $L = a + \frac{3}{4}H$. The first approximation is better than 5% when $H<0.16a$, the last approximation is rather bad and even at $H = 0.01a$ in error by about 10%.

It can also be shown [12] that the force remains attractive if two particles of material 2 are embedded in a medium 1 (see figure 1b).

**a**                               **b**
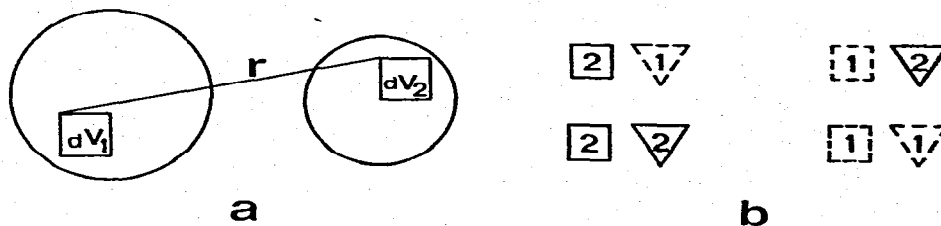
*Figure 1*   *a. Left. Van der Waals attraction is built up additively from pair interactions; see equation (2).*
*b. Right. Two particles of material 2 in a medium 1. In a change in particle distance, the only interactions that change are those between the four pairs shown; see equation (7).*

When the triangular particle is brought close to the square one, a triangular volume of medium has to make the opposite displacement. Inspection of figure 1b shows that all interactions are unchanged, except those amongst the four particles and volumes of medium drawn. At the start we have two 1-2 interactions, and at the end one 1-1 and one 2-2 interaction, all with the same geometrical factor, Geom. Thus we find

$$V_{att}(\text{in a medium}) = - \text{Geom}(A_{22} + A_{11} - 2A_{12}) =$$ 

$$-\text{Geom } \pi^2 (q_2^2 \lambda_{22} + q_1^2 \lambda_{11} - 2 q_1 q_2 \lambda_{12}) = -\text{Geom } \pi^2 (q_2 \sqrt{\lambda_{22}} - q_1 \sqrt{\lambda_{11}})^2 \leq 0$$

(7)

In the last step it has been assumed that $\lambda_{12} = \sqrt{\lambda_{11} \cdot \lambda_{22}}$, which, though not exact, is certainly approximately correct.

Values for the Hamaker constant, $A$, have been derived from theories for $\lambda$, from colloid stability and from macroscopic experiments. Visser [14] gives an extensive survey of data, which we have condensed to table 1.

*Table 1*   *Hamaker constants in air (vacuum) and in water, all in $10^{-20}$ J = 2.5kT.*

|  | in air | in water |
|---|---|---|
| $A$ (water) | 4.4 | 0 |
| $A$ (hydrocarbons) | 4-10 | 0.3-1 |
| $A$ (oxides and halides) | 6-15 | 0.5-5 |
| $A$ (metals) | 15-50 | 5-30 |

Two additional remarks must be made.

1. Since Van der Waals-London forces are in essence based upon electromagnetic oscillations, they show retardation [15] at distances over a few times 10 nm and there they decay faster, viz. as $r^{-7}$ than at shorter distances. In applications retardation is rarely important, because at the distances involved the forces are negligibly small.

2. Van der Waals forces are only approximately additive. Lifshitz and coworkers [16] have formulated a theory of Van der Waals attraction based upon fluctuations of electric field and polarization in macroscopic bodies. This theory allows the calculation of the Hamaker constant if the complex refractive index is known as a function of the wavelength.

The main facts to retain about Van der Waals forces are that they are larger than $kT$ at distances somewhat smaller than the particle size, that they decay as an inverse power of the distance between the surfaces and that, in the presence of a condensed medium, they remain attractive, but usually become smaller.

## Electrostatic double layer forces

In water and in other media which favor electrolytic dissociation, (colloid) particles are usually charged. The suspension as a whole, however, is electroneutral. A charge opposite to that of the particles is carried by small ions in the solution and forms a more or less diffuse electric double layer around each particle, rather similar to the ionic atmosphere known from the Debye and Hückel theory. When colloid particles approach one another the interaction of these double layers causes a repulsion.

Before we discuss the structure of the double layer, we must say a few words about the origin of the particle charge. In clays and other alumosilicates the charge is mostly based on isomorphous substitution of $Si^{4+}$ by $Al^{3+}$ or of $Al^{3+}$ by $Mg^{2+}$. The negative particle charge thus obtained has to be compensated by positive charge in the medium, carried by e.g. $Na^+$ or $Ca^{2+}$. Charge based on this mechanism is rather independent of the composition of the solution. On the other hand the charge may be based on adsorption of ions or on surface dissociation and is then of course quite sensitive to the solution composition. Since like charges repel one another high surface charge densities are only obtained if the ions are strongly adsorbable. In practice this requires the adsorbed ions either to fit into the lattice, as with silver or halide ions on silver halides, and with $H^+$ and $OH^-$ ions on oxides and hydroxides or to be squeezed out of the water, as with surfactant ions, which may give a high charge to a great variety of surfaces.

In the theory of the structure of the diffuse double layer as first given by Gouy [17] and by Chapman [18], the particle charge is considered as a smeared out surface charge on a plane, $x = 0$. The counter-charge is carried by all the ions in the solution which are attracted to or repelled from the surface according to the Boltzmann principle.

$$c_i(x) = c_i(x \to \infty) \exp\left(-\frac{z_i e \phi(x)}{kT}\right) = c_i(x \to \infty) \exp\left(-\frac{z_i F \phi}{RT}\right) \qquad (8)$$

where $c_i$ is the concentration of ions of type i, $z_i$ their charge number, $e$ the elementary charge, and $k$, $T$, $R$ and $F$ have their usual meaning. For high potentials the influence of the counterions (positive exponential) is overwhelming, so that the nature and charge number of the co-ions (negative exponential) is often unimportant.

The electric field in the solution obeys the Poisson equation

$$\nabla^2 \phi = - \frac{\rho}{\varepsilon \varepsilon_0} \tag{9}$$

with $\rho$ = local charge density, $\varepsilon_0$ = permittivity of the vacuum and $\varepsilon$ = relative permittivity (dielectric constant) of the medium. With

$$\rho = \Sigma \; c_i z_i F = (c_+ - c_-) z F \tag{10}$$

where the second equality refers to a single symmetric electrolyte, we find the important Poisson-Boltzmann equation

$$\nabla^2 \phi = - \Sigma \frac{c_i^0 z_i F}{\varepsilon \varepsilon_0} \exp\left(- \frac{z_i F \phi}{RT}\right) = +2 \frac{zFc^0}{\varepsilon \varepsilon_0} \sinh \frac{zF\phi}{RT} \simeq$$

$$\simeq \Sigma \frac{z_i^2 F^2 c_i^0}{\varepsilon \varepsilon_0 RT} \phi = \frac{2z^2 F^2 c^0}{\varepsilon \varepsilon_0 RT} \phi = \kappa^2 \phi \tag{11}$$

where the last equalities are only valid for small $\phi$ ($zF\phi/RT \ll 1$).

The Debye-Hückel length, $1/\kappa$, which in this field is often called the thickness of the double layer is defined as

$$\frac{1}{\kappa} = \left(\frac{\varepsilon \varepsilon_0 RT}{F^2 \Sigma c_i z_i^2}\right)^{1/2} = \left(\frac{\varepsilon \varepsilon_0 RT}{2F^2 I}\right)^{1/2} \tag{12}$$

where $I = \frac{1}{2}\Sigma c_i z_i^2$ is the ionic strength. $1/\kappa$ is proportional to $\sqrt{c}$ and in water at 25°C has the value of 10 nm for a $10^{-3}$ M 1-1 electrolyte solution.

For the double layer on a flat surface $\nabla^2 \phi$ simplifies to $d^2\phi/dx^2$ and then equation (11), especially its linearized form is easily solved. The solution is

$$\phi = \phi(x=0)\exp(-\kappa x) = \frac{\sigma}{\varepsilon \varepsilon_0 \kappa} \exp(-\kappa x) \tag{13}$$

The double layer potential falls off exponentially and the double layer behaves as a parallel plate condensor with a surface charge density $\sigma$, a dielectric constant $\varepsilon$, and a plate distance $1/\kappa$. As the counterion concentration goes up a factor 10 for every $(59/z)$mV increase in the potential, ion concentrations would become unrealistically high near the surface, if the Gouy-Chapman theory is strictly followed. Stern [19] has given a simple solution to this problem by remarking that the centers of counterions cannot approach the interface closer than a distance, $\delta$, of the order of a few Å, the size of hydrated ions. Further refinements take partial dehydration and specific (i.e. non-electrostatic) adsorption into account. The picture of the double layer is then a Gouy-Chapman diffuse layer in which the potential usually remains below 100 mV, separated from the interface by a charge free, relatively low dielectric constant layer, in which the potential drop may be high.

When two particles come close together and their double layers overlap, a rearrangement of charge and potential occurs, resulting in a repulsion, which falls off as $\exp(\kappa H)$, $H$ being the (shortest) distance between the interfaces. The precise value of the repulsion depends on the charging mechanism. With constant surface charge the surface potential goes up, but if the charge is based on adsorption or surface dissociation, the surface potential tends to stay constant and the surface charge decreases. Figure 2 gives a schematic picture of the course of the potential when particles come within distances comparable to $1/\kappa$.

CONSTANT CHARGE    DISTANCE ➡

CONSTANT POTENTIAL    DISTANCE ➡
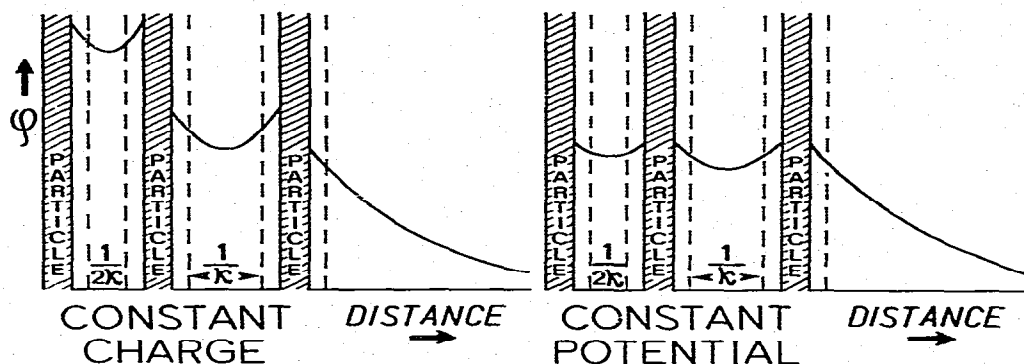
*Figure 2*   *Electrostatic potential, $\phi$, as a function of the distance between particles (shown as flat plates) at constant surface charge (left) and at constant surface potential (right).*

We shall give one equation for the repulsion between two spherical particles, based upon constant surface potential and neglecting the Stern layer effect. In that case the free energy of repulsion, $V_{rep}$, is approximately [5,13,20]
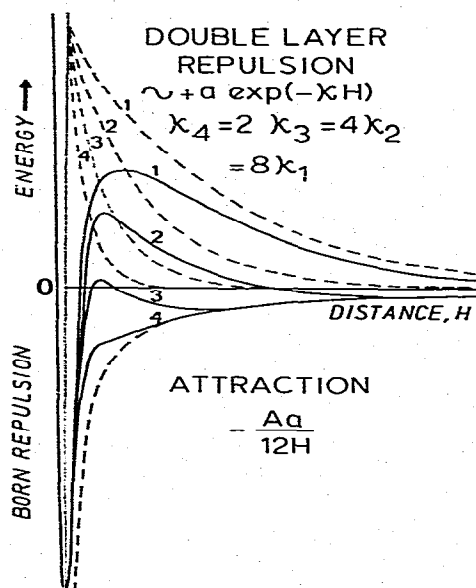
$$V_{rep} = 2\pi\varepsilon\varepsilon_o a\left(\frac{4RT\gamma}{zF}\right)^2 e^{-\kappa H} \simeq 2\pi\varepsilon\varepsilon_o a\phi^2(x=0)e^{-\kappa H} \tag{14}$$

where $\gamma = \tanh(zF\phi(x=0)/4RT)$ and $z$ is the charge number of the counterions. This equation is valid for $H \ll a$ and the second equality is an approximation for low potentials.

## Combination of Van der Waals attraction and double layer repulsion

For electrically stabilized colloids we have to consider the combined influence of Van der Waals attraction and electrostatic repulsion [20, 21]. Whatever the size or shape of the particles, the common feature is that the attraction decays as an inverse first or higher power of the distance, $H$, and the repulsion as an exponential function of this distance. Therefore, the attraction always wins at short distances $(-1/H \rightarrow -\infty)$ and at large distances $(1/H^n > \exp-\kappa H)$, but at intermediate distances $(H \sim 1/\kappa)$ the repulsion may win. The free energy is negative and has a "secondary" minimum at large distance, a deep "primary" minimum at $H=0$ and, if the repulsion is strong enough, a positive maximum in between. The energy does not go to $-\infty$ at $H=0$, because the very steep Born repulsion of the electron clouds sets in when the

surfaces come into molecular contact. Figure 3 shows this schematically for one attraction curve combined with four repulsion curves in which $1/\kappa$, the range of the repulsion, has been varied.

DOUBLE LAYER
REPULSION
$\sim +a \exp(-\kappa H)$
$\kappa_4 = 2 \ \kappa_3 = 4 \kappa_2$
$= 8 \kappa_1$

ENERGY

BORN REPULSION

0

DISTANCE, H

ATTRACTION
$$-\frac{Aa}{12H}$$

*Figure 3*

*Free energy of two particles as a function of the separation, H, between their surfaces. Combination of Van der Waals attraction and double layer repulsion at constant surface potential and at four different ionic strengths.*

The repulsion is made strong by a high surface potential (positive or negative). Low electrolyte concentration gives it a long range. The generally observed loss of colloid stability at the addition of electrolyte is due to the disappearance of the free energy maximum when the range of the repulsion is shortened. This effect is particularly pronounced with counterions of high charge number, which, in addition, may be specifically adsorbed in the Stern layer [22], thus lowering the effective charge.

Both repulsion (equation (14)) and attraction (equation (6)) are approximately proportional to the particle size $(a)$. Therefore the general properties of the combined repulsion and attraction curves are the same for small and for large particles and in particular the transition from a curve with a maximum to one without a maximum (loss of colloid stability) occurs at the same electrolyte composition.

We shall not go further into the theory of colloid stability built on this picture. The interested reader should consult the relevant literature [1,2,3,5,22].

## The influence of large molecules on particle interaction

It has been known for a long time that the addition of large molecules such as proteins or gums protects a colloidal suspension against flocculation by electrolytes. India ink is a classic example. A stable suspension of soot is prepared by rubbing soot, gum arabic and water together. In this suspension the fine soot particles do not coagulate after they have been separated by grinding. Other examples are milk and natural latex. Zsigmondy [23] explained protective action already in 1901 by pointing out that the gum or protein is adsorbed on the

particles, but turns its soluble side towards the solution. When two of these layers of large molecules come together, their solubility prevents the contact from being permanent.

In principle this explanation still holds, but with time it has been made more sophisticated [24,25,26].

In the early days protective action was mainly aimed at aqueous suspensions of electrically charged particles. It should be obvious, however, that electrical stabilization is hard to realize in non-polar media, so that there stabilization by large molecules (called *steric stabilization*) is the primary mechanism.

We now distinguish at least two types of stabilizing large molecules. One is a high molecular weight homopolymer, with a low but finite adsorption energy per monomeric segment. Such a molecule is adsorbed in a configuration consisting of adsorbed segments or *trains* of segments, separated by *loops*, dangling in the solution and two *tails* at the ends of the molecule, which may stick out quite far from the surface.

The other type consists of molecules of relatively low molecular weight, with an *anchor group* that is easily adsorbed and a *tail* that is compatible with the solvent.

Protective action itself also contains two elements as shown in figure 4. When the tails or loops of two surfaces come close to one another the local increase in concentration results in an increase in free energy and thus in a repulsion. This is called the *osmotic effect* and is comparable to the second and higher virial coefficients in the osmotic pressure.



*Figure 4    Illustrating the osmotic effect (left) and the volume restriction effect (right) in steric repulsion.*

At the same time some of the long tails may not fit in the narrow space between two particles, loose a number of conformations and this loss of entropy forms another contribution (the *volume restriction effect*) to the repulsion.

Steric repulsion is steep and strong, at least if desorption is absent, which it usually is. At large separations the Van der Waals attraction still causes a secondary minimum, but a primary minimum cannot be reached.

Steric repulsion can be destroyed by changing the solubility of the
protective chains, which requires rather drastic changes in the sol-
vent or by desorption. Desorption can hardly ever be obtained by
dilution, since the true equilibrium concentrations are extremely low.

At low concentrations polymers or molecules with at least two anchor
groups may lead to bridging between particles and the protective agent
acts as a flocculant in the low concentration region. This is called
sensitization.

Both steric stabilization and sensitization are widely applied. Sta-
bilization in oil based and some water based pigment dispersions,
paints, inks and lacquers, in doped engine oils, in water in oil
emulsions, etc. Sensitization is used in preparing more open and at
the same time rigid and more easily filterable precipitates, and in
improving soil structure, where again an open flocculated structure
is essential for free passage of water and air.

It has been observed fairly recently [26,27,28,29] that polymers in
solution also affect the stability. If the polymer segments show no
tendency to be adsorbed, the polymer as a whole is obviously negatively
adsorbed. In a narrow gap between two surfaces the polymer molecule
cannot be accommodated without an increase in the free energy and it is
pushed out of the gap. This creates a concentration gradient which then
drives the solvent out of the gap and as a consequence the particles
are pushed together and coagulate. At high polymer concentration the
intermediate stage, just before the last layer of polymers is pushed
out of the gap, may act as a kinetic barrier against this attraction
between the particles.

Flocculation by dissolved polymer may be important in suspensions of
sterically stabilized particles, since it promotes an often desirable
weak flocculation and prevents the formation of a dense sediment.

## Magnetic interaction

Particles consisting of a ferromagnetic material are often permanent
magnets, because they consist of only one or a few magnetic domains.
Magnetic attraction between two such particles is high, since the
magnetic moment is high and the interaction decays only slowly (as
$r^{-3}$). As an example we calculate the magnetic interaction between two
spherical particles of iron, with diameters of only 10 nm, magnetic
moments of $p = 10^{-24}$ Vsm (about saturation value), at a distance,
$r = 20$ nm between the centers and using the equation

$$V(\text{magnetic}) = -\frac{p^2}{2\pi\mu_0 r^3} = 16 \times 10^{-21} \text{ J} \simeq 4kT \qquad (15)$$

where $\mu_0 = 4\pi \times 10^{-7}$ Hm$^{-1}$ is the permeability of a vacuum.

It is obvious that the interaction between larger particles or clusters
of particles, that may be far from saturation, will usually be larger
than $kT$, and that thick layers of protective polymers combined with a
high viscosity solvent are necessary to keep the particles separated,
as is desirable during the preparation of sound tapes, video tapes and
similar materials where homogeneous magnetic properties are essential.

## Structural forces

In recent years the old idea [30], that hydration, or solvation in general, might cause repulsion between particles, has been revived. The structure of a liquid near an interface *must* differ from the structure in the bulk, and if the molecules of the liquid are attracted towards the interface, they might indeed prevent actual particle-particle contact. There are now two new developments. Several authors [31,32,33] have used model calculations, e.g. for argon type atoms between ideal flat surfaces and even for a water layer between mica surfaces [33], and found that the disturbance of the liquid structure is periodical and stretches out over about ten layers of molecules. Furthermore a variety of experiments such as the swelling of phospholipid layers in water [34] and actual force measurements [35,36,37] between mica sheets in polar and in non-polar liquids all show a force, oscillating but with an overall decay length of the size of the molecules involved (1 nm for octamethylcyclotetrasiloxane, a few Å for water).

No doubt that *structural forces* (the name given to forces due to solvent structure near the interface) exist, that they can be quite large and that their range is shorter but not much shorter than that of the Van der Waals and electrostatic forces. On the other hand not a single case is known in which colloid stability can be ascribed with certainty to this structural effect. However, the whole issue is very new in its modern form and further developments have to be awaited.

## Repeptization

Redispersion of a flocculated suspension seems to be impossible on account of the deep primary minimum (except, as mentioned, in the case of steric stabilization). Removing the flocculating electrolyte restores the original potential barrier, but now the particles are "on the wrong side" of the barrier and spontaneous repeptization cannot be expected. Even milling or grinding cannot restore the original dispersion, since the shearing force on a pair of particles, which is proportional to $a^2$ ($a$ = radius of primary particles) cannot be made large enough for breaking up aggregates below 0.1 μm.

Nevertheless many examples of repeptization are known. For some sols ($V_2O_5$, other oxides and hydroxides, HgS, Carea Lea's Ag) redispersion is even the traditional method of preparation and most sols can be redispersed directly after flocculation. In those cases redispersion is spontaneous or nearly so. But if the coagulate has stood for an hour or more, redispersibility is lost.

The only reasonable solution to this paradox [38] is that coagulation does not reach the primary minimum, but that surfaces remain separated (at least in the beginning) by a layer of thickness δ, as shown in figure 5. Calculation shows that δ need not be more than a few Å to allow the situation 3 in figure 5 to occur. In this situation the particles are at a positive free energy and not below the energy barrier by more than $kT$ or so. Structural forces may well be responsible for this behavior, although rate effects (see next section) may also be involved. This is a neglected field of research, the more so since repeptization is expected to yield information on the interaction at short distances, information not easily obtained in other ways.
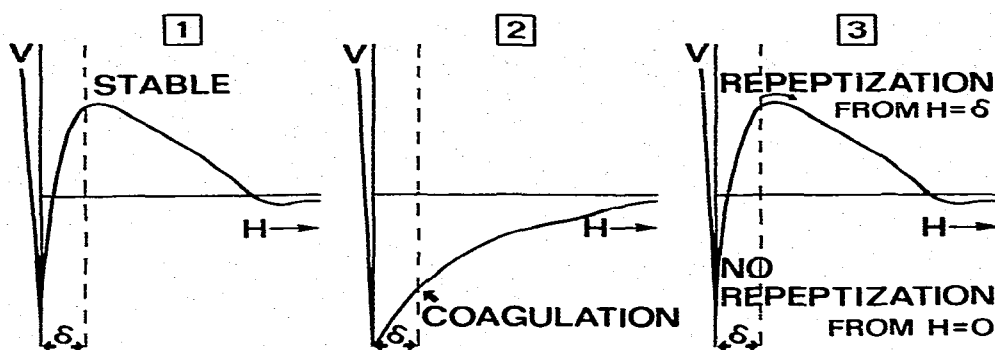
Figure 5 *Repeptization.* [1] *Original interaction curve as in figure 3.*
[2] *After compressing the double layer by addition of electro-*
*lyte.* [3] *After removing the electrolyte repeptization is*
*only possible if the surfaces have remained separated by*
*a distance, δ.*

## Rate effects

So far we have considered interacting particles to be in complete
thermodynamic equilibrium (apart from Ostwald ripening). But this is
not necessarily correct. Van der Waals interactions are rapid, but
electrostatic and polymeric interactions have slow components. Com-
pression of the double layer and rearrangement of the conformations
of polymer chains are usually complete within collision times, but
adsorption and desorption are too slow for that time scale.

After addition of electrolyte to a suspension the double layers will
shrink as soon as the new concentration has been reached. But then
the surface charge should go up and this takes time since it is an
activated process [38]. Therefore coagulation occurs at a surface
charge which is too low. With repeptization the reverse may be the
case and the surface charge remains too high for a short period after
removal of the flocculating electrolyte.

With polymeric stabilization the effect is still more striking. When
the chains are compressed in the gas between two particles, the in-
crease in free energy should lead to desorption and consequently the
protective effect should disappear. Fortunately desorption, even
forced desorption, is such a slow process that protection remains
[25,26].

## Conclusions

Particles, whether in suspension or in air or vacuum *always attract*
each other by Van der Waals forces, sometimes also by magnetic or
purely electrostatic effects. With suspended particles there is *nearly*
*always repulsion* as well, but its magnitude and range can be manipulated.

Since the behavior of suspensions and powders depends strongly on such
interactions, control of the interaction is often desirable and for
this purpose a good understanding of interaction is required.

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