Surface Roughness and Particle Size Effect in Brownian Coagulation
SURFACE ROUGHNESS AND PARTICLE SIZE EFFECT IN BROWNIAN COAGULATION

PROEFSCHRIFT

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Introduction.

The stability of colloidal dispersions against aggregation is one of the fundamental problems of colloid science. Already in 19th century there have been successful attempts to prepare and characterize stable dispersions [1-5]. Although those methods were well developed, the set-up of a rigorous theory that could describe the dependence of the dispersion stability on the main parameters of a system started at the end of 30s. Two papers being the cornerstones of the modern colloid stability theory must be mentioned here. In the first, Smoluchowski described kinetics of rigid particles undergoing either Brownian motion or flow shear [6]. He tried to incorporate an interaction between particles into that description, but was not able to relate the collision probability to physical parameters of the system. Fuchs [7] addressed coalescence of aerosols using the diffusion approximation for calculating the spatial particle distribution. The collision probability became dependent of the electrostatic interaction in that system.

The foundation of the stability theory for particles dispersed in liquid media (colloids) was laid by Derjaguin and Landau, Verwey and Overbeek independently [8,9]. The classical DLVO-theory predicts a pronounced dependence of the stability ratio $W$ for slow coagulation on the radius $a$ of the colloid particles. However, there are many experimental data on different colloidal systems [10-15] to indicate that, generally, there is no such effect (see also review [16]). In particular, the proportionality of $d \log W / d \log c$ with the particle size, has not been found.

To explain away this discrepancy between theory and experimental observation, there have been several suggestions to refine the theory and include extra terms or effects, such as the effect of hydrodynamic interaction on their Brownian motion as particles collide, or extra electrical repulsion between surface charges which are slow to come to equilibrium during a collision. However, this has not been
successful, either because the strong particle size effect remained in the resulting theory, or because the refinements would only reduce the size effects on $W$ for specific sets of parameters, i.e. for specific experimental conditions.

The proposition put forward in the thesis is, that the cause of the above discrepancy between theory and experiment is roughness of the particle surfaces. Surface irregularity is, in larger or lesser degree, present in every macroscopic surface, independent of its size or chemical nature. But the effect of surface irregularities on colloidal interaction will only be felt if their size (amplitude of roughness, for example) is comparable with other length scales in the theory of interaction. Seen from a large distance any particle will appear smooth, but as two particles approach there will "upon closer inspection" be an effect of ever smaller and smaller features of surface irregularity on the interparticle forces. These forces, according to the DLVO-theory, affect the rate of coagulation of electrocratic colloids and its dependence on the electrolyte concentration.

To estimate the consequences of such an effect, one could describe an unstable colloid in terms of a set of characteristic length-scales (e.g. the interparticle distance, the particle radius, the Debye length as a characteristic screening length for interaction forces), and then include the amplitude and the wavelength of the surface roughness in the description. On the basis of this model one can deduce, in terms of the dimensionless ratio of these parameters, under which conditions a factor has a relevant effect.

References.

Introduction.

I. Perikinetic Coagulation in Electrocratic Colloids.

The diffusion approximation in combination with the DLVO theory for the pair interaction in colloidal systems is now the commonly accepted treatment of stability and Brownian coagulation of dilute dispersions. However, it is also known that besides its great achievements, there remain qualitative and quantitative disagreements between the DLVO-theory and a variety of experimental data. Of course, these problems have been, and are attacked by scientists, who try to modify existing descriptions by taking into account additional effects neglected in the original description. Some refinements of the theory may address these approximations, and we briefly repeat here important steps leading from the Langevin equation to the stability diagram. Under circumstance this would improve the agreement between the predictions of the theory and the experimental data.


The original derivations of the Einstein relation for the diffusion coefficient [1], and the Smoluchowski equation for the diffusion of interacting Brownian particles had a phenomenological character. They establish the foundations of the modern stability theory of disperse systems.

Consider a system of n particles with mass m in the medium consisting of much "lighter" components. These big and heavy particles interact with each other via potential \( U (r_1, \ldots, r_n) \), where \( r_i \) gives the position of an i-particle, and bold symbols correspond to vector variables. We may write for such a system (if the time of interaction between "heavy" and "light" particles is small compared to all other characteristic time scales) a set of the Langevin equations
Brownian motion of interacting colloid particles.

\[ m \ddot{\mathbf{r}}_i + \mu \dot{\mathbf{r}}_i + \frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{f}_i(t), \quad (i = 1, \ldots, n), \quad (1.1) \]

where \( \mu \) is the effective friction coefficient, and \( \mathbf{f}_i(t) \) are random forces with the average equal to zero. We may consider these forces of a Gaussian type with the correlation tensor

\[ < f_i^\alpha(t) f_j^\beta(t') > = 2 D \delta_{ij} \delta_{\alpha \beta} \delta(t-t') , \quad (1.2) \]

where \( \alpha \) and \( \beta \) are vector indices. Eq.(1.2) is known as a simplest version of the fluctuation-dissipation theorem [2]. Introducing impulses as

\[ \mathbf{p}_i = m \dot{\mathbf{r}}_i , \]

and using the Hamiltonian function

\[ H = \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \ldots, \mathbf{r}_n), \quad \text{with} \quad \dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \]

equation (1.1) can be rewritten in the form

\[ \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} - \frac{\mu}{m} \mathbf{p}_i + \mathbf{f}_i(t) \quad (1.3) \]

which is more convenient for transition to the Einstein-Fokker equation. This equation describes an evolution of the cooperative probability of site occupancy in the phase space for \( n \)-particles' system. Defining the phase space \( \mathbf{x} = \{\mathbf{r}, \mathbf{p}\} \), and substituting the correlation tensor (1.2)

\[ D_{ij}^{(kl)} = \begin{pmatrix} 0 & 0 \\ 0 & D \delta_{ij} \end{pmatrix} \quad (\text{with } k, l = 1, 2), \quad (1.2a) \]

in eq.(B.18) (see Appendix B for derivation), we write the Einstein-Fokker equation corresponding to (1.2-1.3) in the following form [3]

\[ \frac{\partial P_{(r,p)}}{\partial t} + \sum_{k=1}^{n} \left\{ P_{(r,p)} \right\}_{(k)} - \frac{\mu}{m} \sum_{k=1}^{n} \frac{\partial}{\partial \mathbf{p}_k} \left( \mathbf{p}_k P_{(r,p)} \right) = D \sum_{k=1}^{n} \frac{\partial^2 P_{(r,p)}}{\partial \mathbf{p}_k^2} \quad (1.4) \]
Brownian motion of interacting colloid particles,

with \( \{ \varphi, \psi \} \)_{(k)} = \frac{\partial \varphi}{\partial p_k} \frac{\partial \psi}{\partial r_k} - \frac{\partial \varphi}{\partial r_k} \frac{\partial \psi}{\partial p_k} \) the Poisson brackets for \( k \)-th particle, \( r = \{ r_i \} \), \( p = \{ p_i \} \), and \( D \) is taken constant. \( P_t \) is the probability to find a system of macroscopic particles with the configuration \((p, r)\) in the phase space. The stationary solution of eq. (I.4) has a form of the Gibbs canonical distribution

\[
P_{\infty}(r, p) = \text{Const} \exp(-\beta H)
\]

(I.5)

where \( \beta = 1/k_B T \), and the necessary condition \( D = \mu/\beta \) represents the Einstein relation for the diffusion coefficient of a particle [3,4]. A transition to the stationary distribution (I.5) is made in two stages: in a very short time Maxwell's distribution of velocities (impulses) is established, and after this the respectively slow process of transition to a stationary distribution over coordinates occurs. The latter is described by the Einstein-Smoluchowski equation

\[
\frac{\partial P_t(r)}{\partial t} = \sum_{i=1}^{n} \frac{\partial}{\partial r_i} \left[ \frac{1}{\mu} \frac{\partial U}{\partial r_i} P_t(r) \right] + \sum_{i=1}^{n} \frac{\partial}{\partial r_i} \left[ \frac{D}{\mu^2} \frac{\partial}{\partial r_i} P_t(r) \right].
\]

(I.6)

The derivation of this expression can be illustrated by considering a two-component system. The mutual motion of two particles is described by a system of equations

\[
\dot{p} = -\frac{\partial U}{\partial r} - \frac{\mu}{m} p + f(t), \quad p = m \dot{r}.
\]

(I.3a)

where one of the particles is held in the origin of a coordinate system.

We introduce a new probability function

\[
P_{t}(\rho) = \int dp P_{t}\left(\rho - \frac{1}{\mu} p, p\right)
\]

(I.7)

with substitution of variable

\[
\rho = r + (1/\mu) p.
\]

The system (I.3a) reads in new variables as
Brownian motion of interacting colloid particles.

\[
\rho = -\frac{1}{\mu} \frac{\partial U}{\partial \mathbf{r}} + \frac{1}{\mu} \mathbf{f}(t), \quad \dot{\mathbf{p}} = -\frac{\partial U}{\partial \mathbf{r}} - \frac{\mu}{m} \mathbf{p} + \mathbf{f}(t) \quad \rho = \mu
\]

Having written the Einstein-Fokker equation for this system, we integrated it over impulses, and arrive at

\[
\frac{\partial P_t(\rho)}{\partial t} = \int d\mathbf{p}\left( \frac{\partial}{\partial \mathbf{r}} \frac{1}{\mu} \left[ \frac{\partial U}{\partial \mathbf{r}} P_t(\mathbf{r}, \mathbf{p}) \right] + \frac{\partial}{\partial \mathbf{r}} \frac{D_0}{\mu^2} \left[ \frac{\partial}{\partial \mathbf{r}} P_t(\mathbf{r}, \mathbf{p}) \right] \right) \quad \rho = \mu
\]

(1.8)

with \( D_0 \) the mutual diffusion coefficient. The changes with \( \mathbf{r} \) are slower than those with \( \mathbf{p} \), what allows to exchange integration with differentiation in the r.h.s. of eq.(1.8). We obtain

\[
\frac{\partial P_t(\rho)}{\partial t} = \frac{\partial}{\partial \rho} \left[ \frac{1}{\mu} \frac{\partial U(\rho)}{\partial \rho} + \frac{D_0}{\mu^2} \frac{\partial}{\partial \rho} \right] P_t(\rho) .
\]

(1.9)

Generally, \( D_0 \) and \( \mu \) are functions of the interparticle distance \( \rho \) and other parameters, which may introduce for hydrodynamic effects in the relative particle motion.

1.2 Stability ratio.

Considering dilute dispersions the analysis may be restricted to pair interactions between particles. In this situation it is convenient to separate the many particle distribution function from one-particle distribution function (or the density of particles \( \rho \) at some distance from the origin of the coordinate system). For a many-particle case, eq.(1.9) can be generalized [5], and yields

\[
\frac{\partial P_t^{(n)}}{\partial t} = \sum_i \sum_j \nabla_i D_{ij} \left[ \nabla_j + \frac{1}{k_B T} \left( \sum_{m \neq j} \nabla_j U_{jm} - F_j \right) \right] P_t^{(n)},
\]

(1.10)

where \( F_j \) are external forces acting on \( j \)-th particle, \( \nabla \) is the nabla operator, and the interaction potential depends on the relative distance between two particles.
Again, we perform some elaboration for a simple case, and generalize the deduced expression on a more general situation.

When taking $F_j = 0$ and $D_{ij}$ in a form given by eq.(1.2a), eq.(10) is written as

$$\frac{\partial P_t^{(n)}}{\partial t} = D \sum_i \tilde{V}_i \left[ \tilde{V}_i + \frac{1}{k_B T} \left( \sum_{j=1}^{n} \tilde{V}_j U_{ij} \right) \right] P_t^{(n)} .$$  (I.11)

Integrating eq.(I.11) over all coordinates of particles $2, ..., n$, we obtain [6]

$$\frac{\partial \rho}{\partial t} = D \tilde{V}_1 \left[ \tilde{V}_1 \rho + \frac{1}{k_B T} \int \left( \tilde{V}_1 U_{12} \right) P^{(2)}(r_2) dr_2 \right] .$$  (I.12)

If we rewrite the pair distribution function as

$$P^{(2)}(r_1, r_2) = P^{(1)}(r_1)P^{(1)}(r_2)g(r_1, r_2) ,$$

with $g(r_1, r_2)$ the radial distribution function and $P(r) = \rho(r)$, the generalized diffusion equation acquires the form [7,8]

$$\frac{\partial \rho}{\partial t} = \tilde{V} \left[ D_0(\rho) \tilde{V} \rho + \frac{D_0}{k_B T} \rho \tilde{V} U \right] ,$$  (I.13)

with

$$D_0(\rho) = D_0 \left\{ 1 - \frac{4\pi \rho}{3 k_B T} \int_0^\infty \frac{\partial U}{\partial r} \left[ g + \rho \frac{\partial g}{\partial \rho} \right] r^3 dr \right\} = \frac{D_0}{k_B T} \frac{\partial P}{\partial \rho} .$$

In (I.13), as usual, a spherical symmetry of the particle distribution around a reference particle held at $r = 0$ has been assumed. $g(r, \rho)$ is the radial distribution function of the system with a uniform density $\rho$, $P$ is the osmotic pressure [9,10], and $D_0$ is the mutual diffusion coefficient, which is, generally, a function of $r$. For a low density (or volume fraction of particles) $P$ is proportional with $\rho$, and, as a consequence, $D_0(\rho) \equiv D_0$. These assumptions lead to the well-known phenomenological diffusion equation, which describes the Brownian motion of interacting particles on a macroscopic scale.
Eq. (I.13) in its simplest form was applied by Fuchs [11] to study behavior of aerosol droplets in clouds. Later on, in combination with the DLVO theory, it was extended to the general description of Brownian coagulation (or coalescence) in colloidal dispersions.

Usually, the interaction potential \( U \) is quite complex, and solution of eq. (I.13) is a rather complicated task. However, at a very beginning of the coagulation process the changes of the particle concentration with time are negligible, and a quasi-stationary variant of equation (I.13) may be used. With this quasi-stationary approximation and a spherical symmetry eq. (I.13) is cast as

\[
\frac{1}{r^2} \frac{\partial}{\partial r} r^2 D_0 \left[ \frac{\partial n}{\partial r} + \frac{n}{k_B T} \frac{dU}{dr} \right] = 0. \tag{I.14}
\]

with the boundary conditions

\[
n = n_\infty \quad \text{as } r \to \infty,
\]

\[
n = 0 \quad \text{at } r = 2a,
\]

where \( n \) is the number concentration of colloidal particles. The solution of eq. (I.14) is convenient to write down in the following form

\[
n = n_\infty \frac{\exp[-U(q)] \int_0^\infty D(\infty) D(q) \exp[U(q)] \frac{dq}{q^2}}{W}, \tag{I.15}
\]

\[
J = \frac{16\pi D(\infty)n_\infty a}{W}, \tag{I.16}
\]

\[
W = \int_0^\infty \frac{D(\infty)}{D(q)} \exp[U(q)] \frac{dq}{q^2}. \tag{I.17}
\]

Here \( q = r/2a \) is the dimensionless distance between centers of two interacting particles, \( a \) is the particle radius, \( U(q) \) is the interaction energy scaled with \( k_B T \), \( J \) is the total flux of particles towards the surface of a central particle that expresses the initial rate of coagulation, \( W \) is the stability ratio. We also accounted for the hydrodynamic correction in the diffusion coefficient.
1.3. Coagulation kinetics.

To understand the meaning of the stability ratio, let us consider a case without any interaction between colloidal particles, i.e., $U = 0$ and $D = \text{Const}$. Then

$$J_0 = 16 \pi D n_\infty a$$

is the flux that gives the initial rate of rapid coagulation, if it is assumed that every collision between particles leads to adherence. The stability ratio $W$ shows how the interaction energy alters the coagulation rate in the system. At the very initial stage of coagulation ($t \to 0$) one can estimate how the numerical concentration $n_\infty$ of colloidal particles changes in time. Supposing only binary collisions (only a little number of doublets, triplets, etc. present in the system), the continuity equation is

$$-\frac{dn_\infty}{dt} = \frac{1}{2} Jn_\infty,$$  \hspace{1cm} (I.18)

where the pre-factor $1/2$ allows to avoid the double counting of pair collisions because of an arbitrary choice of a particle in the origin of the coordinate system. The flux is given by eq.(I.16), and with

$$n_\infty (t = 0) = n_0 = \text{Const}.$$  

as the initial condition, the solution of eq.(I.18) is

$$n_\infty (t) = \frac{n_0}{1 + t/T},$$  \hspace{1cm} (I.19)

The characteristic time $T = W/8\pi D n_0 a$ is called the coagulation time. Actually, after $t = T$ the resulting concentration of particles is half of the original concentration $n_0$. All the above-equations concerning the coagulation rate apply for small $t$, when the number of doublets (etc.) is much smaller than that of original particles.

$W$ is a very important characteristic in the description of the coagulation rate. In a dilute dispersion of particles without interaction ($W = 1$) the characteristic
time of rapid coagulation is of the order of seconds (see chapter III). In slow coagulation ($W >> 1$) the repulsion energy stabilizes colloid significantly. Though, hydrodynamic corrections may affect the stability ratio, the main contributor to $W$-factor is the interaction energy which enters into eq.(1.17) exponentially.


Direct measurement of colloidal forces is a very complicated and time-consuming procedure. When the stability theory was developed, such measurements were technically impossible. Observation of the particles' flocculation from a dispersed into an aggregated state, and then interpreting the rate of flocculation in terms of interaction forces was the most direct possibility. That could be done by direct counting the number of particles through an ultramicroscope (or electron microscope), or by following the growing average size of particles using light scattering techniques. In this way it was established how, in electrocratic systems, the rate of change in the number $n_o$ of colloidal particles in an electrolyte solution varies with the coagulating electrolyte concentration.
The classical result is schematically represented by Fig.I.1 (see elsewhere [21]). Increase of the electrolyte concentration entails a compression of the double layer; the colloid becomes more unstable; the rate of coagulation increases. Above the concentration $c_c$, the rate of coagulation will not change anymore. At that particular concentration the effect of the interaction between particles on the coagulation rate vanishes. At this concentration the transition occurs from the regime of slow ($W > 1$) to rapid ($W = 1$) coagulation. Actually, Fig.I.1 illustrates the behavior of the total flux of colloidal particles to a reference particle. Relating that flux in the region of rapid coagulation ($c \geq c_c$) to the flux at a particular electrolyte concentration ($c < c_c$), the stability ratio $W$ can be calculated as a function of the main parameters. For a direct comparison of experimental data with what the DLVO theory predicts, log $W$ as a function of log $c$ should be plotted [92].

Conversion of Fig.I.1 into log $W$ - log $c$ diagram is shown in Fig.I.2. Following definition of $W$, the behavior of log $W$ as a function of main parameters is linearly related to the dependence of the total interaction energy on those parameters (log $W \sim U$). However, experimental results on different systems depart very much from what is drawn in Figs. I.1 and I.2.
In particular, the dependence of the slope of the log $W$- log $c$ diagram on the electrolyte concentration, which is expected (following the theory) to be proportional with the particle size, is almost never found in experiments. Moreover, this contradiction has not only quantitative character, but also the qualitative behavior may be completely different.

1.5. **The pair interaction energy in colloidal dispersions.**

The DLVO theory described originally the pair interaction between particles in electrostatically stabilized (electrocratic) systems [12,13]. This approach was later extended to more general cases. According to the theory, the total interaction energy is represented as a sum of repulsive and attractive components (additivity) which can be calculated separately. In the original version, there are two contributions: attraction due to van der Waals forces, and repulsion due to electrostatic forces.

1.5.1. *Van der Waals attraction.*

In the calculation of the attraction energy, our attention will mostly be focused on the dependence of this energy on the interparticle distance, and on the particle size. For an elaborate discussion of microscopic and macroscopic approximations in the calculations of attractive forces we refer to [14-17].

In van der Waals forces, there are three components: the dipole-dipole interaction (or the Keesom forces), the dipole-induced dipole interaction (or the Debye forces), and the dispersion interaction (or the London forces). The two first types assume at least one permanent dipole moment of two interacting molecules. The dispersion forces arise due to the interaction between two temporary dipole moments resulting from fluctuations of the electron density in
Pair interaction energy.

atoms (molecules). The dependence of all these forces on the distance between molecules is the same (for rather large separations), and only the constant prefactors are different [14,18]. In colloids the London forces are the most relevant factor in the interparticle interaction. Restricting the discussion to the dispersion component only, the interaction energy of two molecules can be written in the form (see [14])

\[ \varepsilon(r) = -\frac{\Lambda_{11}}{r^6}, \]  

(I.20)

for two identical molecules. Here, \( \Lambda_{11} = 3/4 \pi \omega_0 \alpha_2^2(0) \); \( \omega_0 \) and \( \alpha_2(0) \) are the resonance frequency and static polarizability of a molecule, respectively.

Hamaker pioneered the calculation of the attraction energy between two macroscopic bodies of same nature, employing the method of pairwise summation. Assuming additivity of intermolecular forces, the total interaction energy can be obtained by integrating over the volumes of two bodies:

\[ U_A = -\int_{V_1} \int_{V_2} \frac{\Lambda_{11} \rho_1^2}{r_{12}^6} \, d\tau_1 \, d\tau_2, \]  

(I.21)

with \( \rho_1 \) the density of molecules, and \( r_{12} \) is the distance between the volume elements \( d\tau_1 \) and \( d\tau_2 \) of volumes \( V_1 \) and \( V_2 \), respectively. To demonstrate how the method works, consider the interaction between two infinite slabs of thickness \( \alpha_1 \) and \( \alpha_2 \) (Fig.1.3).

Because of infinite extension of the plates in this model, we calculate the interaction energy per unit area \( u_A \) which is defined by the following relation

\[ \int_{dS} u_A \, dS = U_A. \]  

(I.22)

The distance between two interacting elements \( d\tau_1 \) and \( d\tau_2 \) is given by \( r_{12}^2 = R^2 + (h - x_2 + x_1)^2 \) where \( x_1 \) and \( x_2 \) are absolute values (see Fig.1.3). Using eqs.(I.20-I.22), we may write
Pair interaction energy.

\[ u_A = -\Lambda_{11} \rho_1^2 \int_0^{a_2} dx_2 \int_0^{a_1} dx_1 \int_0^{2\pi} R dR \int_0^1 \frac{1}{R^2 + (h - x_2 + x_1)^2} d\varphi, \]  

(I.23)

where transition to the polar coordinates in the plane of the surface 2 was made. One sees that integration is trivial if performed in the sequence presented in eq. (I.23). Introducing a new parameter, the Hamaker constant

\[ A_{11} = \pi^2 \rho_1^2 \Lambda_{11}, \]

the interaction energy (I.23) acquires the following form

\[ u_A = -\frac{A_{11}}{12\pi} \left[ \frac{1}{h^2} - \frac{1}{(h + a_1)^2} - \frac{1}{(h + a_2)^2} + \frac{1}{(h + a_1 + a_2)^2} \right]. \]  

(I.24)

Now we will apply this method to two spheres. The surface with cross-section ABC at the distance \( r \) from an atom at P (see Fig. I.4) is given by

\[ S_{ABC} = 2\pi \int_0^\theta r^2 \sin \theta d\theta, \]

with \( \theta \) determined from equation representing the cosine theorem.
Pair interaction energy.

\[ a_1^2 = x^2 + r^2 - 2xr \cos \theta. \]

Thus, \( S_{ABC} = \pi r/x [a_1^2 - (x - r)^2] \), and since the volume differential is \( d\tau_1 = S_{ABC} \, dr \), we may write for the potential energy of interaction between an atom at \( P \) and a sphere with its centre at \( O \):

\[ \varepsilon_a = -\int_{r-a_1}^{r+a_1} \frac{\rho_1 \pi A_{11}}{r^6} \frac{r}{x} \left[ a_1^2 - (x - r)^2 \right] dr. \]  

(1.25)

Integrating eq.(1.25) over all molecules of another particle

\[ U_A = -\int_{R-a_2}^{R+a_2} \varepsilon_a \, \rho_2 \pi \frac{x}{R} \left[ a_2^2 - (R - x)^2 \right] dx, \]

where \( R \) is the distance between centers of two particles, we obtain for two interacting spherical particles with radii \( a_1 \) and \( a_2 \)

---

Fig.1.4. Illustration of a spherical geometry.
\[ U_A = -\frac{A_{11}}{6} \left\{ \frac{2a_1a_2}{R^2-(a_1+a_2)^2} + \frac{2a_1a_2}{R^2-(a_1-a_2)^2} + \ln \frac{R^2-(a_1+a_2)^2}{R^2-(a_1-a_2)^2} \right\}. \] (I.26)

We have used the pairwise summation method to derive expressions (I.24) and (I.26). The main purpose was to understand how a geometry of the problem enters into the consideration. As it was shown by Lifshitz and co-workers [19,20], for a proper calculation of the dispersion interaction energy a macroscopic approach has to be used to account for collective effects within a macroscopic body. Pairwise summation is only a simplified case of this more general approach when all the collective effects are neglected (for discussion see, for example, [14]). Nevertheless, the microscopic approach gives the right particle size and interparticle distance dependence of the van der Waals interaction between two macroscopic bodies. The macroscopic consideration does alter the definition of the Hamaker constant. In this definition the intermicellar solution can be taken into account. The latter leads to change of \( A_{11} \) in eq.[I.26] for an effective value \( A_{131} \) [14,16,21].

The dependence of the interaction on the interparticle distance can significantly be affected by electromagnetic field retardation. That occurs when the distance between the molecules of interacting macrobodies (roughly speaking the interparticle distance) is significantly larger than the wavelength of electromagnetic radiation associated with electronic transitions in molecules. This problem was treated by Casimir and Polder [22] They derived an expression for the interaction between two molecules at large separations, which falls with distance as \( 1/r^7 \). It is, however, a special case beyond interest of our discussion, and we refer to [14,17,21] for a review.

1.5.2. Electrostatic interaction.
In electrocratic colloids the main stabilizing factor is the electrostatic interaction resulting from an overlap of two double layers around particles when they approach each other. The double layer around a particle is formed at the particle-solution interface to compensate a charge on the surface of this particle. Particles can acquire the surface charge due to adsorption of potential determining ions from the electrolyte solution, recombination of surface groups, etc. [23,24].

The repulsion between charged interfaces may conveniently be expressed in terms of the disjoining pressure $\Pi$.

The change of the interparticle distance leads to the redistribution of ion densities between slabs. The excess pressure (acting on the plate surface) due to this redistribution, can be calculated on the basis of equilibrium thermodynamics. In such a way, the colloid stability problem was first brought onto rigorous thermodynamic basis that made possible to measure all parameters, which are relevant for the interaction, experimentally.

Consider two plates immersed into an electrolyte solution, and separated by a thin gap (Fig.I.5). According to [25], we write for the Gibbs free energy differential per unit area (dealing with the interfacial forces, after Gibbs, it is more convenient to use this thermodynamic potential):

$$dg = -sdT + vdp + \mu d\mu - \Pi dh + \psi_1 d\sigma_1 + \psi_2 d\sigma_2,$$  

(I.27)
where $\psi_1$ and $\psi_2$ are surface electrostatic potentials, $\sigma_1$ and $\sigma_2$ are charges at the surfaces 1 and 2, respectively, and other symbols have their usual meanings. Performing a Legendre transformation, eq.(1.27) may be rewritten as

$$d(g - \mu n - \psi_1 \sigma_1 - \psi_2 \sigma_2) = -sdT + v dP - nd\mu - \Pi dh - \sigma_1 d\psi_1 - \sigma_2 d\psi_2,$$  
(1.28)

and Maxwell's rule gives

$$\frac{\partial \Pi}{\partial \psi_1} \bigg|_{n,\psi_2} = \frac{\partial \sigma_1}{\partial h} \bigg|_{\psi_1,\psi_2},$$  
(1.29)

This equation serves as the thermodynamic definition of the disjoining pressure $\Pi$. It relates the disjoining pressure to electrostatic properties of the intermicellar solution.

To find the dependence of the disjoining pressure on the distance between two flat plates, the distribution of the electrostatic potential must be known. For that purpose a set of the Poisson-Boltzmann equations

$$\nabla^2 \psi^l = \kappa^2 \sinh(\psi^l),$$  
$$\nabla^2 \psi^s = 0,$$  
(I.30a)

has to be solved, which is subjected to the boundary conditions

$$\left. \psi^l \right|_S = \left. \psi^s \right|_S,$$

$$\left. \frac{d\psi^l}{dr} \right|_S - \left. \frac{d\psi^s}{dr} \right|_S = -\frac{2\sigma F}{\varepsilon^l \varepsilon_0 RT}.$$  
(I.30b)

System (I.30a,b) is written here for a binary symmetrical electrolyte and identical plates with $\sigma_1 = \sigma_2 = \sigma$. Superscripts $l$ and $s$ denote the liquid and solid phases, $S$ is the particle surface, $n$ is the outer normal to the particle surface, $\gamma = zF \psi / RT$, $R$ is the gas constant, $\kappa = (2F^2 z^2 c_0 / \varepsilon^l \varepsilon_0 RT)^{1/2}$ is the Debye-Hückel parameter, $c_0$ is the concentration of an electrolyte in solution, $F$ is the Faraday
Pair interaction energy.

constant, $\nabla^2$ is the Laplace operator and other symbols have their usual meanings. Solution of system (I.30) is a very complicated task and a progress in analytical elaboration can be made using some approximations. Before discussing different approximations acceptable for different systems, we recast eq.(I.29) to a form more suitable for calculations. First the integral electroneutrality condition must be satisfied [21,25,26]

$$\sigma = \int_{h}^{h+\delta h} \rho(h) dh ,$$  \hspace{1cm} (I.31)

which says that a charge within a volume restricted by the plane located at the distance $h$ from the surface of a slab is neutralized by the bulk-ion density $\rho$ beyond that plane. Having integrated eq.(I.29), we substitute expression (I.31) into the final result, and obtain

$$\Pi(h) = \int_{\psi_b}^{\psi_m} \rho \, d\psi - \int_{\psi_m}^{\psi_b} \rho \, d\psi = \int_{\psi_b}^{\psi_m} \rho \, d\psi ,$$  \hspace{1cm} (I.32)

where it was taken into account that the disjoining pressure becomes zero at infinite separations. $\psi_b$ and $\psi_m$ are electrostatic potentials at the surface and mid-way point between surfaces, respectively (Fig.I.5) (they are generally functions of the separation).

Eq.(I.32) shows that the disjoining pressure arises due to the changes of the counterion density $\rho$ between two slabs when the latter approach each other. The formal expression for the counterion density can be taken from the Poisson-Boltzmann equation (first in eq.(I.30a)), and substituted into eq.(I.32). The final expression for the disjoining pressure, after a simple integration in (I.32), reads

$$\Pi(h) = 2 c_o RT (\cosh y_m - 1) .$$  \hspace{1cm} (I.33)

If only pure electrostatic effects stabilize the system, the change of the Gibbs energy with the interparticle distance can be transformed into the change of the
interaction energy, and we may write for the energy density per unit area [25,27]

\[
    u(h) = -\int_0^h \Pi(h)dh = \int_h^0 \Pi(h)dh .
\]

(1.34)

Actually, this transition is defined by the equality \((\delta U)_S = (\delta G)_T\) [28], where \(\delta\) is a small variation. If the entropy factor is important for the system under consideration (like in rather concentrated dispersions or micro-emulsions), it must be included. In some cases the additivity [29] of the forces of different kind is still applied, but in other cases the situation becomes more complicated [30,31]. Then, more advanced statistical thermodynamics of electrolyte solutions must be involved.

In the DLVO theory the electrostatic component of the total free energy is calculated by substituting (I.34) into (I.22), i.e., by integrating over the particle surface. One can see that the energy of electrostatic interaction is completely then determined by the distribution of electrostatic potential in the gap between the two surfaces. As mentioned above, the calculation of this distribution is a very complex problem, and we shall restrict our elaboration to the case of flat parallel plates of same nature. Actually, eq.(I.30a) is written in the Debye-Hückel approximation, which is justified for low electrolyte concentrations or low electrostatic potentials, i.e.,
\[ y_m < y_b < 1. \] (I.35)

The coordinate system for solving (I.30) in a one-dimensional situation is chosen as presented in Fig.I.6, with \( x = \kappa h/2 \), and \( \xi \) is a dummy variable, and \( h \) is the distance between two surfaces. After multiplying the first equation in (I.30) by \( 2 \frac{\partial y}{\partial \xi} d\xi = 2dy \), it can be transformed into [32]

\[ \left( \frac{dy}{d\xi} \right)^2 = 2(\cosh y - \cosh y_m), \] (I.36)

with formal solution

\[ \xi = \int_y^{y_b} \frac{dy}{\sqrt{2(\cosh y - \cosh y_m)}}. \] (I.37)

Using conditions (I.35), one may expand hyperbolic cosine in the Taylor series truncated at the first non-zero term as

\[ \xi = \int_y^{y_b} \frac{dy}{\sqrt{y^2 - y_m^2}}, \] (I.38)

whence

\[ \xi = \text{Arcosh} \left( \frac{y}{y_m} \right) \bigg|_{y}^{y_b} \Rightarrow x = \text{Arcosh} \left( \frac{y}{y_m} \right) \bigg|_{y}^{y_b}, \]

and

\[ y_m = \frac{y_b}{\cosh x}, \] (I.39)

where the symmetrical boundary conditions at the surface of particles were used.
Pair interaction energy.

Eq. (I.39) gives the relation between electrostatic potentials at the mid-way point and at the surface. For a low surface potential the disjoining pressure can be written as

\[ \Pi(h) = c_0 RT \, y_m^2. \] (I.40)

From (I.39) and (I.40) it follows that the electrostatic interaction can be calculated if the behavior of the surface electrostatic potential is known as a function of the distance between two surfaces.

In the theory of the electrostatic colloid forces different descriptions of the surface charge (or electrostatic potential) are widely accepted. Historically, the case of constant surface potential (assuming an electrochemical equilibrium was considered first. In (I.39) we assign \( y_b = y_0 = \text{Const.} \), and the disjoining pressure (I.40) can readily be integrated as in (I.34)

\[ u' = \frac{2}{\kappa} c_0 RT \, y_0^2 [1 - \tanh x]. \] (I.41)

A discussion of applicability of the constant surface potential approximation arose later on. As an alternative regime interaction at constant surface charge was introduced implying that the charge at interfaces of two interacting particles cannot relax during the final Brownian jump leading to coagulation of this couple. The rigorous mathematical formulation of this problem was done in [27,33,34,97], and is repeated here in terms of our approximations. The integral electroneutrality condition is used in the following form [21]

\[ \eta + \sigma_b = - \sigma_d, \] (I.42)

where \( \eta \) is the permanent charge density on the particle surface (which can also be an effective charge representing a charge distribution within the volume of a colloid particle), \( \sigma_b \) is the surface charge density due to adsorption (or surface complexation), and \( \sigma_d \) is the double-layer charge per surface unit, which
neutralizes the total charge density at the particle-solution interface. Eq.(1.42) has a general form, and it is representing the second boundary condition in (I.30), which is now expressed in terms of a charge density. Supposing that the charge at surfaces is changing only a little, one may approximate the l.h.s of eq.(1.42) by a constant value $\eta_0$. The double-layer charge density per unit area can be determined using the known definition (see, for example, [21,26]) that follows from the last equality in system (I.30)

$$\sigma_d(h) = \varepsilon' \varepsilon_0 \kappa RT \left( \frac{dy}{d\xi} \right)_{\xi=x},$$

(I.43)

After substitution of (I.36), eq.(I.43) acquires the form

$$\sigma_d(h) = \frac{\varepsilon' \varepsilon_0 \kappa RT}{2zF} \sqrt{2(\cosh y_b - \cosh y_m)}.$$

(I.44)

Again, expanding hyperbolic cosine into series, and using expression (I.39) for the mid-way potential, we obtain

$$\sigma_d = \frac{\varepsilon' \varepsilon_0 RT \kappa}{2zF} |y_b| \tanh x.$$

(I.45)

Introducing a new dimensionless constant

$$\delta_1 = \left| \frac{2zF \eta_0}{\varepsilon' \varepsilon_0 RT \kappa} \right|,$$

(I.46)

we write for the absolute value of the surface electrostatic potential

$$|y_b| = \frac{\delta_1}{\tanh x}.$$

(I.47)
After substituting, sequentially, (I.47) into (I.39), and (I.39) into (I.40), the integration over interparticle distances (I.34) gives

\[ u^\sigma = \frac{2}{\kappa} c_0 RT \delta_i^2 \left[ \coth x - 1 \right]. \quad (I.48) \]

If surface charge is formed due to a process like adsorption, for example, some kind of a balance equation must be written representing that process. This idea was applied to recombination of ionizable surface groups [35,36], and called the charge regulation modeling. In [37] it was pointed out that mathematical formalism is quite the same as in the case of a sorption-desorption process, and the latter is somewhat simpler and more illustrative. For the sake of brevity, the surface charge density caused by physical adsorption of potential determining ions will be described with a Stern-layer, Henry-type, adsorption isotherm valid at low degrees of surface occupancy:

\[ \sigma_b = \sigma_0 \exp \left[ -|y_b| \right], \quad (I.49) \]

with

\[ \sigma_0 = zF \Delta_b c_b \exp(-\omega_b), \]

where \( \Delta_b \) is the width of the potential well of depth \( \omega_b \) scaled with \( k_B T \), \( c_b \) is the ion concentration next to a slipping plane. This description corresponds with the Martynov model for surface-bound ions [38]. Substituting (I.49) into the integral electroneutrality condition (I.42) (\( \eta = 0 \) is taken) and expanding exponential into Taylor's series, we derived

\[ |y_b| = \frac{\delta}{\delta + \tanh x}, \quad (I.50) \]

and
\[
\delta = \frac{2zF}{e' \varepsilon_0 RT \kappa} \cdot
\]

The interaction energy per unit area reads in this case as

\[
u_0 = \frac{2}{\kappa} c_0 RT \frac{\delta^2}{(1+\delta)} \frac{1 - \tanh x}{\delta + \tanh x}.
\] (I.51)

Deriving eqs. (I.41), (I.48), and (I.51) for different models of electrostatic interaction, we used a bit different notations. To compare the final results, these expressions must be rewritten in terms of parameter \(\delta\)

\[
y_b^V = \frac{\delta}{1+\delta},
\]

\[
y_b^G = \frac{\delta}{(1+\delta) \tanh x},
\]

\[
y_b^\omega = \frac{\delta}{\delta + \tanh x}
\] (I.52)

with \(y_0 = \delta_1 = \delta / (1 + \delta)\), and \(\delta < 1\). Finally, the three model potentials acquire a form

\[
u^V = \frac{2}{\kappa} c_0 RT \frac{\delta^2}{(1+\delta)^2} [1 - \tanh x]
\]

\[
u^G = \frac{2}{\kappa} c_0 RT \frac{\delta^2}{(1+\delta)^2} [\coth x - 1]
\] (I.53)

\[
u^\omega = \frac{2}{\kappa} c_0 RT \frac{\delta^2}{(1+\delta)} \frac{1 - \tanh x}{\delta + \tanh x}
\]
The comparison of these interaction potentials is given in Fig.I.7 for $\delta = 0.5$, what corresponds to $\psi \equiv 8 mV$. As it is seen, the difference between interaction potentials becomes very pronounced when the distance between interacting surfaces diminishes. The interaction at constant surface charge tends to infinity as $h \to 0$, whereas the interaction at constant surface potential has a finite limit. The interaction corresponding to the totally equilibrated double layers finds itself in an intermediate region. At distances of about $2/\kappa$ the differences in interaction potentials almost disappear.

Shilov [39] performed a qualitative analysis of the complete system (I.30) for spherical colloid particles. It was shown that for dielectric particles in an aqueous electrolyte solution ($\varepsilon^s / \varepsilon^l \to 0$) formation of the double layer is governed by the distribution of the surface charge only, whereas for metallic particles ($\varepsilon^s / \varepsilon^l \to \infty$) the distribution of the electrostatic potential in the bulk of a particle influences rather significantly the build-up of double layers. As a consequence, the constant surface charge regime is almost coinciding with the constant surface potential case.

More exact calculations were published by Ohshima [40] for different geometries. Using our notations, one can rewrite his results for two identical slabs of thickness $\sigma$ as
\[ u^\sigma = \frac{2c_0RT}{\kappa} \frac{\delta^2}{(1+\delta)^2 \tanh x + 1} \left[ 1 + \frac{1}{\left( 1 + \frac{\kappa a \varepsilon^l}{\varepsilon^s} \right)} \left[ 1 - \tanh x \right] \right], \]  

(I.54)

and

\[ u^\omega = \frac{2c_0RT}{\kappa} \frac{\delta^2}{(1+\delta)^2} \left[ 2 + (1+\delta)\kappa a \frac{\varepsilon^l}{\varepsilon^s} \right] \left[ 1 + \frac{1}{1 + (1+\delta)\kappa a \frac{\varepsilon^l}{\varepsilon^s}} \left[ \tanh x + \frac{\delta}{1+\delta} \right] \right] \left[ 1 - \tanh x \right]. \]  

(I.55)

These two types of interaction are compared with the constant surface potential regime for \( \delta = 0.5 \) in Fig.I.8 \( a \) and \( b \), respectively.

---

\( u \frac{\kappa}{2c_0RT} \)

- \( \psi_b = \text{Const} \)
- \( \sigma_b = \text{Const, } \varepsilon^l / \varepsilon^s = \infty \)
- \( \sigma_b = \text{Const, } \varepsilon^l / \varepsilon^s = 0 \)

**Fig.I.8.** Influence of the nature of particles on the electrostatic repulsion at \( \sigma_b = \text{const} \) (a), and \( \omega_b = \text{const} \) (b).
Pair interaction energy.

It was already demonstrated, that the difference between the models reduces strongly for the electrostatic interaction energy of metallic particles. Moreover, one can show that variation of the $\delta$-parameter will almost eliminate the differences between the constant surface potential and the charge regulation cases.

In Fig.I.9 we have compared two situations: $a$ - $\delta = 0.5$ what corresponds to $\psi_0 \sim 8 \text{ mV}$, and $b$ - $\delta = 3$ what corresponds to $\psi_0 \sim 19 \text{ mV}$.

First case is a model one and it fulfills the requirements imposed on the system ($\gamma \ll 1$). Formally, the second case satisfies this approximation too, albeit approaching the limits of its applicability. The latter means that the calculations are more shifted in the qualitative area, and reveal only the tendency in the
dependence of the interaction energy on the surface electrostatic potential. On the other hand, the second case more adheres to the real experimental situation, and it is quite obvious that the difference between interactions at a constant surface potential and that one governed by the charge regulation is becoming negligible when the surface potential grows.

However, to describe interaction in a real colloid, a more advanced geometry has to be involved.

1.6. Derjaguin's approximation.

Derjaguin (see [32], and references therein) pointed out that for the interaction between macrobodies it is mostly sufficient to consider small (relative to particle size) separations only. This approximation allows to obtain interaction potentials for complex geometries from those between half-spaces.

Consider two identical spherical particles (see Fig.I.10). The distance between two local regions at the azimuthal angle \( \phi \) from the line connecting centers of two interacting particles can be written as

\[
H = h + 4a \sin^2 \phi / 2. \tag{I.56}
\]

We envisage the situation

\[
\kappa a \gg 1, \text{ and } x \leq 1, \tag{I.57}
\]

i.e., the systems with relatively thin double layers compared to \( a \).
Derjaguin’s approximation.

Fig. I.10. Geometry of two spherical particles. Cylindrical symmetry of a problem.

The integral over the particle surface of an arbitrary function which depends on the distance $H$ is written then

$$
\int_S S f(H) = 2a^2 \int_0^{\pi/2} d\vartheta \int_0^{\kappa a} f(H) d\vartheta \sin \vartheta.
$$

(Making a simple transformation $d\vartheta \sin \vartheta = 2 \sin \vartheta/2 \cos \vartheta/2 \ d\vartheta = 2d \sin^2 \vartheta/2$, and introducing a new dimensionless distance $X(\vartheta) = \kappa H/2$, we rewrite (I.58) as

$$
\int_S S f(H) = 4\pi a^2 \kappa^{-1} \int_{\kappa}^{a} f(X) dX.
$$

Here, following (I.57), the upper limit of integration can as well be infinity, and the integral over the particle surface finally becomes
Derjaguin's approximation.

\[ \int f(H) dH = \frac{4\pi a}{\kappa} \int f(X) dX. \] (I.59)

The main conclusion drawn from this simple elaboration is, that the integral over the surface of a particle with some advanced geometry can be converted into an integral with respect to the interparticle distance, which is multiplied by some geometrical factor.

However, the Derjaguin approximation does not stick down to the geometrical effect only (as it is often encountered in text books on colloid and physical chemistry). The system schematically represented by Fig.I.10 has a cylindrical symmetry, i.e., the Laplace operator in (I.30) contains derivatives with respect to the interparticle distance and azimuthal angle as well. Because of condition (I.57), the derivative with respect to the azimuthal angle \( \vartheta \) is a small correction (of the order of about \( 1/\kappa a \)) in calculations of the electrostatic potential distribution. As a consequence, the problem becomes essentially one-dimensional, and the interfacial curvature can indeed be introduced by exchange of \( h \) for \( H \) in the case of two thick flat plates. The rigorous procedure of the solution of linearized Poisson-Boltzmann equations, and comparison with the Derjaguin approximation has been established in [41] and extended on variety of systems in a sequence of papers [42]. The main result is that the Derjaguin approximation works well, until \( h << a \) and \( \kappa h \) is not close to zero. For \( \kappa a \) of about ten times larger than \( \kappa h \) the calculation error (comparing with exact numerical solution) does not exceed 5%.

We have already pointed above that the solution of a set of the Poisson-Boltzmann equations in the case of spherical metallic particles is a rather complicated task, and we restrict our analysis here to dielectric particles. The total repulsive energy between spherical particles can be written in our notations as
Derjaguin's approximation.

\[ U_R^{\psi} = \frac{4\pi a_0 c_0 N_A}{\kappa^2} \frac{\delta^2}{(1 + \delta)^2} \ln(1 + \exp[-2\delta]), \]

\[ U_R^{\sigma} = -\frac{4\pi a_0 c_0 N_A}{\kappa^2} \frac{\delta^2}{(1 + \delta)^2} \ln(1 - \exp[-2\delta]), \tag{I.60} \]

\[ U_R^{\omega} = -\frac{4\pi a_0 c_0 N_A}{\kappa^2} \frac{\delta^2}{1 - \delta^2} \ln \left( 1 - \frac{1 - \delta}{1 + \delta} \exp[-2\delta] \right), \]

with \( N_A \) the Avogadro number.

The van der Waals component in this approximation reads

\[ U_A = -\frac{A_{11} \kappa a}{24k_B T} \frac{1}{x}. \tag{I.61} \]

All the interaction potentials are scaled to \( k_B T \).

The total pair interaction potential is a sum of repulsive and attractive components

\[ U_{\text{tot}} = U_R^{(\psi,\sigma,\omega)} + U_A, \tag{I.62} \]

and depends on the repulsion regime chosen. The three repulsion regimes are compared in Fig.I.11 for \( \delta = 0.5 \). The picture is similar to the interaction between flat plates, where the repulsive energy at a constant surface charge basically differs from the two other types of the pair interaction potential.

Again, we have to draw here attention to the particle size dependence of the total interaction energy. All components [eqs.(I.60) and (I.61)] of this energy
Derjaguin’s approximation. are proportional with $a$. This is independent of the electrostatic regime chosen, and implies that the stability ratio $W$ must strongly and systematically be influenced by the particle size in colloidal dispersions. We have, however, to draw already here attention to the fact that the surface of colloidal particles has a complex geometry. When we are looking at the particle shape from separations compared with (or larger than) particle size, they, perhaps, may be modeled as ideal spheres. However, at a closer inspection (on length-scales compared with the radius of action of colloidal forces), the local curvature may deviate significantly from the overall curvature embodied in the particle radius as per the DLVO theory. This effect is obviously not included into the standard description, and deserves much more attention.

1.7. Consequences of the DLVO theory, and extensions of the standard description.

The great achievement of the classical DLVO theory was (and is) the prediction of the influence of the measurable parameters (which describe colloidal dispersion) on the stability against coagulation. The dependence of the interaction energy on such parameters as the surface charge (electrostatic potential), the Hamaker constant, the concentration and the valency of coagulating electrolyte is well understood now, and the theoretical anticipation is in a rather good agreement with experimental observations (see [21] and references therein).

The repulsive component of the pair interaction potential increases with growing (surface) $\zeta$-potential, and dispersion becomes more stable. The way around, increasing Hamaker’s constant makes the system more unstable.
The influence of the electrolyte concentration on the interaction energy is demonstrated in Fig.I.12, where abscissa is given in terms of $1/\kappa$. Growing concentration reduces the electrostatic barrier, and at a certain concentration this barrier becomes zero. That electrolyte concentration is called the critical coagulation concentration $c_c$. It can be calculated using a system of equations

$$\frac{U_{\text{tot}}}{k_B T} = 0 \quad \frac{dU_{\text{tot}}}{dx} = 0 , \quad (I.63)$$

if all other parameters remain the same. In this particular situation we have performed calculations for $T = 300$ K, $A = 2 \times 10^{-20}$ J, $y_0 = 0.8$, $a = 25$ nm, obtaining $c_c = 36$ mmol / L. These two equations are required to find the position of a maximum and deduce the dependence of $c_c$ on other parameters. One can see that the critical coagulation concentration is independent of particle size, because both the pair interaction energy and its derivative are proportional with particle’s radius. This proportionality predicts a strong and systematic dependence of the interaction energy and stability of dispersions on the particle size, as it is illustrated by Fig.I.13.
Later on, a number of experiments showed deviations of experimental results from what was expected following this stability theory. The theory predicted higher values for the stability ratio than those found in experiments, and qualitative dependence of the stability ratio on particle size differed from theoretical expectations. Stability ratio was slightly (if not at all) sensitive to the variation of particle diameter, and critical coagulation concentrations were particle size dependent. There have been attempts to modify this standard description involving new features not accounted for in the original consideration. These new parameters had to alter the theoretical particle size dependence of the interaction between macroscopic particles.

Fig. I.13. Typical classic stability diagram.

First, attention was drawn to the hydrodynamic effects. Considering capture of a spherical particle by an infinite slab, the expression for the hydrodynamic resistance of the liquid film between two macrobodies to their approach has been derived in [43]. This resistance was proportional to the particle size, and stabilized the system. Ideologically analogous derivation has been performed for different geometries, and correction was included into description of the coagulation process [44-46]. Usually, it is presented as a dependence of the diffusion coefficient on the distance between interacting particles, and, dealing with colloid stability problem, this correction is written in the following form [46]
\[
\frac{D(\infty)}{D(h)} = 1 + \frac{13}{12} \frac{\kappa a}{x} + \frac{1}{12} \left( \frac{\kappa a}{x} \right)^2 \left( 1 + \frac{1}{3} \frac{\kappa a}{x} \right).
\] (1.64)

However, the hydrodynamic correction enters the stability ratio linearly (see (1.17)), whilst the interaction energy, that is also proportional to the particle radius, contributes exponentially. Thus, expression (1.64) may be considered as a necessary correction, but it does not solve the problems.

Also, so-called secondary minimum coagulation [47-52] was considered as a possible reason for discrepancies. This type of coagulation affects stability of a system if the secondary minimum is deep enough, i.e., in rather coarse dispersions with \( a > 500 \text{ nm} \). The occurrence of the secondary minimum coagulation of coarse particles can easily be detected observing steeper slope of log \( W \) - log \( c \) curves for smaller particles coagulating in the primary minimum. However, for rather fine particles dependence of the stability on particle size still deviates significantly from what predicted by the standard description [51,53], and that cannot be attributed to the secondary minimum coagulation.

As a next serious correction we discuss a so-called dynamic approach to colloid particle interaction, meaning that the DLVO theory is essentially static, while coagulation is a dynamic process. There have been considered a few qualitatively different models[54-57]. All these models have the same basis, i.e., dynamics introduces into description a new parameter the Deborah number (De). The latter gives a relation between the time needed for a system to relax to the equilibrium situation, and the characteristic time of a process. If \( De \ll 1 \), the system is always in equilibrium, and at \( De \gg 1 \) the system is totally disequilibrated. In connection to colloid stability problem we can define the Deborah number as relation between the time that double layers need to relax,
and the average time which particles need to overcome the separation equal to the extent of these double layers [58].

The electrokinetic relaxation processes were included into hydrodynamic correction as well as into description of the interaction between particles [59,60]. First elaboration gives only slight correction to the interaction curve. The second consideration settled all regimes of the electrostatic repulsion on the unified basis with the constant surface charge interaction corresponding to the total disequilibrium, and with the charge regulation regime (with a constant surface potential as the lowest limit) corresponding to equilibrium. The real situation is always somewhere between these two model interactions.

It was theoretically shown that the dynamic approach to colloid particle interaction can contribute to solution of the long-standing problem if the difference between equilibrium and nonequilibrium interaction is sufficient. From the above consideration dispersions of dielectric particles charged due to the physical adsorption of potential-determining ions [23] or the recombination of surface ionogenic groups [24] are systems for which this approach can significantly alter the particle size dependence of the pair interaction energy. As soon as smaller particles experience more intensive Brownian motion than bigger ones, they have less time for the double-layer relaxation, and, as a consequence, they interact with a potential next to the constant surface charge regime, while the interaction between bigger particles occurs in a more equilibrium situation. The difference in the interaction due to the geometrical effect is counterbalanced by the difference in interaction regimes. Unfortunately, this description has lack of independent data on coagulation kinetics and exchange constants governing relaxation processes. Without these data it is difficult to see whether these processes will generally alter the interaction in colloidal dispersions or work on an especially chosen system only.
It is worth to mention here refinements invoking advanced statistical models of intermicellar electrolyte solution [61-63], which account for ion correlations, the intrinsic size of ions, and effect of the image forces. Although the latter effect increases the electrostatic repulsion [64,65], two first give rise to the electrostatic attraction, which can be explained in terms of ion-"correlation hole" interaction [66], for example, when intrinsic ion size is taken into account.

On the basis of the ion correlation effects the restricted swelling of calcium clays was explained with a rather good agreement between experimental results and theoretical anticipation [61]. Also approaches based upon hypernetted chain approximation (HNC) [61,62] demonstrate quite good agreement with Monte Carlo simulations. As it was mentioned in [30], it is not consequent to account for correlations considering the van der Waals interaction, and neglect correlations in electrolyte solution at all.

It should be pointed out that a rather solid effort is required when involving electrolyte statistics into the colloid stability problem, and all the solved models deal with interaction between two infinite semispaces or slabs. Although it is difficult to speak about particle size effect on the stability at this stage of the development of theory, results of these considerations are quite attractive. Also, it is worth to point out here that for colloidal particles with a low surface potential (charge) which are immersed into diluted electrolyte solution, trends of the disjoining pressure calculated on the basis of the DLVO theory corresponds well with HNC approximation [93,94].

A variety of approaches to the colloid stability problem can be found in the literature concerning heterogeneity of the characteristics describing colloidal dispersions. Every monodisperse suspension has some standard deviations in size and surface charge distribution. As a consequence, heterocoagulation theory (see elsewhere [67]) must be applied to calculate the interaction between
Strong and weak points of the standard description. Refinements.

particles with different characteristics. The stability ratio stems from the averaging over interactions between particles with all possible combinations of the particle characteristics obeying, for example, a Gaussian type of distribution. In [68] it was shown that these deviations cause reduction of the stability ratio, however if they are not large (let say within 15±20 %) this reduction is not pronounced (within about 10 %). Again, as a correction in the description of the coagulation process, which is related to absolute value of the stability ratio, these calculations bring closer stability curves described theoretically and observed experimentally. Usually the deviations in characteristics for coarser particles are larger than for smaller ones, and the averaging procedure results in a more pronounced reduction of the stability ratio for larger particles. However, this correction cannot explain a slight dependence of stability on the particle radius and critical coagulation concentrations dependent of particle size.

This approach accepts an idea that every individual particle has ideal characteristics, but, in general, these characteristics are not uniform through suspension. Other refinements discussed this rather idealistic approach meaning that in reality particles may not be represented as ideal spheres with smeared out surface charge (potential). There were different approaches to introduce a more realistic description of the interface into the stability problem. One has demonstrated that the discreteness of adsorbed ions will reduce the disjoining pressure [69,70]. Different models have been to account for heterogeneity of the surface charge, that can be represented by different regular fluctuating functions, or using patch-wise analogues [70-75,96]. However, the theoretical description of the particle size effect on the stability ratio (or collision efficiency) remained still unclear, while experiments showed virtually independent colloid stability (or capture under unfavorable chemical conditions) of this characteristic.
Comparison of this theoretical approach with experimental results was performed in [76], where authors combined ideas about heterogeneity of the surface electric potential with the heterocoagulation theory. The possible combinations of the particle-to-particle orientations were averaged with the distribution function of a Gaussian type for both surface potentials. It was shown that varying the standard deviation of a local surface potential with respect to its averaged value the theoretical stability curve can be fitted to the experimental data. The experiment was carried out for different colloids (latex, silica, and cerium oxide), and a fitting procedure was performed. Particle size effect on the stability diagram was explained by different factors, i.e., for latex particles the hydrophobic forces in the exponential form have been involved into description. Stability of silica colloids, presumably, was affected by the surface roughness represented by averaged protrusion with characteristic size determined, again, using a fitting procedure. Although the exponential decay of the non-DLVO forces (due to hydrophobic/hydrophilic, structural, etc. effects) has been manifested both theoretically and experimentally [77-79], the description of required constants, as functions of particle size, for example, is not quite clear. Also, recent extensive experimental study on rapid coagulation of ferric oxide (hematite) particles could be matched by theoretical calculations if a local deviations from the overall curvature (described by the particle diameter) was accounted for [95].

Unfortunately, in all descriptions mentioned above, very important parameters have been used as fitting constants without drawing any physical background, which will clarify why one or another value of these constants was chosen for calculations. Moreover, additional effects were needed to complete the picture of colloid stability.

The heterogeneity of the interface may purely have geometrical character, at least a geometrical effect can mostly be pronounced. The surface of every
The theory based upon Derjaguin's approximation for the van der Waals interaction between roughened surfaces has been presented in [82] where different shapes of the characteristic surface protrusion were analyzed. The averaging over all possible orientations of one surface with respect to another at the calculation of the dispersion component is considered in [83]. In those papers the calculated values of the dispersion interaction were compared with experimental results on macroscopic quartz plates, manifesting much better agreement when the surface irregularity is accounted for. The direct relation between adhesion forces and the surface roughness is demonstrated using a relatively new technique - atomic force microscopy (AFM) [84] - when studying adhesion of particles to a surface [85].
Introduction of the surface roughness into calculations of an electrostatic component of the total interaction energy is a more difficult task. Serious problems arise already when deriving distribution of the electric potential around an isolated charged colloid particle immersed into an electrolyte solution [86]. If the deviations in a local curvature are not much pronounced this problem can be simplified. Representing surface features by an ideal array (as in the case with the van der Waals interaction), the electrostatic energy can be calculated. This was done for different geometries, i.e., for inclined slabs [87], protrusions of different shapes [88], regular "waviness" analyzing dependence of the interaction energy on the position of one surface with respect to the other [89], etc. Also the numerical simulations have been carried out [81,90].

Comparison of the interaction between roughened bodies with the interaction between smooth analogies showed a right trend, i.e., improves agreement between theory and experiment. However, all those descriptions do not allow to analyze the particle size dependence of the colloid stability when the surface roughness is accounted for. The necessary order has to be established in the description of surface features for particles of different radii but same nature.

We briefly reviewed above the main refinements able to modify the standard theory significantly. Those are aimed at the solution of a long-standing problem of the stability theory - the particle size dependence of the stability ratio. Still various considerations remained beyond discussion of this chapter (see [96]). We have skipped such refinements where, for example, next order of $h/a$ parameter is taken into account in the van der Waals term, and is neglected in the repulsive component [91].
Conclusions.

The colloid stability is a very complicated problem approached by Derjaguin and Landau, Verwey and Overbeek in a rather simple way. At that stage of the development in other fields of science and technology this theory presented "a state of the art" in colloid chemistry, moreover, it was able to predict the major trends of the stability of colloidal dispersions, depending on the main parameters describing these systems.

There have been different refinements of the theory to solve discrepancies between theoretical description and experimental observations, in particular, those concerning the particle size effect on the colloid stability. However, majority of those modifications suffer from overwhelming of fitting parameters introduced, but not measured independently. Moreover, those new ideas are mostly working on the very special systems only.

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   Elsevier, Amsterdam, 1952.
II. Surface Roughness and the Particle Size Effect on the Brownian Coagulation of Monodisperse Colloid Particles. Theoretical.

Real colloidal particles are not ideal spheres (or objects of any ideal shape) with averaged out surface characteristics. Every macrobody possesses some surface irregularities; the question is only whether those irregularities have visible influence on the behavior of a system.

Here we can turn to a geographical analogy after [1]. From a point of view of a pilot, leading his modern airplane a few miles above the earth, the topological features are as good as flat. It does not really matter whether we travel on this plane over a mountain archipelago or the surface of an ocean. However, the nearer our plane approaches the surface, the more often the pilot should take care of mathematical imperfection of the earth surface. In other words, whether an ideal shape may be assigned to a surface depends on what we are going to do with this surface.

It is not the surface irregularity as such which enters into the theory, but the aspects of this irregularity which are relevant in the context of this theory. The relevant length scales of the surface roughness are determined by a typical range of the interaction in the stability theory.

All models which have been introduced to involve surface features into the calculations of the pair interaction between particles have the problem that they cannot give a uniform description of surface roughness of colloidal particles with different size. Therefore, the particle size effect could not be analyzed in terms of these models.

II.1. Scaling concept in description of surface irregularity.

In this section we would like to outline underlying basic ideas of our description of surface irregularities. These irregularities represent deviations from an ideal
geometry of the interface between colloidal particles and an electrolyte solution, i.e., disorder of the particle surface. Depending on the system, the disorder can be rather weak or strong. A system is weakly disordered if the disorder vanishes as the system is probed at progressively smaller or larger scales. In strongly disordered systems, the disorder remains as we are going to smaller or larger scale. (As well-known examples we can mention here stepped crystals in the first case, and the perimeter of a coast in the latter.)

Fractal (or strongly disordered) systems can be represented as a repetition of some structure within the same structure. Fractals are characterized by fractal dimension $D$ reflecting the fact that disordered systems with a structure within the relevant structure must occupy more space than simply a chain of regular surfaces. If $D$ coincides with the topological dimension of the system $D_{\text{top}}$ ($D_{\text{top}} = 0$ for a dust, $D_{\text{top}} = 1$ for a curve, $D_{\text{top}} = 2$ for a surface, and $D_{\text{top}} = 3$ for a solid body), then the system will be called Euclidean (or non-fractal). If $D$ differs from $D_{\text{top}}$, then the system will be called fractal. For strongly disordered systems $D > D_{\text{top}}$, whereas $D = D_{\text{top}}$ for ordered or for weakly disordered systems.

If a solid has a surface with fractal dimension $D$, many properties depend not only on $D$, but also on the scaling behavior of characteristics such as the mass (alloys), the pore space, etc. Therefore, all these systems are subdivided into classes describing how the surface scales alike, i.e., mass-, pore-, and surface-fractals, which are characterized by the relevant fractal dimension. However, also a non-fractal surface can still possess many irregularities. To describe this situation, a new dimension $D_{\text{irreg}}$ is introduced, which gives the fractal dimension of a set-creator of surface features. In this case the definition of the fractal dimension is [2]

$$D = \max\{D_{\text{irreg}}, D_{\text{top}}\}.$$
Return now to fractals. These can be subdivided into two groups: self-similar and self-affine systems. Self-similar systems have one scale factor repeating at all length-scales. In a more general case of self-affine systems there may exist a few different scaling factors in different directions. All these types of interface are illustrated by Fig.II.1 (see also [2]).

<table>
<thead>
<tr>
<th>Disorder Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>no disorder</td>
<td>dilation and translation invariance</td>
</tr>
<tr>
<td>weak disorder</td>
<td>local dilation and translation invariance</td>
</tr>
<tr>
<td>(anisotropic) strong disorder</td>
<td>dilation invariance; macroscopic translation invariance</td>
</tr>
<tr>
<td>(isotropic) strong disorder</td>
<td>dilation invariance; no translation invariance</td>
</tr>
</tbody>
</table>

Fig.II.1. Different types of disorder.

Although scaling representation of rough surfaces is, of course, an idealization, this concept brings some order into description of disordered systems, that allows to study complex effects of the surface roughness related, for example, to the coagulation process in colloidal systems. Moreover, bringing
stochastic deviations into ideal constructions of Fig.II.1, structures matching more closely the real situation may be obtained.

To demonstrate how the profile of a complex shape can be constructed using the scaling concept, and how the fractal dimension of this profile is calculated the Koch curve will be used [3,4]. Consider a piece of the surface profile measured with a stiff “yardstick” of length $\lambda$ (see Fig.II.2). We define a generator which describes deviations from the original, ideally smooth interface. In this example the generator consists of four regular sections with length $\lambda/3$ each. As the following step, each section is represented by the same generator scaled down, however, to the length of this section. Repeating this procedure $n$ times, we can draw a rather complex profile, that is demonstrated by Fig.II.2 for $n = 3$, for example. In principle, this insertion of a structure into the same structure can be repeated to infinite extent so, that infinitely fine surface features can be modeled. Actually, real profiles consist already of features on different scale, and the profile construction in nature is often going just the way opposite to that described above. However, it is easy to illustrate how this manner of modeling the surface features is reproduced in an experimental investigation.
Consider, again, a classical example: monolayer adsorption of molecules with different cross-sections at the same solid surface [5,6] (see Fig.II.3). The perimeter of the surface profile, which is measured in the first situation will be much smaller than that obtained with smaller molecules. The size of larger molecules does not simply allow them to fill all cavities in the solid surface. This means that the effective surface area measured with adsorption of molecules with different cross-section (or “yardstick”) will be different, and the fractal dimension reflects that. The example is, of course, correct if the surface possesses scaling properties on the molecular scale. (We are speaking here about the homogeneous adsorption, however, for discussion of a heterogeneous case see [7]).

The length of a profile is determined as (see elsewhere [3], [6])

\[ \text{Length} = \lim_{r \to 0} N_{\text{ball}}(r) 2r , \]  

(II.1)

where \( r \) is the radius of a molecule (or “yardstick”), and \( N_{\text{ball}} \) is a number of “balls” covering this profile.

\[ N_{\text{ball}}(r) \sim 1/r^D , \]  

(II.2)

where \( D \) is the dimension of a system. For a regular profile \( D = 1 \), and the profile length remains always the same.
Scaling concept.

We shall calculate this dimension for the Koch curve constructed above. As a first step the curve was represented by four copies of itself scaled down by a factor of $1/3$. After $n$ steps we have $4^n$ copies scaled by a factor $3^{-n}$. The profile length can be measured after each step by one yardstick of the length $\lambda$, by four yardsticks of the length $\lambda/3$, by 16 yardsticks of the length $\lambda/9$, etc. Thence, a number of balls is given as a function of the ball size by

$$N_{\text{ball}} \left( \frac{\lambda}{2} \right) = 4^n = \left( \frac{1}{3^n} \right)^{\ln 4 / \ln 3}. \quad (\text{II.3})$$

Comparing eqs. (II.2) and (II.3), we come up then with

$$D = \ln 4 / \ln 3.$$

Fig.II.4. The Cantor dust.

We should note that the characteristic feature of the Koch curve is that it retains scaling invariance at every scale, and starting at every point of the curve.

Most crystal surfaces exhibit a weak disorder. They can be represented as step-fractals, or subfractals. The description of these system is also nontrivial, and to demonstrate this, we have chosen another classical example, i.e., the Cantor (or devil) staircase [2-4]. Using a simple example of the Cantor dust, it is easy to understand how the generator is chosen in this particular situation, and how the fractal dimension (not integer) can be calculated.

The Cantor dust is constructed as follows. An original interval of length $\lambda$ is cut in three equal pieces, and the middle one is removed. This procedure is repeated with each of the segments left, as illustrated by Fig.II.4. Calculation analogous to the first example of this chapter gives $D = \ln 2 / \ln 3$. The basis of the Cantor dust is so-called Cantor's set, which serves as a starting platform for the generation of a variety of different intricate structures.
We shall return now to the devil staircase, and consider how using the Cantor set one can compose one of the possible constructions. We take a box of some height $\delta$, and length $\lambda$, and choose a generator in the following way: plateau with the width of $\lambda/3$ is located at the half-height of the box (as it is drawn in Fig.II.5a). On the next stage, each of the steps is represented by the same construction scaled to the size of this step (Fig.II.5b). After already a few repetitions, a rather complicated structure is obtained. (It is not difficult to see that the generator used resembles very much the Cantor set, i.e., plateaus in this construction correspond to the removed segments in the example with the Cantor dust.) Some aspects make this system different from classical fractal systems (the Koch curve as an example). First of all Devil’s staircase is not a self-similar construction. Moreover, the actual dimension is position-dependent. The latter means that if we probe the interface with a progressively decaying yardstick at the plateau position, the local dimension will be equal to the topological dimension $D_{\text{top}} = 1$. The definition of the fractal dimension leads to $D = D_{\text{top}} = 1$, and can also be obtained by covering profiles in Fig.II.5 with balls and using
eqs.(1),(2) [2,3]. Thus the staircase has a finite length. However, the breakpoints remind about presence of irregularities. The latter can be characterized by a dimension $D_{\text{irreg}}$.

The value for $D_{\text{irreg}}$ is non-trivial. A possible interpretation [3] of this dimension is as follows. Consider the monolayer coverage of the profile by balls (spherical molecules) of the same size, and calculate pores' volume for sets of balls with progressively small radius. Under the term "pore" the volume around the curve that is not accessible to a ball of radius $r$ should be understood. Every end-point of a plateau produces an irregularity with some pore size.

The fractal dimension of these irregularities is then commensurate with the fractal dimension of the Cantor set, i.e., $D_{\text{irreg}} = \ln 2 / \ln 3$.

This or another staircase may serve as a basis for modeling the surface roughness. For example, it was shown that the equilibrium shape of the crystal facets is a subfractal of a type alike one considered above [8-11].

It has been demonstrated that the disorder (or irregularity) of an interface can be presented in different manners, having the same profile length and different fractal dimension, or just the other way around. Fig.II.6 visualizes this difference (picture is similar to [3, p.336]), showing different profiles of same length but different fractal dimensions. The smaller is the "negative" (or inaccessible) volume, the less is the fractal dimension of a profile.

Having considered a few examples of modeling the surface irregularities, we would like to demonstrate that for different systems the surface roughness can have different descriptions, which best corresponds with the nature of a system.
under consideration. One might consider capillary waves in liquid surfaces or surface fractality, or deal with almost "regular" surface irregularities in a weakly disordered or subfractal systems. But, the surface irregularity is an inherent property of every macroscopic body, whatever the fractal or non-fractal nature of the surface. In the above-models one common feature is essential - the scaling behavior of the irregularities. The scaling concept can be illustrated by a schematic picture given in Fig.II.7 (see, also, [12]).

Scaling of surface features alleviates the description of surface roughness at different length-scales, i.e., it allows to introduce some system into modeling of surface roughness for particles of different size. In the scaling description of surface irregularities there is always a lower and an upper limit for the important parameters characterizing the system. Generally, we can set up the upper limit at the characteristic system length, and the lower one at the atomic bond length. But, mostly, the real limits are not commensurate with these lengths, and depend on the system. For example, measuring monolayer adsorption, we will never get lower than, let say, the cross-section of nitrogen molecules. Modeling of surface
features below this limit is without any sense. Also, a system may be a fractal at a small length-scale, and non-fractal at larger scales (molecular roughness), or the way around. A good example is the microporous system, where the fractal regimes starts at the size of the maximal pore diameter, and goes down to the molecular level. An even more complicated situation may exist when different fractal laws are applied on different length-scales. An example of this is found in aggregates of colloidal particles (in silica, for instance), where a change of fractal dimension must necessarily occur at the transition from the bigger yardstick (on the length scale of an aggregate) to the smaller yardstick proportional to the size of primary particles.

II.2. Theoretical modeling of the interaction between rough surfaces.

In the previous section we have shown how even a rather simple generator can produce quite complex profiles. However, the study of the particle size effect in the interaction between colloidal particles is already so complicated that a model to be chosen for the description of surface roughness must make this study feasible. That is why, adhering to the scaling concept, we will further deal with a simplified view on the matter. In the kinetics of coagulation a random spatially homogeneous distribution, i.e. spherical symmetry of the boundary conditions and the interparticle forces, is assumed [13]. Strictly speaking, this implies completely "smooth" particle surfaces, i.e. homogeneous surface characteristics influencing the interaction of the particles. However, surface inhomogeneities will only become relevant for the interaction at interparticle distances of the order of the range of interacting forces. Because the mean distance between colloidal particles in the dispersion is much larger than the range of interaction, the treatment of coagulation kinetics in terms of numbers of effective binary collisions between Brownian particles in a homogeneous sol remains valid. Inhomogeneity of
surfaces is only affecting the detailed structure of the potential energy diagram for two colliding particles, but not the distribution of the trajectories, along which Brownian particles approach each other.

All the particles in our model colloid will have the same surface properties, double layer potentials, etc. The particles are monodisperse spheres of diameter \( d \). The surface roughness is superimposed as a uniform pattern of "waviness" or "hills" [14] on the sphericity of the particle surfaces. To represent the finer features of the surface texture, each of the hills is considered as a set of \( N \) steps and \( N \) plateaus of a characteristic width \( \lambda \) and height \( \delta \). Each of the plateaus, in turn, is then corrugated in the same way as the macroscopic surface of the particles, i.e. as the same set of steps and plateaus, scaled down according to the same law (Fig.II.8). The height of the steps \( \delta \) and the width of the plateaus \( \lambda \) are independent length scales. These can be adapted to represent different degrees of surface roughness. In such a model, the influence of the surface roughness on coagulation kinetics may be investigated under different experimental conditions, in particular when the characteristic range of interaction varies because of the changes in the electrolyte concentration.

Having introduced this description of roughness of the surfaces into the model, one may use the traditional DLVO theory, including Derjaguin's approximation to calculate the interaction between two "spherical" particles. However, we may not now change the summation over the surface elements (as per Derjaguin's
approximation) for the integration because of discrete structure of the surface
features. In slow coagulation the potential energy of interacting electrical double
layers will be described under the assumptions of low surface potential and a
constant surface charge [15-17]. Then, the interaction between quasi-flat elements
of the two surfaces is given by the energy density per surface unity (see Chapter I):

\[ u_{\text{attr}}(X) = \frac{A \kappa^2}{48\pi k_B T} \frac{1}{X^2} \equiv \frac{B}{X^2}, \]  

\[ u_{\text{rep}}(X) = \frac{2 c_0 N_A y_0^2}{\kappa} (\coth X - 1) \equiv G(\coth X - 1), \]

\[ X = x + 2\kappa a \sin^2 \left( \frac{\theta}{2} \right), \]

(Defining the quantities \( G = 2 c_0 N_A y_0^2 / \kappa \); \( B = A \kappa^2 / (48 \pi k_B T) \)).

Here, \( c_0 \) is electrolyte concentration in the intermicellar solution, \( N_A \) is Avogadro's
number, \( y_0 = z e \psi_0 / (k_B T) \), \( \psi_0 \) is the surface potential of a single particle, \( z \) is the
counterion valence, \( A \) is
Hamaker's constant, \( X \) is the
dimensionless distance between
two curved surfaces at azimuthal
angle \( \theta \). Eq.(II.4) represents the
energy density per unit area of
van der Waals forces, and
eq.(II.5) is the repulsion energy
density per unit area between the
surfaces with constant surface charge. Eq.(II.6) is the basis for the Derjaguin
approximation (valid for \( \kappa a > 1, x < 1 \)). The interaction forces in the system decay
rapidly with the distance between two surface elements. Therefore in eq.(II.6), the
interaction decreases strongly with increasing \( \theta \). Only the area of the surface near
to the line which connects the centers of two particles contributes significantly to
the interaction.

Fig.II.9. Maximal double-layer overlap.
Interaction between rough surfaces.

Usually, this significant surface area is described by introducing a (cutoff) azimuthal angle \( \vartheta_m \) (Fig. II.9). This is not only so for smooth particle surfaces of radius \( a \), but also for the corrugated surfaces of our model:

\[
\vartheta_m^2 = \frac{2}{\kappa a}.
\]  

(II.7)

The final step in the procedure is then the integration of the interaction energy over the significant area. Since the distances \( X \) for \( \vartheta > \vartheta_m \) are large relative to the range of interaction forces, the upper boundary of the integration may just as well be infinity. In the presence of an electrolyte the behavior of a van der Waals part of the potential energy changes drastically for \( x > 1 \). It decays exponentially with distance (see [27], chapter 7), resembling thereby the behavior of an electrostatic component. Therefore, an error introduced by using the cut-off angle in the calculations of the total energy can easily be estimated. It is of about 10% in each of the components. Moreover errors in both components nearly cancel each other. The interaction between the rough surfaces in our model is then obtained as the sum of interaction energies over all the sets of steps and plateaus which describe the surfaces of the particles. In this summation each plateau has its own height, size and position in space, which is determined by the topography of the underlying coarser structure, such as curvature of the particle surface. The number of complete sets of interacting plateaus, which contribute to the interaction energy, is determined by the degree of double layer overlap (Fig. II.10). It is, according to eq.(II.7), a function of particle
radii. For obtaining the total potential energy of interaction for a set which consists of \( N \) steps and \( N \) plateaus, we write, according to eqs. (II.4 - II.7)

\[
U_{\text{tot}}(x) = \sum_{\vartheta=0}^{\vartheta=0} \sum_{\alpha_i=0}^{N-1} \sum_{\alpha_n=0}^{N-1} G S_0 n(\vartheta) (\coth[x + z(\vartheta) + \alpha_1 \Delta_1 + \ldots + \alpha_n \Delta_n] - 1)
\]

\[
- \sum_{\vartheta=0}^{\vartheta=0} \sum_{\alpha_i=0}^{N-1} \sum_{\alpha_n=0}^{N-1} \frac{B S_0 n(\vartheta)}{[x + z(\vartheta) + \alpha_1 \Delta_1 + \ldots + \alpha_n \Delta_n]^2}
\]

with \( z(\vartheta) = \kappa a \vartheta^2/2 \), \( \Delta_i = \delta_i \kappa / 2 \), \( \delta_i \) is the height of step in \( i \)-set, \( S_0 \) is the surface area of plateau in the lower limit of scaling, \( \alpha_i \) is a running parameter, and \( n(\vartheta) \) is the coordination number of "hills" (Fig.II.11). This number is completely defined by the packing of the hills in the particle surface [18]. In this scaling approximation for the surface texture a step in the \( i \)-th set can always be represented in relation to the upper limit of scaling by:

\[
\Delta_i = \frac{\Delta_i}{N^{(i-1)}}.
\]

In the simplest version of the model, for \( N = 2 \) and constant \( S_0 \)

\[
U_{\text{tot}}(x) = G S_0 \sum_{\vartheta=0}^{\vartheta=0} \sum_{\alpha_i=0}^{1} \sum_{\alpha_n=0}^{1} n(\vartheta) (\coth[x + z(\vartheta) + \alpha_1 \Delta_1 + \ldots + \alpha_n \Delta_n] - 1)
\]

\[
- B S_0 \sum_{\vartheta=0}^{\vartheta=0} \sum_{\alpha_i=0}^{1} \sum_{\alpha_n=0}^{1} \frac{n(\vartheta)}{[x + z(\vartheta) + \alpha_1 \Delta_1 + \ldots + \alpha_n \Delta_n]^2}
\]

and
\[ \Delta_i = \frac{\Delta_1}{2^{(i-1)}}. \]  

(II.11)

In these equations \( z(\mathcal{G}) \) is a discrete function of \( \mathcal{G} \) which can separately be calculated for a specific roughness profile. For densely packed spherical caps, coordination numbers and corresponding distances from a reference hill to \( n \)-th neighbor are given in Table II.1.

<table>
<thead>
<tr>
<th>( n(\mathcal{G}) )</th>
<th>( \xi ) (distance to a neighbor)</th>
<th>( \mathcal{G} ) (corresponding to this distance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>central &quot;hill&quot;</td>
<td>( \xi [0,0] = 0 )</td>
<td>0</td>
</tr>
<tr>
<td>first coordination number</td>
<td>( \xi [0,1] = 2 \lambda )</td>
<td>( 2 \lambda / a )</td>
</tr>
<tr>
<td>second coordination number</td>
<td>( \xi [0,2] = 2\sqrt{3} \lambda )</td>
<td>( 2\sqrt{3} \lambda / a )</td>
</tr>
</tbody>
</table>

In principle, a number of sets \( \alpha_n \) can be infinite (as we have already mentioned above), however, there is always a lower and an upper limit of such a scaling. These limits determine the relevance of the chosen scaling regime for the description of the physical behavior of the system. In the DLVO description of slow coagulation the lower limit must be chosen at the interparticle distance where the pair interaction energy of colloidal particles has its maximum. If the particles succeeded to pass this maximum they coagulate very rapidly, and it is no use to model fine surface textures on this scale. Thus, surface roughness can only affect coagulation rate if its effect is measurable at this or larger interparticle distances. The upper limit becomes an additional free parameter in the geometrical description of the system. Both \( \lambda \) and \( n(\mathcal{G}) \) can be adapted to represent more closely the actual features of surface roughness.

If surface roughness is to be included into geometrical factor while calculating the total interaction energy, we must also measure the characteristic amplitude and
lateral length of irregularities by the "yardstick" of the characteristic range of the interaction forces. To apply the Derjaguin approximation for our elaboration, these additional roughness parameters have to satisfy the following relation

$$a > \lambda >> \delta \approx h/2.$$  \hspace{1cm} (II.12)

We have performed calculation for different sets of parameters representing diverse relation between particle's size and surface corrugations, and results are reported and discussed in the following section.


In this section we present the calculations of stability diagram, involving the surface irregularity, and compare those with the classical results. The stability ratio as a function of the electrolyte concentration can be obtained on the basis of eq.(I.17), where the hydrodynamic correction is left in its usual form (see eq.(I.64)), and eq.(II.10) is used for the pair interaction energy. The dense packing of the hills modeling the coarsest roughness details has completely determined $n(\mathcal{G})$ and $z(\mathcal{G})$ in eq.(II.10). To embrace different degrees of surface corrugation we have carried out calculations with different combinations of particle's size $d$, and the surface roughness parameters $\delta$ and $\lambda$. Here we represent results for two parameter sets, where set b) is typical for colloidal systems.
Particles with rather rough and uneven surface characteristics are described by the set:

a) \( T = 300 \, \text{K}, \, A = 2 \times 10^{-20} \, \text{J}, \, \psi_0 = 0.3 \) (\( \approx 8 \, \text{mV} \)), \( \delta_1 = 12 \, \text{nm} \), \( \delta_{\text{lower limit}} = 0.75 \, \text{nm} \), \( S_0 = 3.9 \times 10^{-15} \, \text{m}^2 \). The horizontal size of the upper limit set (Fig.II.8) was taken \( \lambda = 200 \, \text{nm} \) and scaled down with four steps.

Rather smooth particles are represented by the parameter set:

b) \( T = 300 \, \text{K}, \, A = 2 \times 10^{-20} \, \text{J}, \, \psi_0 = 0.8 \) (\( \approx 20 \, \text{mV} \)), \( \delta_1 = 3 \, \text{nm} \), \( \delta_{\text{lower limit}} = 0.19 \, \text{nm} \), \( S_0 = 7.7 \times 10^{-18} \, \text{m}^2 \). It was scaled down as in the previous case from \( \lambda = 8.8 \, \text{nm} \).

Stability diagrams corresponding to these two sets are plotted in Figs. II.12 and II.13, respectively. (Some points in Fig.II.12 are drawn to alleviate graph reading, and they should not be understood as an experimental verification.) These results can be compared with calculations based upon the classical version of the theory discussed in chapter.
one. For this purpose we shall use parameter set (b) that corresponds to truly colloidal system. The classical stability diagram for this case is plotted in Fig.II.14. It is quite obvious that diagrams in Figs. II.13 and II.14 have a totally different character. If surface roughness is accounted for, the slope of curves is almost insensitive to the variation of particle radii, and only for rather coarse dispersions the particle size dependence of log $W$ - log $c$ curves becomes pronounced.

However, for those (rather large) colloidal particles behavior of the stability ratio $W$ still departs very much from the case of an ideally smooth sphere. First of all, at a particular electrolyte concentration corrugated particles have much lower stability than ideal spheres, and also the log $W$ - log $c$ dependence deviates very much from the linear one (for details see [19]).

Another important feature of our modeling is the particle size dependence of such an important characteristic as the critical coagulation concentration ($c_c$). $c_c$ is higher for finer particles, and lower for coarser ones, what is demonstrated in Fig.II.15 being inset A of Fig.II13. This phenomenon that cannot be predicted by the classical theory, but found in experiments (see, for example, [20,21]), is called fractionated coagulation [21], and is used to separate large from small particles in bimodal distribution.

If dispersions are coarse enough (or surface roughness is rather fine), we see trends to the standard behavior of the stability diagram. This suggests, that the dependence of the stability ratio $W$ on the particle size, that is implied by the classical DLVO theory, can only be observed in two limiting cases. The first corresponds to rather small colloidal particles, when the characteristic
parameters of surface features fall below the lower limit of scaling. These particles may be considered as perfect spheres, and should behave in the way predicted by the DLVO theory. When the particle radius is rather large (second limiting case), the surface region corresponding to the overlap of two double layers will include a large number of hills setting up the upper limit of surface corrugation. Therefore, particle size (via number of hills in the overlap region) will significantly affect the interaction between surfaces of those particles. However, this is still a case of the interaction between rough surfaces, and it cannot be described in terms of pure particle size effect.

In the intermediate region of particle radii, i.e., for normal colloids, the stability ratio $W$ is only slightly sensitive to variations in particle size, because of surface roughness commensurate with the characteristic range of the interparticle forces. At close range the textural features of approaching particles begin to contribute to details of the interaction. At separations where the interaction energy reaches its maximum it is not the particle diameter $d$ (which is always very large relative to $h_{\text{max}}$) that makes the difference, but the geometry of hills (protrusions) determining roughness of the particle surfaces.

In slow coagulation the energy maximum is usually located at rather small interparticle distances. Thus, fine details of the surface structure are involved into description of the interaction energy. A scaling law defines then the size of surface irregularities which are relevant for the interaction between particles be they small or large. This can schematically be illustrated by

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Fig. II.16. Interparticle distance as a “yardstick” for surface features.
Fig.II.16. When the finer details of one single hill are the only relevant geometrical factor in the interaction, this nearly eliminates the influence of particle radius on the stability ratio.

At rather low electrolyte concentrations the electrostatic repulsion acts between all surface details of the particle surface in the overlap region. Thus, only the configuration of surface features defines whether the contribution of that or another asperity is significant for the particle interaction. A slight dependence of the stability ratio on the particle size comes from a difference in the overlap region for particles of different diameter. However, because the scaling behavior of surface irregularities is independent of particle size, this difference is not pronounced.

At rather high electrolyte concentrations, the situation becomes more complicated. The secondary minimum of the interaction energy is now found at rather short interparticle distances, and its contribution to the interaction must be accounted for. So, valleys of the surface corrugation can then experience an attractive interaction while protrusions repel each other. For rather coarse particles and sufficiently large valley area within the overlap region this may result in a lower stability ratio (than for finer particles) (Figs. II.12 and II.13). Of course, precise behavior of theoretical log \( W \) - log \( c \) curves depends on a model chosen for featuring the particle surface.

A simple criterion that separates stability curves with the slope being insensitive to particles’ diameter from curves with the particle size dependent slope can be derived [19]. It shows that the boundary between these regimes is at

\[
L = \frac{\lambda^2}{\delta d} = 1. \tag{II.13}
\]

This dimensionless quantity relates the surface area occupied by one (coarsest) roughness element (one hill) at the upper limit of the scaling regime to the surface region which contributes significantly to the interaction. When \( L \geq 1 \), we deal with one-hill regime of the interaction (schematically illustrated by
Fig. II.17). If the area of double layer overlap is large enough compared to the characteristic size of surface features, \( L \) becomes much smaller than one (\( L \to 0 \)), and the irregularities become almost negligible. All other situations correspond to the interaction between rough interfaces.

\[
S_{\text{overlap}} \sim \pi r_m^2 \sim \pi \delta d \quad S_{\text{hill bottom}} \sim \pi \lambda^2
\]

The calculations for a rather primitive model, which we have presented, may serve as a basis of the qualitative, physical understanding of the influence of surface irregularities on the dispersion stability, and elucidate the role of particle size in this problem. The derivation of eq.(II.13) is based upon spherical symmetry of colloidal particles at the macroscopic scale (spherically shaped colloidal particles), and it can scarcely be applied for colloidal particles of a complex geometry without modifications. Moreover, in the calculations of the pair interaction potential an averaging over all possible configurations of one surface with respect to the other is required. However, the configuration considered will have the greatest weight in the averaged interaction potential. As a circumstantial proof of this paper [22] may be referred to. Our description is based on a step-like model. However, this is not the only possibility. Other classes of generators may be used to describe the real situation more closely. As an example, those based on the Mandelbrot-Weierstrass function worth to be mentioned [23-26].
References.

III. Surface Roughness and Particle Size Effect on the Rate of Perikinetic Coagulation. Experimental.

III.1. *Surface roughness and a model electrostatically stabilized system.*

In this chapter experimental study of the coagulation kinetics in electrocratic suspension is combined with the direct observation of surface roughness. The coagulation kinetics can be followed using different experimental techniques, which are dependent of the system under investigation. Some are based on a simple particle count [1], while others take advantage of more sophisticated methods involving light scattering [2], transmittance [3], or absorbance [4] measurements. The influence of different parameters describing colloidal systems can be studied by varying one of those parameters, while others are kept constant. So, the Schulze-Hardy rule, for example, can be checked by changing the valency of a coagulating, indifferent electrolyte and looking at the concentrations where coagulation rates are equal [5]. In same manner, the influence of the particle size on the stability of dispersions is studied on colloidal dispersions with different particle size, while other parameters (nature of particles, surface characteristics, coagulating electrolyte, etc.) are kept the same.

Our experimental investigation of the particle size effect on the rate of Brownian coagulation is focussed on the role of surface roughness in the stability of monodisperse colloidal particles of different radii.

In the preceding chapter, we have analyzed on the basis of the DLVO theory which length-scales are relevant for the interaction of two colliding particles. It was concluded that the surface roughness (with reasonable average characteristics) rather than the particle size determines the geometrical factor in the interaction energy of approaching particles. The range of interaction forces
is of a very different order of magnitude than the particle radius, but certainly comparable to the characteristic parameters which describe the surface roughness of particles.

In general, the size of the corrugations on the surface of a particle is determined by other conditions than the particle size. Therefore surface roughness and particle size may be considered as independent characteristics of a colloidal system. Two different regimes can be distinguished. In most colloids the particles are large compared with the range of the interaction, whereas geometrical properties of the surface which are relevant for the strength of the interaction forces should be of the order of that range. The analysis showed that the geometry of the interaction between approaching particles is best described by a model in which smaller and smaller features (with the wavelength $2\lambda$ and amplitude $2\delta$) of the surface roughness become relevant as the interparticle distance ($h$) diminishes. In such systems the stability ($\log W - \log c$) diagrams have a slope that remains almost independent of particle size. The scaling aspect of the surface roughness determines the interaction energy of colliding particles as a function of their separation. The other regime is when particles are very small, or when the corrugations are very fine. Then the total interaction of the particles becomes related to the number of roughness waves - or "hills" - per unit area of particle surface. In this case the ratio $d/h$ determines how many of the individual hills participate in the interaction. In this second regime there is a rather strong dependence of the slope on the particle size. Although this might seem to resemble the classical result for perfect spheres in some aspects, the difference with the classical theory is that the strength of the interaction forces is not just related to the constants of van der Waals attraction and double-layer repulsion alone, but also depends strongly on the characteristics $\delta$ and $\lambda$ of the surface roughness.
Choice of a model system.

In the preceding chapter a situation was considered when the maximal double-layer overlap region includes about one "hill" of the coarsest surface corrugation. The surface roughness is an additional parameter for the system, and the maximal overlap depends on both the overall and local curvature (local curvature was imposed upon overall one). The relation between characteristic size of the surface features and area of the maximal double layer overlap is embodied in parameter $L = \frac{\lambda^2}{\delta d}$, with $d$ the particle diameter. The transition between the two above-discussed regimes is when the number $L$ is of the order 1. When the experimental conditions of coagulation are changed, e.g. when electrolytes are added to an electrocratic colloid and reduce the range of interaction, the characteristics of the relevant surface corrugations scale as the range of the surface forces. This should determine the appearance of log $W$ - log $c$ diagram.

To demonstrate the relevance of including the effect of surface roughness into the theory of colloid stability, our experiment explores the differences in stability diagrams for one and the same colloidal material, on both sides of predicted boundary at $L = \frac{\lambda^2}{\delta d} = 1$ between the two geometrical regimes.

For this a real colloid had to be found which can be used in the relevant experimental conditions. Most particles are very large compared with the range of their interaction, and their surfaces are, generally, not exceptionally smooth. Then, the surface roughness model predicts that the dependence of the stability diagram on the size of the particles is small. But, of course, it is the result that most coagulation experiments are known to show anyway. What we need is a real electrocratic colloid with a rather special combination of particle size and surface roughness, so that its coagulation can be studied on either side of the boundary at $L = 1$. The differences between the two types of stability diagrams for the two regimes of coagulation would then be predicted by our theory.
The surface roughness of particles is of sub-colloidal dimensions. It has almost never been quantified in the literature on coagulation rates and stability diagrams for colloidal materials. But for relating the size and also the surface roughness of particles with the range of interaction forces these characteristics must be measured. The characteristic dimensions $\delta$ and $\lambda$ of surface roughness are, almost by definition, much smaller than the particle size. Also, the roughness structure is (presumably) more or less independent of it. With very fine, monodisperse electrocratic colloidal systems, in which particles of different diameters $d$ can be obtained it should be possible to investigate the properties of the two regimes. Moreover, we wish to investigate a boundary between two geometrical regimes (one which would be a very special case) by measuring coagulation rates at different electrolyte concentrations with particles of different sizes. In that experiment the magnitude of $\delta$ and $\lambda$, which has to be related to the Debye length $1/\kappa$, and of diameter $d$ must be measured and known as independent variables.

Colloidal gold, prepared with the citrate method, is a sol which is well characterized [7-14]. It can be used for such an experiment. It has monodisperse particles of nanometer size. The diameter $d$ is determined by the number of nuclei generated during the preparation, and can be measured precisely from electron micrographs. Surface corrugations depend rather on the preparation, but not on the size of the particles. Gold particles have a high contrast in transmission electron microscopy. Details of their geometry can be identified (to a certain extent) at very high magnifications. It is then possible to measure $\delta$ and $\lambda$ of the surface roughness directly, well into the nanometer range of resolutions, and with the same methods as the diameter $d$. In gold sols it is, therefore, possible to evaluate $L$ without duplicities in the meaning of the lengths $d$, $\delta$ and $\lambda$, as could result from different measuring techniques. Fine surface irregularity of crystalline gold surfaces has been investigated [12,15], and the surface roughness of gold
surfaces can be described on the molecular scale as a fractal-step system [16]. Monodisperse colloidal gold particles can be prepared in the right size relative to the characteristics of the surface roughness and to the Debye length $\kappa^{-1}$, so that $L$ in coagulation experiments is just above or slightly below the transition at $L = 1$, depending on the particle size. Moreover, it is known that colloidal gold shows anomalous particle size effect on the critical coagulation concentration [11,17], which has never been explained satisfactorily.


Fig. III.1 is a representative micrograph of spherical particles in a monodisperse gold sol prepared with the citrate method (the average diameter is of about 42 nm). The preparation method [10] for obtaining monodisperse sols with chosen particle sizes uses concentrations of reducing agent which are much lower than in the earlier methods described by Turkevich et al. [8]. The citrate concentrations during the preparation determine the size of the monodisperse spherical particles. Series of standard colloids were prepared for our experiments in the range of particle diameters ($20 \text{ nm} < d < 100 \text{ nm}$). All suspensions were diluted to satisfy requirements of experiments based on light scattering techniques.
Particle diameter $d$ in the gold sols was measured with a Coulter N4 Submicron Analyzer, and also estimated from electron micrographs. The former technique (known as a Photon Correlation Spectroscopy) is based on measurements of the time auto-correlation function that supplies with an information about diffusion coefficient of a single particle (if dispersion is diluted enough). If particles are spherical, the diffusion coefficient can easily be recalculated into the particle radius using the Einstein-Stokes relation. A typical histogram is presented in Fig.III.2.

Electrophoretic mobilities of the sols were measured with a Coulter DELSA 440

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**Fig.III.2.** Typical particle size distribution in a sol.

**Fig.III.3.** A typical mobility measurement. Peaks on the left side are end of correlations.
Particle preparation and characterization.

instrument. This technique utilizes the Doppler effect for calculation of velocity of particles moving in an external field. The incident signal from a laser is compared with that scattered by dispersion, and the particle velocity is directly related to the shift in frequency of the received beam with respect to the original one. Typical results are represented by Fig. III.3 (where positions of peaks and the average mobility are given). Measurements of the electrophoretic mobility have been carried out in a very diluted dispersions, i.e. the solvent may be considered as a plane water.

Knowing the particle size, the electrophoretic mobilities can be recalculated into \( \zeta \)-potentials using Henry’s series [18] (in colloid stability experiments \( \zeta \)-potential is usually assigned to the surface electrostatic potential used in our theoretical elaboration).

Stable gold dispersions have clear colors, ranging from light orange for fine particles (with \( d \sim 15-20 \) nm) through saturated red-wine (with \( d \sim 40-50 \) nm) to grayish-violet for rather coarse suspensions (\( d \sim 100-150 \) nm). For such kind of colloids a rather important characteristic is the absorbance of light [19]. The absorption spectra of each colloid used in our experiments on coagulation kinetics were measured by a Shimadzu UV 150-02 double-beam spectrophotometer. These spectra (Fig. III.4) demonstrate once more that rather fine dispersions are monodisperse spheres (a perfect Gaussian shape of peaks), and that rather coarse
suspensions may have both a slight deviation in particle shape and a wider particle size distribution (slightly skewed peaks).

<table>
<thead>
<tr>
<th>sol</th>
<th>( d ), nm</th>
<th>( \mu ), ( \mu m-cm/V-s )</th>
<th>( \zeta ), mV</th>
<th>( l_{\text{max}} ), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>22±5</td>
<td>2.4±0.3</td>
<td>48±6</td>
<td>520</td>
</tr>
<tr>
<td>b</td>
<td>35±7</td>
<td>2.6±0.6</td>
<td>51±12</td>
<td>523</td>
</tr>
<tr>
<td>c</td>
<td>42±7</td>
<td>2.4±0.4</td>
<td>48±8</td>
<td>527</td>
</tr>
<tr>
<td>d</td>
<td>83±19</td>
<td>2.5±0.5</td>
<td>49±10</td>
<td>540</td>
</tr>
<tr>
<td>e</td>
<td>92±23</td>
<td>2.2±0.7</td>
<td>46±13</td>
<td>553</td>
</tr>
</tbody>
</table>

All these experimental data are collected in Table III.1. One may conclude that all sols chosen for the experiment on coagulation kinetics have almost the same characteristics. And, if an indifferent coagulating electrolyte is used, only the particle size can influence the course of the coagulation process.

The kinetics of coagulation was determined from the rate of change in the absorption spectrum of the sols, at different concentrations of 1-1 (indifferent) electrolyte (NaNO₃). The rate of decrease of the absorption maximum is proportional with the coagulation rate in these sols. The absorption spectra of the sols and the measured rates of coagulation were reproducible at each electrolyte concentration. The whole set of experiments was completed - from the preparation of series of standard colloids to the construction of stability diagrams - and then repeated with a newly prepared set of standard colloids, in order to establish the reproducibility of the experimental data.

At the adsorption maximum the Lambert-Beer law is obeyed by each sol. Before coagulation starts the extinction maximum is proportional to a number of the primary particles in the sol. To follow the kinetics of coagulation, we have recorded a decrease in the absorption maximum as a function of the time after addition of the coagulating electrolyte (see Fig. III.5). The rate of decrease (always extrapolated to \( t = 0 \)) is a measure of the coagulation rate [5,20].
Coagulation kinetics.

At a given concentration the stability factor $W$ is defined as the ratio of the rate of rapid coagulation at high electrolyte concentrations and the coagulation rate at that particular concentration. For electrolyte concentrations $c < c_c$ the stability ratio $W$ is obtained as the ratio of the rates of decrease of the absorption maximum at the concentrations $c$ and $c_c$. Plotting these results in stability diagrams, we obtained Fig.III.6 for five gold sols with different particle sizes.

Indeed, two regimes can be distinguished in Fig. III.6: one group of diagrams contains the smaller, and the other - the bigger particles. For the smaller particles the slopes of the stability curves may slightly depend on the particle size at relatively high electrolyte concentrations (near $c_c$). They level off, and bunch together at lower salt concentrations. In sols with coagulation times of the order of minutes ($W$ is typically about 10) they are almost independent of the particle sizes in the colloids $a$, $b$ and $c$. 

Fig.III.5. Extinction as a function of time after addition of the coagulating electrolyte.
The diagrams for the coarser particles indicate lower $c_c$ values, and much steeper slopes. The stability diagrams for the finer and the coarser sols intersect near $W \sim 100$. This is at electrolyte concentrations which are smaller than $c_c$ by an order of magnitude. The Debye length $\kappa^{-1}$ where the diagrams of the coarser and the finer sols intersect is of about $6 \div 7$ nm.

In the range of electrolyte concentrations between $c_c$ for the smaller particles and the intersection of the diagrams there is a possibility for fractionated coagulation, which is when coarser particles can be coagulated out of polydisperse sols [11].

It is quite obvious that the qualitative behavior of the stability diagram measured experimentally resembles very much that one calculated theoretically in previous chapter. To prove that the two different types of log $W$ - log $c$ curves reflect the postulated impact of the surface roughness on the kinetics of slow coagulation we must measure the relevant length parameters $d$, $\lambda$, and $\delta$ for the particles, and show that the boundary between the two regimes lies at $L = 1$.

### III.3. Particle size and surface roughness.

Although the techniques have already been developed to measure surface roughness on the molecular scale [15,21-23], characterization of surface details
of colloidal particles on a nanometer scale is still troublesome. It is known for example, that beads of colloidal gold are used for a calibration of such instruments as a scanning tunneling microscope [24]. Therefore, a procedure has to be developed that will allow us to pull out some information about characteristics of surface features on the scale of colloidal forces’ range.

Fig III.7 illustrates how the surface profile can be extracted from a high resolution TEM micrograph of a gold particle from one of our sols. Transmission electron microscopy became a standard tool for direct observation of colloidal particles on a nanometer scale [12,13]. The original high contrast micrograph (magnification 500,000) is processed electronically into a "trace profile", that traces the projection of the particle on the background. From each colloid a large number of particles was scanned in this way. The trace profiles contain the information about the particle diameter $d$ and the corrugation parameters $\lambda$ and $\delta$ [6].

The average particle diameter $d$ and the standard deviation in each sol were obtained as the mean of the inscribed and the circumscribed circle diameters for the trace profiles. These values checked with the experimentally determined particle sizes of the sols.

We have introduced the range of the double-layer repulsion as a yardstick for the characterization of the surface roughness. Such a yardstick is the same and applicable in each individual sol, independent of the particle size. Our interest lies in the range of electrolyte concentrations where there is a distinct effect of the
particle size $d$ on the stability diagrams of Fig.III.6, i.e., $3 < c < 30$ mmol/L. Aspects of the surface roughness can only play a role in colloid stability when they are commensurate with the interparticle distance at the maximum in the potential energy of two colliding particles in this range of electrolyte concentration. The order of this distance is determined by $\kappa^{-1}$. Using predictions of our theoretical approach, the yardstick $\lambda$ can be defined as the maximal overlap of two double layers around particles where the slope of log $W$ - log $c$ curves is almost independent of particle radii. In our experimental span of parameters this gives the lateral yardstick in the range (as defined in the DLVO theory) between 4 and 10 nm.

The concentration range where the interception of two very different sets of log $W$ - log $c$ curves occurs is very interesting. In this region of electrolyte concentrations the surface structure of particles with different diameters renders the interparticle interaction in the same way. This is possible when the interaction between particles of different size is determined by the one hill-regime, i.e., with only one hill trapped in the maximum overlap region. In this way, the largest corrugation wave that is relevant for the stability diagram (i.e., of the order of the Debye length) defines, actually, the yardstick $\lambda$. The lateral length that follows from this consideration is of about 7-8 nm.

One can see that the selection of one cut-off value as a yardstick to be applied in all the sols is a bit arbitrary. For the finest sols the particle radius and the Debye lengths in the investigated range of concentrations differ only by a factor of 3. We have chosen $\lambda = 7$ nm (in proportion with the range of the double-layer repulsion) as our yardstick for the corrugations on the surface of the particles. Should we have selected another constant yardstick in our range than it would be found that the measured amplitude $\delta$ would be changed accordingly so that the particle size
where \( L = 1 \) is hardly affected. We have verified that by calculating \( L \) with different values of \( \lambda \).

To obtain the roughness characteristics of the particles from the trace profiles we compared the real trace profile and an ideal arc of a curvature \( R_i \). The arc and the trace profile had both a common chord of length \( 2\lambda = 14 \text{ nm} \). The amplitude \( \delta \) of the largest relevant corrugation mode follows then - geometrically - from \( \delta_i = 1/2 \left( R_i - \left(R_i^2 - \lambda^2\right)^{1/2} \right) \), where \( R_i \) is a local curvature of the idealized profile (Fig.III.8).

Locally, the curvature of the trace profile, and, as a consequence, also the corresponding amplitude \( \delta \) vary over the projection of the particle. Therefore \( \delta \) was averaged for all the values from each particle out of one sol. Also, values of \( L \) were calculated in the same way. All results are represented in Table III.2.

### Table III.2. Particle size and roughness characteristics

<table>
<thead>
<tr>
<th>sol</th>
<th>( d, \text{ nm} )</th>
<th>( \delta, \text{ nm} )</th>
<th>( L = \lambda^2 / d\delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>29±1.3</td>
<td>0.76±0.11</td>
<td>2.20±0.28</td>
</tr>
<tr>
<td>( b )</td>
<td>38±1.3</td>
<td>0.70±0.15</td>
<td>1.80±0.29</td>
</tr>
<tr>
<td>( c )</td>
<td>55±1.7</td>
<td>0.62±0.13</td>
<td>1.44±0.21</td>
</tr>
<tr>
<td>( d )</td>
<td>85±3.7</td>
<td>0.62±0.09</td>
<td>0.93±0.12</td>
</tr>
<tr>
<td>( e )</td>
<td>99±3.3</td>
<td>0.62±0.11</td>
<td>0.80±0.14</td>
</tr>
</tbody>
</table>

### III.4. Comparison of experimental results with the theoretical predictions.

The results of the experiments are summarized in Fig.III.6 and Table III.2. We have already noticed that the stability diagrams for the different monodisperse
Experimental results, and comparison with theory.

Gold sols form two distinct groups - for coarser and for finer colloids. The difference in the critical coagulation concentration $c_c$ for the two groups had already been described before, and our data reproduce the earlier result [11] quite well.

The most striking feature of the stability diagrams is, that, although particle sizes and electrolyte concentrations are varied in a continuous fashion, there is a sudden transition in the shape of the log $W$-log $c$ curves at a particle size of approximately $d = 70$ nm.

The combination of these two observations shows that the transition is indeed at $L = 1$, and it means [6] that at this transition there must be a change from the situation where the interaction is dominated by one "hill" of roughness on the surfaces of the smaller particles, to that which is representative for larger, relatively smooth spherical particles. For these coarser particles the curvature of the surface determines the number of "hills" participating in the interaction. With the smaller particles all the hills but one have disappeared below the horizon of the interaction range. It must be noted here that our model colloid was chosen because the particle surfaces were known to be extremely smooth. In most colloids the surface details are at least one order of magnitude larger in comparable circumstances. This is why in all these colloids the interaction is, again, dominated by one characteristic "hill" in the surface roughness geometry, and then the rate of coagulation becomes independent of the particle size like in the sols $a$, $b$ and $c$ of our experiment.

We have attempted to further probe the relevance of surface corrugations in a quantitative theoretical calculation of stability diagram from the available experimental data. For these computations the Hamaker constant, which determines, actually, the attractive component, must be known. An effective value of this characteristic can be found using a classical route, i.e., by setting $W = 1$ at the critical coagulation concentration $c_c$ for a colloid. We can use the
Experimental results, and comparison with theory.

![Diagram](image)

Fig. III.9. Theoretical stability diagram computed with parameters measured.

Experimental data from Table 1 for colloid particles of 42 nm, for example, and introduce all parameters into our "scaling" model of the chapter two (see also [6]). The surface roughness is described by the experimental characteristics $\delta$ and $\lambda$ for the upper cutoff values. Scaling procedure was repeated exactly as in chapter two, giving for the lower limit plateau a surface area of 10 nm$^2$. In this way the experimental value $A = 1.1 \cdot 10^{-19}$ J is obtained. With this $A$ as a constant (see, however, [17]) it is possible to reconstruct theoretical stability diagrams for all sols used in experiments. Two representative colloids with particles' diameter 42 and 83 nanometers have been chosen.

In our calculations the model of a constant surface potential has been used, which is a rather good approximation in the case of metallic particles (see Chapter I). The result is shown in Fig. III.9.

III. Conclusions.

In an experiment with spherical monodisperse colloidal gold particles there is a sudden transition in the shape of the log $W$ - log $c$ diagrams which are measured for finer and for coarser sols. The surface roughness of the gold particles, as characterized by the length scales $\lambda$ and $\delta$ is independent of the particle diameters $d$. The transition occurs at $L = \lambda^2/\delta d = 1$. This is what would be expected when
the surface roughness of the particles, rather than their average particle size, determines the geometrical aspects of the interparticle interaction in the kinetics of slow Brownian coagulation of electrostatically stabilized colloidal particles. Moreover, comparison of the experimental stability diagram (Fig.III.6) with theoretical one (Fig.III.8) shows that it becomes possible to fit theoretically the experimental data without the need for any adaptable parameter.

References.

20. H. Reerink, "De Uitvloksnelheid als Criterium voor de Stabiliteit van de Zilverjodensolen."
References.

IV.1. Theses.

The Conclusions of this dissertation can be given in a form of the following theses:

i) The particle size effect in the stability diagrams for lyophobic colloids, that is predicted by the DLVO theory, is, generally an artifact, which has been introduced by the Derjaguin approximation.

In the Derjaguin method the particle size is introduced into the theory as the only relevant length scale for the description of the particle geometry near the point of a closest approach of two surfaces. The relevant geometrical yardstick, however, must be that which is commensurate with the range of the interparticle forces.

ii) In electrocratic colloids the relevant length scale is set up by the range of the electrostatic interaction, and is typically of the order of a few nanometers. This determines the upper limit in the description of the local surface geometry which renders the interparticle interaction.

The surface of colloidal particles is never ideal, i.e., some irregularities are always present. These surface corrugations have to be looked at through a prism of the colloidal forces. So, the particle size effect can only enter (as the main geometrical parameter) into the interaction energy when surface roughness is shallow compared to the characteristic length of the interaction.
iii) For most colloidal systems surface protrusions rather than the overall particle curvature (radius) determine a geometrical factor in the interaction energy of a couple of colloidal particles.

Which features of the surface texture must be included into the computation of the interaction forces between particles depends on the distance $H$ between particles' surfaces. In a stability diagram the slope of $\log W - \log c$ curves, and values of the critical coagulation concentration are determined by the surface details with characteristic sizes between the upper and lower limits of the scaling description. They are defined, respectively, by the Debye length (as the range of an electrostatic component of the interaction) and the interparticle distance corresponding to the maximum of the electrostatic barrier. If the particles overcome this barrier, nothing can alter a course of the coagulation anymore.

iv) Particle size effect can only be seen in colloids consisting of rather coarse, or, contrary, of very fine particles.

The former case falls within the frame of our phenomenological description. The particle size effect can be significant, but it is expressed through a number of coarsest features trapped within a region of the maximal double-layer overlap, which depends on the overall curvature, i.e., the particle radius. In very fine dispersions, the particle radius may be commensurate with the range of the interparticle forces, and,
therefore, its effect on the interaction should be pronounced.

v) A rather simple criterion has been derived to discriminate between situations when the particle size effect is significant, and when the interaction is altered by surface corrugations sufficiently.

We have derived a dimensionless construction that joined relations between characteristic lateral and horizontal lengths of a "coarsest corrugation", and the particle size. This elaboration has been made for $\kappa a > 1$. Therefore, this criterion indicates when particles become coarse enough to make the interaction energy sensitive not only to local surface features, but, also, to the area of the surface periphery, participating in the interaction.

vi) New important parameters introduced into a standard theory should not be used as fitting variables (constants), but measured independently in well-defined experiments.

Very often in experiments on coagulation kinetics, stability diagrams are measured and then fitted using additional parameters, which adopt one or other new feature prescribed to a system. However, there may be different reasons why this system deviates from the behavior expected according to the standard consideration. Only independent experiments can reveal whether a new parameter is relevant for the process under consideration, or there is something else which is what bothers the system.
Het is algemeen gebruikelijk om de stabiliteit van colloïdale systemen op basis van de klassieke (DLVO) theorie te beschrijven. Deze theorie kan de manier waarop de vertragingsfactor $W$ (of de uitvloktijd $T \sim W$) afhangt van belangrijke experimentele factoren (zoals de elektrolytconcentratie, de oppervlaktebelading/oppervlaktepotential, de Hamakerconstante, enz.) voorspellen.

Volgens deze theorie moet ook de deeltjesgrootte een sterke invloed op de vertragingsfactor hebben: dispersies, bij gelijke samenstelling, zijn stabiler als de deeltjesstraal groter is. Echter, experimenteel is dat effect nooit gevonden.

Daarom zijn er inmiddels verschillende uitbreidingen van de theorie voorgesteld, maar ze konden de situatie alleen voor specifieke systemen verbeteren.

In het klassieke model wordt meestal verondersteld, dat colloïdale deeltjes perfecte bollen zijn. Dit heeft als gevolg, dat de deeltjesstraal $a$ als de enige relevante lengteschaal in de interactieenergie voorkomt. Reële colloïdale deeltjes zijn nooit perfect: er zijn andere lengteschalen (kromtestralen) in de oppervlaktegeometrie, die vergelijkbaar met de karakteristieke reikwijdte van de interactiekkrachten kunnen zijn. Deze oppervlaktegeometrie beschrijven eerder de oppervlakteruwwedheid dan de vorm van de colloïdale deeltjes. Juist details van de geometrie die vergelijkbaar zijn met de reikwijdte van de interactie tussen twee deeltjes kunnen de karakteristieke uitvloktijd $T$ sterk beïnvloeden.

Het modelleren van de oppervlakteruwwedheid is in onze benadering op een zogenaamd "schaalconcept" gebaseerd. De oppervlakteruwwedheid heeft een complex karakter. Er zijn oppervlaktegeometrie aanwezig op verschillende lengteschalen. Maar voor de stabiliteit van colloïdale deeltjes zijn alleen die relevant welke van de orde van de reikwijdte van colloïdale krachten zijn. Deze
reikwijdte wordt bij electrocratische colloïden door de Debijelengte $\kappa^{-1}$ bepaald.
Feitelijk bepaalt deze lengte een karakteristieke bovengrens in onze beschrijving van de oppervlakteruwheid.

Berekeningen laten zien, dat de wisselwerking tussen twee deeltjes bijna ongevoelig wordt voor veranderingen van de deeltjesstraal, in een vrij breed interval van deeltjesgroottes. Voor dat hele interval wordt de interactie tussen deeltjes door oppervlaktedetails van dezelfde grootte orde bepaald. Dus oppervlakteruwheid verbergt het effect van de deeltjesgrootte.

Bij een bepaalde kritische waarde van de deeltjesstraal komt er een nieuwe lengteschaal in de theorie, die resulteert in een overgang naar een ander type stabiliteitsdiagram. Hoe zo'n diagram eruit ziet hangt af van de verhouding tussen de deeltjesstraal en de structuur van de ruwheid. De overgang tussen de (twee) verschillende regimes kunnen we voorspellen op basis van karakteristieke parameters die de oppervlakteruwheid beschrijven. Dat is door de waarde van het dimensieloze getal $L$ gegeven

$$L = \frac{\lambda^2}{d\delta}$$

met $d =$ deeltjesdiameter,

$\lambda = $ karakteristieke "golflengte" van de ruwheid,

$\delta = $ karakteristieke "amplitude" van de ruwheid.

Het is duidelijk dat zo'n criterium een belangrijk rol kan spelen in technologische processen. Wij hebben dit expliciet bevestigd voor één modelsysteem.

In een goudsol kan de deeltjesstraal de enige variërende parameter zijn. Experimenten met een serie goudsolen van verschillende deeltjesgrootte laten zonder twijfel zien dat het genoemde criterium werkt. Voor $L < 1$, dus bij extreem gladde oppervlakken (ergelijkbaar met de deeltjesgrootte), wordt $W$ afhankelijk van de deeltjesstraal. In normale dispersies, met de deeltjesgrootte tussen 100 nm en 1 $\mu$m, is de oppervlakteruwheid altijd van de orde van
Samenvatting.

(tientallen) nanometers (de typische schaal van de colloïdale krachten). Dit heeft tot gevolg, dat de oppervlakteruwheid de interactie tussen colloïdale deeltjes bepaalt. Er kan wel (voor \( L < 1 \)) een effect van de deeltjesgrootte aanwezig zijn, maar dit wordt uitgedrukt in termen van het aantal "ruwheidskoppen", dat aan de wisselwerking tussen twee oppervlakken bijdraagt.

Experimenten met het colloïdale goud laten zien dat het opnemen van de oppervlakteruwheid in de berekening van de potentiële energie de discrepantie tussen theoretische resultaten en de experimentele gegevens elimineert.
Appendix A. Basic definitions in the theory of functionals.

In this appendix the basic definitions and transformation rules of the functional theory, which are involved into description of the diffusion approach to the random processes, will shortly be listed.

A.1. Definitions and examples

First, we will define what is the functional. Following some determined rule, the functional relates a function to a number. The simplest example is

\[ F[\varphi(t)] = \int_{t_i}^{t_f} dt a(t)\varphi(t) \]  

(A.1)

where \( a(t) \) is a known function. Also, a more complex relation can be defined as

\[ F[\varphi(t)] = \int_{\tau_i}^{\tau_f} d\tau_1 d\tau_2 B(\tau_1, \tau_2)\varphi(\tau_1)\varphi(\tau_2) \]  

(A.2)

or

\[ F[\varphi(t)] = f(G[\varphi]) \]  

(A.3)

where \( f \) is a function, and \( G \) is a functional. We can define now the functional derivative, evaluating the difference in the same functional at two points (for two functions) \( \varphi(\tau) \) and \( \varphi(\tau) + \delta \varphi(\tau) \), where \( \delta \varphi(\tau) \neq 0 \) when \( t - 1/2 \Delta t < \tau < t + 1/2 \Delta t \). The variation of a functional is the linear with \( \delta \varphi(\tau) \) term in the difference

\[ \delta F[\varphi] = \{ F[\varphi + \delta \varphi] - F[\varphi] \} \]

which can schematically be

![Diagram of function perturbation](image)

Fig.A.1. Perturbation of function \( \varphi \) on the interval \( \Delta t \).
explained by Fig.A.1, where a perturbation of $\phi(\tau)$ on the interval $\Delta t$ is shown.

The functional derivative is called the following relation

$$\frac{\delta F[\phi]}{\delta \phi} = \lim_{\Delta t \to 0} \frac{\delta F[\phi]}{\int_{-\Delta t}^{+\Delta t} d\tau \delta \phi} \quad . \quad (A.4)$$

Using the above definitions, the variations and the functional derivatives can be calculated for examples (A.1-A.3).

Case (A.1);

$$\delta F = \int_{t_1}^{t_2} d\tau a(\tau) \delta \phi(\tau) = \int_{-1/2\Delta t}^{1/2\Delta t} d\tau a(\tau) \delta \phi(\tau)$$

According to the mean value theorem (see elsewhere [1]), which is applicable if $a(t)$ and its first derivative are continuous on the integration interval, we may write

$$\delta F = a(t') \int_{\Delta t} d\tau \delta \phi(\tau), t' \in [t_1, t_2] .$$

Substituting this expression into the definition of the functional derivative, we arrive at

$$\frac{\delta F[\phi]}{\delta \phi(t)} = a(t) . \quad (A.5)$$

Case (A.2) yields

$$\frac{\delta F[\phi]}{\delta \phi(t)} = \int_{t_1}^{t_2} d\tau [B(\tau,t)+B(t,\tau)] \phi(\tau) = 2 \int_{t_1}^{t_2} d\tau B(\tau,t) \phi(\tau) , \quad (A.6)$$

where symmetrical kernel $B$ suits most of the physical problems.

For the last case (A.3) we readily derive

$$\frac{\delta F[\phi]}{\delta \phi(t)} = \frac{\partial}{\partial \phi(t)} F_1[\phi] G[\phi(t)] , \quad (A.7)$$

The functional derivative satisfies also the following relations

$$\frac{\delta}{\delta \phi(t)} F_1[\phi] F_2[\phi] = F_1[\phi] \frac{\delta}{\delta \phi(t)} F_2[\phi] + F_2[\phi] \frac{\delta}{\delta \phi(t)} F_1[\phi] , \quad (A.8)$$
and
\[
\frac{\delta \phi(\tau_0)}{\delta \phi(\tau)} = \delta(\tau - \tau_0) \quad .
\] (A.9)

As an example consider the functional of a type given by eq.(A.3)
\[
F[\phi] = \int_0^t d\tau \mathcal{Z}(\tau, \phi(\tau), \frac{d\phi(\tau)}{d\tau})
\]

which is often encountered in the problems concerning the distribution of coordinates and impulses in many-component systems.

The functional derivative of this functional can be found using the above relations
\[
\frac{\delta F[\phi]}{\delta \phi(t)}^{(A.7)} = \int dt \left[ \frac{\partial }{\partial \phi} \mathcal{Z} + \frac{\partial }{\partial \phi} \frac{d}{d\tau} \right] \frac{\delta \phi(t)}{\delta \phi(t)}^{(A.9)} = \int dt \left[ \frac{\partial }{\partial \phi} \mathcal{Z} + \frac{\partial }{\partial \phi} \frac{d}{d\tau} \right] \delta(\tau - t) =
\]
\[
= \left( - \frac{d}{dt} \frac{\partial }{\partial \phi} + \frac{\partial }{\partial \phi} \right) \mathcal{Z}(t, \phi(t), \frac{d\phi(t)}{dt}) .
\]

Having introduced the functional derivative, and evaluated a few examples, we can also define the Taylor expansion in a series with respect to a small parameter \( \eta \to 0 \) for an arbitrary functional that
\[
F[\phi(t) + \eta(t)] = \exp \left\{ \int dt \eta(t) \frac{\delta}{\delta \phi(t)} \right\} F[\phi(t)] ,
\] (A.10)

where under the exponential we have to understand an operator written as
\[
\exp \left\{ \int dt \eta(t) \frac{\delta}{\delta \phi(t)} \right\} = 1 + \int dt \eta(t) \frac{\delta}{\delta \phi(t)} + \frac{1}{2!} \int dt dt_1 \eta(t_1) \eta(t_2) \frac{\delta^2}{\delta \phi(t_1) \delta \phi(t_2)} + ... =
\]
\[
= 1 + \int dt \eta(t) \frac{\delta}{\delta \phi(t)} + \frac{1}{2!} \left\{ \int dt \frac{\delta}{\delta \phi(t)} \right\}^2 + ...
\] (A.11)

The last property, that we need to manipulate with expressions containing functionals, concerns a transformation of the functional derivatives at the
functional transition to new variables. We define the following substitution of variables

$$\varphi(t) = G[\psi(\tau); t]$$ and $$F[\varphi(\tau)] = F[G[\psi(\eta); \tau]] = F[\psi(\tau)].$$ \hfill (A.12)

It can be shown that [2]

$$\frac{\delta F[\psi(\tau)]}{\delta \varphi(t)} = \int dt' \frac{\delta F[\varphi(t')]}{\delta \varphi(t')} \frac{\delta G[\psi(\eta); t']}{\delta \psi(t)}. \hfill (A.13)$$

For example, consider the transition from the functional argument to its Fourier transformation

$$\varphi(t) = \int d\omega \: \psi(\omega) \: \exp(i\omega t) = \varphi[\psi(\omega); t].$$

Then

$$\frac{\delta \varphi[\psi(\omega); t]}{\delta \psi(\omega')} = \exp(i\omega't),$$

whence

$$\frac{\delta F[\varphi(\psi(\omega); t)]}{\delta \psi(\omega')} = \int dt' \frac{\delta F[\varphi(t')]}{\delta \varphi(t')} \exp(i\omega't). \hfill (A.14)$$


The random variable $\xi$ is completely characterized by its characteristic function defined as follows

$$\chi(\lambda) = \langle \exp(i\lambda \xi) \rangle \hfill (A.15)$$

with $\lambda$ an arbitrary variable. Using this function, we can obtain the probability density with the Fourier transformation as well as all moments

$$\langle \xi^n \rangle = \left( \frac{1}{i} \frac{d}{d\lambda} \right)^n \chi(\lambda) \bigg|_{\lambda=0}, \hfill (A.16)$$
cumulants (semi-invariants)
Characteristic functional.

\[ K_n = \left( \frac{1}{i} \frac{d}{d\lambda} \right)^n \ln[\chi(\lambda)] \bigg|_{\lambda=0} \quad (A.17) \]

etc. These are very important characteristics in the description of random processes [2-4].

In the case of many dimensional variables \( \xi = (\xi_1, \ldots, \xi_n) \) we can write

\[ \chi(\lambda) = \langle \exp \left( i \sum_k \lambda_k \xi_k \right) \rangle . \quad (A.18) \]

Corresponding cooperative probability density results from the Fourier transformation of the characteristic function

\[ P(x_1, \ldots, x_n) = \frac{1}{(2\pi)^n} \int d\lambda_1 \ldots d\lambda_n \chi(\lambda_1, \ldots, \lambda_n) \exp \left( -i \sum_k \lambda_k x_k \right) = \langle \delta(\xi_1 - x_1) \ldots \delta(\xi_n - x_n) \rangle \quad (A.19) \]

In the same way the characteristic functional can be defined for the random function of a continuous type \( z(t) \)

\[ \Xi [v] = \langle \exp \left( i \int d\tau \ v(\tau) \ z(\tau) \right) \rangle \quad (A.20) \]

where \( v(\tau) \) is an arbitrary "good" function. All characteristics can be determined in the same way; moments, for example, are given by

\[ \left( \frac{1}{i} \right)^n \frac{\delta}{\delta v(t_1)} \ldots \frac{\delta}{\delta v(t_n)} \Xi . \quad (A.21) \]
Appendix B. Diffusion approximation in the description of the random processes.

In this appendix the Einstein-Fokker equation corresponding to its Langevin analogue with a Gaussian random force field is deduced. In our derivation we follow the method described in [3], although it is not only approach and other formalisms can be used.

B.1. The Einstein-Fokker equation. I.

Consider some variable $\xi(t) = \{\xi_1(t), ..., \xi_n(t)\}$ which obeys the following set of equations

$$\frac{d\xi_i(t)}{dt} = v_i(x, t) + f_i(x, t) ,$$

with $\xi(0) = \xi_0$, and $v_i(\xi, t)$ are some determined functions, but $f_i(\xi, t)$ are random functions of $(n + 1)$ variables, which satisfy the following conditions:

- $f_i(x, t)$ is a random Gaussian field in $(n + 1)$ dimensional space $(x, t)$;
- $\langle f_i(x, t) \rangle = 0$.

All the statistical characteristics of this field are completely described by its correlation tensor

$$B_{ij}(x, t; x', t') = \langle f_i(x, t) f_j(x', t') \rangle$$

where the averaging is taken over all possible realizations of field $f = \{f_i\}$.

$\xi_i(t)$ depends on $f_i(x, t)$ only in a finite time interval $0 \leq t' \leq t$, and as a consequence

$$\frac{\delta \xi_i(t)}{\delta f_i(x, t)} = 0, t' < 0, t' > t .$$

(B.2)
This is so-called the causality condition, i.e., our process depends only on a “short” history, but does not on pre-history and future.

The general solution of eq.(B.1) can be written as

\[ \xi_i(t) = \xi_{i0} + \int_0^t \int dx' \left[ v_i(x', \tau) + f_i(x', \tau) \right] \delta(x' - \xi'(\tau)) . \] (B.3)

We introduce now the probability density for solution \( \xi(t) \) of the system (1).

\[ P_t(x) = \langle \delta(x - \xi(t)) \rangle \] (B.4)

where \( \xi(t) \) is a solution of the set (B.1) which corresponds the determined realization of \( \mathbf{f}(x, t) \), and the averaging is taken over all possible realizations of \( \mathbf{f} \).

We differentiate eq.(B.4) with respect to \( t \)

\[ \frac{\partial P_t(x)}{\partial t} = -\frac{\partial}{\partial x_k} < v_k(\xi(t), t) + f_k(\xi(t), t) \delta(x - \xi(t)) >, \] (B.5)

with summation over repeating indices, and substitution of eq.(B.1). Using properties of \( \delta \)-function, and liberating the nonrandom components (which stay under averaging), we can write

\[ \frac{\partial P_t(x)}{\partial t} = -\frac{\partial}{\partial x_k} \{ v_k(\xi(t), t)P_t(x) \} - \frac{\partial}{\partial x_k} < f_k(\xi(t), t)\delta(x - \xi(t)) >. \] (B.6)

The last term on the r.h.s. represents correlations of \( \mathbf{f}(x, t) \), with \( \delta(x - \xi(t)) \) which depends on the solution of eq.(B.1), and, as a consequence, is a function of \( \mathbf{f} \). Our next task is the calculation of that average.

**B.2. The average value of the multiplication of two functionals.**

To obtain equation for the probability of the realization of \( \xi \), we have to evaluate the average on the r.h.s. of eq.(B.6). The consideration here will be restricted to the one-dimensional case, and the final result can be generalized on the many-dimensional variables.
Consider an average \( <F[z(\tau)] \cdot R[z(\tau)]> \), where \( F[z(\tau)] \) depends explicitly on \( z(\tau) \), and \( R[z(\tau)] \) does not necessarily depend on \( z(\tau) \) directly. We shall calculate \( <F[z(\tau)] \cdot R[z(\tau) + \eta(\tau)]> \) (where \( \eta(\tau) \) is a known function), and the needed correlations are obtained letting \( \eta(\tau) \equiv 0 \).

Functional \( R[z(\tau) + \eta(\tau)] \) can be expanded into the functional Taylor series in terms of \( z(\tau) \)

\[
R[z(\tau) + \eta(\tau)] = \exp \left\{ \int d\tau z(\tau) \frac{\delta}{\delta \eta(\tau)} \right\} R[\eta(\tau)]
\]

or

\[
<F[z]R[z + \eta]> = <F[z] \exp \left\{ \int d\tau z(\tau) \frac{\delta}{\delta \eta(\tau)} \right\} > R[\eta].
\]

It is convenient now to introduce a new functional

\[
\Omega[v(\tau)] = \frac{<F[z(\tau)] \exp \left\{ \int d\tau z(\tau)v(\tau) \right\}>}{<\exp \left\{ \int d\tau z(\tau)v(\tau) \right\}>}.
\]

Then eq.(B.7) can be cast as

\[
<F[z]R[z + \eta]> = \Omega \left[ \frac{\delta}{i\delta \eta(\tau)} \right] <R[z(\tau) + \eta(\tau)]>.
\]

We change the differential with respect to \( \eta(\tau) \) into \( z(\tau) \), and let \( \eta(\tau) \equiv 0 \).

Finally, we can write

\[
<F[z(\tau)]R[z(\tau)]> = \Omega \left[ \frac{\delta}{i\delta z(\tau)} \right] <R[z(\tau)]>.
\]

\[
\textit{Calculation of } \Omega\textit{-functional.}
\]

As a following step we perform transformation of the functional \( \Omega \). For most physical situations one may imply rather low intensity of fluctuations, what makes the case \( F[z(t)] = z(t) \) important to consider. Then
Average of two functionals.

\[ \Omega_{\tau'}[\psi(\tau)] = \frac{\langle z(\tau') \exp\{i[d \tau z(\tau) \psi(\tau)]\} \rangle}{\exp\{i[d \tau z(\tau) \psi(\tau)]\}} = \]
\[ = \frac{1}{\Xi[\psi(\tau)]} \frac{\delta}{i \delta \psi(\tau')} \Xi[\psi(\tau)] = \frac{\delta}{i \delta \psi(\tau')} \Theta[\psi(\tau)] \]

where \( \Xi \) is a characteristic functional, and \( \Theta[\psi(\tau)] \) is defined as \( \exp\{\Theta[\psi]\} \). The introduction of \( \Theta \)-functional is very convenient, because i) the average value of the multiplication of two functionals can be written in a rather simple form using definition of \( \Theta \), ii) \( \Theta \) is easily expressed in terms of the cumulants. The latter can be shown if we apply the Taylor expansion into series in terms of function \( \psi \). We have

\[ \Theta[\psi(\tau)] = \sum_{n=1}^{\infty} \frac{i^n}{n!} \int dt_1 \ldots dt_n K_n(t_1, \ldots, t_n) \psi(t_1) \ldots \psi(t_n). \]

We are substituting now the expressions obtained into eq.(B.10)

\[ \langle z(\tau') R[z(\tau)] \rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \int \ldots \int dt_1 \ldots dt_n K_{n+1}(t', t_1, \ldots, t_n) \left( \frac{\delta^n R[z]}{\delta z(t_1) \ldots \delta z(t_n)} \right). \quad (B.11) \]

If the distribution of \( z(t) \) is of a Gaussian type, the only cumulant \( K_2 = \sigma^2 = \langle z^2 \rangle \) is not equal to zero, and we write

\[ \langle z(t') R[z] \rangle = \int d\tau < z(t') z(\tau) > \left( \frac{\delta R[z]}{\delta z(\tau)} \right) \quad (B.12) \]

for \( t' \leq t \). Having generalized eq.(B.12) on the multi-component case, we deduced

\[ \langle z_{i_1 \ldots i_n}(r) R[z] \rangle = \int dr' < z_{i_1 \ldots i_n}(r) z_{i_1 \ldots i_n}(r') > \left( \frac{\delta R[z]}{\delta z_{i_1 \ldots i_n}(r')} \right). \quad (B.13) \]
B.3. The Einstein-Fokker equation. II.

Using result (B.13) from the previous section, eq.(B.6) can be transformed into

\[
\frac{\partial P_i(x)}{\partial t} = -\frac{\partial}{\partial x_k} \{v_k(x,t)P_i(x)\} - \frac{\partial}{\partial x_k} \int_{-\infty}^{\infty} d\tau <f_k(x,t)f_i(x',\tau)> \left( \delta \frac{\partial}{\partial f_i(x',\tau)} \delta(x - \xi(t)) \right)
\]

\[
- \frac{\partial}{\partial x_k} \{v_k(x,t)P_i(x)\} + \frac{\partial}{\partial x_k} \int_{-\infty}^{\infty} d\tau <f_k(x,t)f_i(x',\tau)> \frac{\partial}{\partial x_m} \left( \delta(x - \xi(t)) - \delta \frac{\partial}{\partial f_i(x',\tau)} \delta \frac{\partial}{\partial f_i(x',\tau)} \right). \tag{B.14}
\]

The functional derivative staying on the r.h.s. of eq.(B.14) must be calculated, and for this purpose we differentiate eq.(B.3)

\[
\frac{\delta \xi_i(t)}{\delta f_j(x,t')} = \delta_{ij} \delta(x - \xi(t')) + \int_{-\infty}^{\infty} d\tau \int d\xi' \left[ v_i(x',\tau) + f_i(x',\tau) \right] \frac{\partial}{\partial x_k} \delta(x' - \xi'(\tau)) \frac{\delta \xi_i(\tau)}{\delta f_j(x,t')} , \tag{B.15a}
\]

where eq.(A.9) has been used. It is clear that considering eq.(B.14) with eq.(B.15), we shall make our task too complicated. To alleviate the further consideration, \(t' = t\) will be taken (for discussion see [3]), then

\[
\frac{\delta \xi_i(t)}{\delta f_j(x,t)} = \delta_{ij} \delta(x - \xi(t)) . \tag{B.15b}
\]

In eq.(B.15) the lower limit has been changed to \(t'\), following condition (B.2), and \(v_i\) does not depend directly on \(f_j\).

To make a progress we shall a bit simplify the correlation tensor, i.e., the effective tensor will be introduced

\[
B_{ij}^{\text{eff}}(x,x';t,t') = 2\delta(t-t')D_{ij}(x,x';t) , \tag{B.16}
\]

where the new tensor \(D_{ij}\) can formally be found, for example, from the identity of two time integrals

\[
D_{ij}(x,x';t) = \frac{1}{2} \int_{-\infty}^{t} dt'B_{ij}^{\text{eff}}(x,t;x',t'). \tag{B.17}
\]
Expressions (B.16) and (B.17) are of applied interest when dealing with processes whose characteristic time is much larger than the time-correlation radius of a random process.

Using definitions (B.16) and (B.17), and substituting the functional derivative (B.15b), eq.(B.14) can be transformed into

$$\frac{\partial P_i(x)}{\partial t} = -\frac{\partial}{\partial x_k} \left[v_k(x, t) P_i(x)\right] + \frac{\partial}{\partial x_k} \int dxx'D_{kl}(x, x'; t) \frac{\partial}{\partial x_m} \delta(x-x(t))\delta(x'-\xi(t))\delta_{ml}.$$

and, finally, we arrive at the Einstein-Fokker equation

$$\frac{\partial P_i(x)}{\partial t} + \frac{\partial}{\partial x_k} \left[v_k(x, t) + A_k(x, t) \right] P_i(x) - \frac{\partial^2}{\partial x_k \partial x_l} [D_{kl}(x, x; t) P_i(x)] = 0 \quad (B.18)$$

with

$$A_k(x, t) = \frac{\partial}{\partial x_l} D_{kl}(x, x'; t) \bigg|_{x = x'}.$$

This equation must be accompanied by the initial condition

$$P_0(x) = \delta(x - \xi_0), \quad (B.19a)$$

or a more general one, as

$$P_0(x) = W_0(x). \quad (B.19b)$$

A few remarks about terms included in equation (B.18) can be made in addition. We shall first consider terms $A_k$ and $D_{kl}$, which are dependent of fluctuations $f_i(x, t)$. If the field $\mathbf{f}$ is stationary, $A_k$ and $D_{kl}$ are time independent. Moreover, if $\mathbf{f}$ is homogeneous and isotropic, then $D_{kl} = \text{const}$, and this corresponds to the constant diffusion coefficient (consequently, $A_k = 0$). However, dependence of $A_k$ and $D_{kl}$ on $x$ can be introduced with the use of a curvilinear system of coordinates.

It is also shown that if homogeneous fluctuations are rather small, and $\mathbf{v}$ is linear with $\xi$, a closed set of equations alike eq.(B.18) can be obtained for all the moments of $\xi$. 
For a more general approach based on the master equation formalism we refer to [4].

References.

Curriculum Vitae

Shulepov Sergei Yurjevitch was born 4 of April, 1965, in Kiev (the Ukraine). In 1982 he entered the Kiev State University. After military service (1984 ÷ 1986) he proceeded with study, and in 1989 he graduated from the University as a Physicist/Lecturer, completing the full University course with “Optics and Spectroscopy”, and “Theoretical Physics” as the major disciplines. During the diploma work at the group of theoretical physics (Institute of the Metals Physics), he has carried out an investigation on the influence of small deformations on the structure of a solid lattice. An emphasis was on transitions between a “homogeneous” and a multy-layer lattice structure, with the latter as a possible matrix for superconductors.

From 1989 till 1993 he was working at the Institute of Colloid and Water Chemistry, in the group of Electrochemistry of Membranes and Dispersions leaded by Prof. S.S. Dukhin. Main research interests were concerned the relaxation processes at the particle-solution interface in colloidal systems, with relation to the colloid stability problem, floatation, etc.

From February 1, 1993 he started as a Ph.D. student at the Delft University of Technology, Laboratory of Physical Chemistry (Prof. dr. G. Frens), where he carried out theoretical and experimental research described in this thesis.
It is well known that the surface roughness can play an important role in technology. At the same time, scaling aspects of surface topography are often neglected. However, "...it is unlikely that an airline whose pilots where encouraged to treat the earth as mathematically flat would attract a great deal of custom." cited from "Surface Topography in Engineering. A State of the Art and Bibliography.”
T.R. Thomas, and M. King.

In the literature on the coagulation of electrocratic colloids very often two limiting regimes are compared. These are the interaction at a constant surface potential, and the interaction at a constant surface charge. However, from general boundary conditions of classical electrodynamics, the double layer theory for these regimes cannot be applied for colloid interaction in the form it is mostly used in the literature, unless the dielectric properties of the particles and the medium are explicitly accounted for.

It is unlikely that colloidal particles with a particle diameter of about a few hundred nanometers can make a distance of $2 \kappa^{-1} \sim 20$ nm in one Brownian jump. This means that there is always a possibility of a double-layer relaxation, which realization depends on the kinetic parameters responsible for the relaxation processes.

Very often important theoretical proportionality "constants" are used as fitting parameters to reproduce one or another experiment. A set of experiments should be set up in a way that all these parameters must be determined independently in order to eliminate any uncertainty about a possible influence of other effects.

Recent developments in hard- and soft-ware made a personal computer more friendly to a user. However, simultaneously, the same user has to spend much more time practicing with those developments.

A tendency is that the "technology" is going to substitute the "science". Nowadays, there are many publications in different journals, which deal with the same systems but describe these with slightly different parameters.

Table tennis as a kind of sport has a very special atmosphere, which is what makes social contacts much easier.

Sometimes, mostly in the morning, coffee only keeps research going.