

The bottom size of colloids

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Abstract. A review is given on a number of colloidal phenomena with special reference to their applicability to nanoparticles. Phenomena addressed include preparation, electric double layers and their characterization, electrokinetics, van der Waals and Lifshits forces, electric and steric particle interaction.

Key words: colloid stability, electrokinetics, nanoparticles, electric double layers, polymer and polyelectrolyte adsorption, steric interaction.

1. Nanoparticles, or colloids, a matter of definition

“Nanoparticles are small colloidal particles, but not all small colloidal particles are nanoparticles.” This opening statement may be used to define the topic and scope of the present paper. In practice, the definition is sometimes more a matter of habit than of general acceptance. Colloid science has a long history; it dates back to halfway the nineteenth century. The name was coined by Thomas Graham in 1861 after the Greek word $\kappa\omicron\lambda\lambda\alpha$, meaning glue, because some of his colloidal systems were glue-like. Nowadays we know that most colloids are not glue-ish, but the name has stuck. Graham’s nomenclature did not imply a reference to the size range, which had to wait till codification by IUPAC. In the relevant document, prepared for publication by Everett [1], the size of colloids is defined as being between roughly 1 and 1000 nm, i.e. from the nanorange up to that of microns. In line with this, a substantial amount of competent research on nanoscience *avant la lettre* can be found in the classical journals of colloid scientists, as will readily be confirmed by those who search the literature beyond web pages under the key nano.

However, besides claiming on the basis of formal arguments that nanoscience is part of colloid science, it must also be appreciated that over the past decades a number of novel nanostructures have been developed, that cannot be found in the classical colloidal literature. Several industries and, not to forget, financial sponsors, have therefore embraced terms like nanoscience, nanotechnology, etc. to suggest the impression of novelty. Indeed, the quality of the pertaining literature varies between top notch innovation to unwitting reproduction or extension of existing science, be it of good or poor quality.

The present paper addresses these crossroads. In order to define the issue, we shall reserve the name “nanoparticles” to those systems where the physical material properties differ substantially from their macroscopic counterparts, say carbon in buckyballs as compared to carbon black or diamond. In this vein, “small colloids” are defined as systems having small particles, down to the nanometer range, of materials that also exist in macroparticles. Essentially, our distinction is based on phys-

ical material properties, rather than on size scales. The theme will be: “what has classical colloid science to offer when the particles become smaller?”

To concentrate on this question we shall mostly consider spherical particles.

2. Preparation strategies

Two different approaches exist for preparing materials in the colloidal size range:

1. Start with big particles and break them down by brute force, such as milling (so-called dispersion or comminution methods). These procedures are routinely carried out in industries. A typical example is the comminution of pigments in the paint industry to obtain samples in a size range compatible with optical (reflectivity, hiding power, ...) and rheological specifications. Although it is possible to prepare in this way materials down to the nanometer size range we would, according to our definition, not classify the obtained product as “nanoparticles.” By dispersion methods it is difficult to obtain homodisperse sols (all particles having the same sizes and shapes), although by fractionating size distributions can be narrowed down.

2. Prepare particles by precipitation from solution (condensation methods). For the present theme such procedures are relevant because, on their growth path from dissolved molecules via small nuclei and embryos to larger particles, they pass through a state that, according to size and properties, belongs to the nanoparticle domain. Nucleation is achieved by making the solute insoluble, say by a chemical reaction, a change in temperature, or quenching by a non-solvent. Over the past decades colloids scientists have learned to prepare homodisperse sols, essentially by controlling the rates of nucleation and growth, exploiting the Gibbs-Kelvin (or Gibbs-Thomson) rule. This rule states that for nucleation a much larger supersaturation is needed than for growth of existing nuclei. The origin of this difference results from the large surface-to-volume ratio of very small particles which therefore carry a high excess interfacial Gibbs energy and hence are better soluble. Recipes for the preparation of homodis-

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perse sols typically involve a step in which nucleation is suddenly inhibited by lowering the supersaturation, after which all nuclei grow gradually with equal rate till the desired size is attained. The classical example is the preparation of homodisperse sulfur sols by La Mer and Barnes [2]. This method is based on the slow formation of S from $\text{Na}_2\text{S}_2\text{O}_3$ by acid, according to $\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{S}$. After mixing the ingredients S is slowly formed till all through the system nuclei are formed. As a result the supersaturation drops so that no new nuclei are formed and any newly created S deposits on the growing particles. Growth can be stopped at any desired moment by titrating the unreacted $\text{S}_2\text{O}_3^{2-}$ with a solution of iodine in KI. The growth of the particles is easily followed by colour changes in the scattered light in the visible part of the spectrum.

Even better control can be achieved by replacing the above step of homonucleation by heteronucleation, i.e. by adding nuclei of a different kind to a slightly supersaturated solution. Then, only growth on the nuclei will take place; no new nuclei are formed and the sols become increasingly homodisperse upon further growth. A typical older illustration is Watillon's technique of preparing Se sols, using small colloidal Au particles as the nuclei [3]. From the point of view of colloidal properties (say, electrophoretic mobility) the resulting sols behave as a Se sol, but with a heart of gold. For a review of this matter a recent chapter by Philipse [4] is recommended; it also contains some recipes.

It is obvious that nanoparticles serve well as condensation nuclei. A variant is the synthesis of inorganic nanoparticles in the cores of microemulsions, droplets which by their very nature are homodisperse. In this way sizes are readily controlled, but characterization of the surfaces may be problematic because the stabilizers of the microemulsions will remain sitting on the particles. Another variant, allowing preparation of particles of a variety of specific shapes (cylinders, plates, disks, etc.) involves inhibition of the growth of certain crystal planes [5].

One of the main challenges is the characterization of growing nuclei, the problem being that they are short-lived. An illustration is the study of transient complexes in the nucleation of iron oxides, alumina oxides and calcium phosphates, using conductometry and scattering techniques, by de Bruyn and co-workers [6–9]. Another issue is quantifying which part of the adjacent liquid is stagnant, and to what extent or, for that matter, establishing the position of the slip plane.

3. Electrical characterization

Nanoparticles and larger colloids have in common that, in order to describe their interaction, it is mandatory to characterize their surfaces electrically. Two types of surface charge have to be distinguished

(i) the real surface charge, σ^0 , caused by charges that are so tightly bound that they may be considered as belonging to the surface. Examples are H^+ and OH^- ions for oxides and covalently sulfate groups bound to polystyrene latex spheres. These charges can be experimentally obtained by acid-base

titration and conductometrically, respectively. Another possibility, more typical for nanoparticles, is inclusion of ions of a special type in the solid matrix of the particle, e.g. inside cages. The colloidal equivalent is that of clay platelets which through isomorphic substitution ($\text{Si}^{4+} \rightarrow \text{Al}^{3+}$, $\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$) acquire a negative bulk charge, compensated by cations outside the platelets. For such systems the ion exchange capacity (i.e.c.) can be experimentally determined. Surface charges are mostly recorded as charge densities ($\mu\text{C cm}^{-2}$).

(ii) electrokinetic charges, σ^{ek} , obtainable from electrophoresis and other electrokinetic techniques. These techniques measure the electrokinetic or ζ potential, which is readily converted into σ^{ek} values, using Gouy-Chapman theory. For flat surfaces this can be carried out analytically but for small spheres tables are available [10]. For a review of electrokinetics, including the effect of particle size, see ref. [11].

The two charges σ^0 and σ^{ek} are by no means identical, they can even have different signs. The interpretation of this difference is fairly well known for colloids and may be also applied to nanoparticles. Upon tangential motion of a liquid with respect to a solid, or conversely, typical for all electrokinetic phenomena (electrophoresis, streaming potential, electro-osmosis, ...), a thin adjacent layer of the liquid behaves as if it were stagnant. Slip takes place at the outer side of this stagnant layer. For practical reasons the change of the liquid fluidity from virtually zero at the solid wall to its bulk value is usually replaced by a step function at the slip plane. The thickness of the stagnant layer is about a few molecular cross-sections, more or less corresponding to the first two oscillations in the radial density distribution $\rho(z)$ of the fluid near the wall, and more or less coinciding with the Stern layer thickness (the Stern layer is the non-diffuse part of the countercharge in solution). In this picture the ζ potential is the potential at the slip plane. Its value is close to that of the diffuse double layer potential ψ^d , and hence $\sigma^{ek} \approx \sigma^d$. Molecular dynamics studies have helped to understand the slip process better [12].

For the purpose of electrical characterization of nanoparticles the following points are relevant (i). At fixed conditions with respect to temperature, pH and salt concentration, σ^0 and σ^{ek} are both well-defined characteristics. Of these, σ^0 is perhaps academically the most relevant, but this quantity can only be measured when the charge-determining mechanism is fully understood. When this is not the case, ζ and/or σ^{ek} can usually be measured. Although this is not such a fundamental characteristic as σ^0 , it remains a very useful parameter because it controls the diffuse part of the double layer and this is the part that controls particle interaction.

(iii). The difference between σ^0 and σ^d is determined by the amount of countercharge σ^i , residing in the stagnant (or Stern) layer. The most frequent situation is that a substantial fraction of the countercharge resides in this layer. Surface charges can be as high as several tens of $\mu\text{C cm}^{-2}$ but σ^d rarely exceeds $5 \mu\text{C cm}^{-2}$. So, the countercharge in the stagnant layer is often substantial; σ^i can be obtained experimentally from charge balance if σ^0 and σ^{ek} are both measured. Situations in which $|\sigma^i| > |\sigma^0|$ are not rare. They may occur by specific adsorption that is strong enough to overcome the elec-

tric repulsion from the surface. Ionic surfactants, either added intentionally or present as a result of the synthesis belong to this category, and so do multivalent counterions, which over a specific pH-range adsorb strongly as hydrolyzed products. (Sometimes the ensuing overcharging is attributed to ion correlations but as far as the author is aware there is no unambiguous experimental evidence for that.) The term overcharging is in classical colloid science sometimes referred to as charge reversal, which is sloppy because as a result of strong specific adsorption of counterions the absolute value of σ^0 increases, because of better screening. The reversal only applies to the electrokinetic charge or to ζ . In the older colloid literature the term irregular series in the critical coagulation concentration is known; this phenomenon should also exist for nanoparticles.

Regarding the properties of the stagnant layer, no major differences between colloids and nanoparticles are to be expected, apart from material idiosyncracies. Because of their large area-to-volume ratio nanomaterials typically show a high surface conductivity. Study of this, in conjunction with measurements of σ^0 and ζ may help to characterize the electric double layer around the particles.

4. Van der Waals attraction between nanospheres

In this field an interesting transition takes place between colloids and nanoparticles. There are two approaches for describing the (London-) van der Waals attraction between two spheres, the microscopic and macroscopic way, originated by Hamaker and de Boer, see [13] and Lifshits et al. [14], respectively. According to the former, the particles are considered to consist of atoms or molecules, additively attracting all the atoms or molecules in the other particle according to the London attraction between isolated pairs. The latter theory pictures the particles as macroscopic phases, of which the electron density fluctuates. Upon interaction with another particle attractive modes occur more frequently than repulsive ones, so that eventually overall attraction ensues. It is immediately realized that in the mesorange transitions from macroscopic to microscopic (molecular) must be expected. To elaborate and illustrate this it is expedient to write some basic equations [15].

The interaction energy u_{11} between two atoms or molecules of nature 1 across a vacuum is, according to van der Waals,

$$u_{11} = \frac{-\beta_{11}}{r^6} \quad (1)$$

where β_{11} is a material-specific constant of units $\text{J} \cdot \text{m}^{-3}$. Three interpretations of β_{11} have been forwarded, by Keesom, Debye and London. Only those by London are more or less additive and therefore only those have to be considered for colloids. For the (hetero-)interaction between molecules of nature 1 and nature 2

$$u_{12} = \frac{-\beta_{12}}{r^6} \quad (2)$$

where, according to the Berthelot principle

$$\beta_{12} \approx (\beta_{11}\beta_{22})^{1/2} \quad (3)$$

Assuming perfect additivity, Hamaker and de Boer derived equations for various geometries. All of them contain some Hamaker constant A_{11} for homo-interaction, A_{12} for hetero-interaction and $A_{12(3)}$, etc., for interaction across a medium 3. These are material constants, independent of the particle shape, and tables are available For reviews by Lyklema and by Israelachvili, see [15–17]. Definitions are

$$A_{11} = \pi^2 \beta_{11} \rho_{N1}^2 \quad A_{12} = \pi^2 \beta_{12} \rho_{N1} \rho_{N2} \quad (4)$$

$$A_{12(3)} = A_{12} - A_{13} - A_{23} + A_{33} \quad (5)$$

with

$$A_{12} \approx (A_{11}A_{22})^{1/2} \quad (6)$$

Here, ρ_{Nj} is the number density of molecules in phase j . Hamaker constants have the dimensions of energy. Often they are expressed in units of kT . Mostly they are of order of a few to a few tens of a kT unit. Equation involves Archimedes' principle: it accounts for the process underlying the approach of the two particles from infinity, which involves medium transport the other way round. In this sense (5) anticipates Flory-Huggins' χ parameter for polymer segments.

Of the family of equations derived by Hamaker and de Boer (or by others, using the same assumptions) the following, applying to two spheres, is the most appropriate for our present purpose

$$U(s) = -\frac{A_{11(3)}}{6} \left[\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right] \quad (7)$$

in which s is a dimensionless distance parameter

$$s = \frac{r}{a} = \frac{h + 2a}{a} \quad (8)$$

where a is the particle radius, r the distance between the particle centres and h the shortest distance between the surfaces. In (7), as in all formulas of the Hamaker-de Boer type, the interaction energy is written as the product of a material constant and a function of distance and geometry.

We return to (7) but first discuss the macroscopic theory. In this approach the material is considered as a continuum, characterized by macroscopic properties, in particular their complex (i.e. frequency-dependent) dielectric permittivities, $\hat{\epsilon}(\omega)$, which reflect the local fluctuations in electron density. The amplitudes and frequencies of these fluctuations depend on the densities and strengths of binding, so they are material properties. As is typical for fluctuations, the average field strength $\langle E \rangle$ is zero, but $\langle E^2 \rangle$ is finite. The fluctuations extend beyond the particles to an extent depending on ω and on the dielectric permittivity of the medium, $\hat{\epsilon}_3$. Upon overlap with the fluctuating field of a second particle attractive and repulsive correlations occur, of which the former prevail, hence the negative (attractive) Gibbs energy of interaction. Quantitative elaboration requires quantum electrodynamics and is rather abstract. Quantitative prediction of $G(h)$ or $G(s)$ rests upon knowledge of the spectrum for all wavelengths; such spectra are called dispersion spectra, and hence the name dispersion forces for the macroscopic counterpart of the microscopic theory.

Lifshits theory is more general (phenomenological) and more abstract than Hamaker-de Boer theory. One of the typical differences is the dependence on particle shape, where the product-rule of (7) no longer holds. The explanation is that for two interacting spheres a variety of distances between the surfaces is involved (h being the shortest of these) and each react to different parts of the spectrum.

Otherwise stated, shape and size are implicitly accounted for. Similarly, the role of the medium (entering via the Archimedes principle in the microscopic theory) is now quantified via differences in spectra ($\hat{\varepsilon}_1(\omega) - \hat{\varepsilon}_2(\omega)$, etc.). For Lifshits theory the additivity of London forces between molecules is not needed, which is (another) advantage over the microscopic theory, though at the price of less “visibility”. Over the last decades Lifshits-like interpretations have become more amenable, mostly because of better availability of spectra and better insight into the range of the spectra that are relevant for each material. Much of this has its roots in pioneering work by Ninham and coworkers [18].

How well do these two theories match? Let us first consider macroscopic objects, because otherwise Lifshits theory would not work. For two flat plates, a distance h apart, Lifshits’ approach gives an expression similar to that of Hamaker and de Boer, with instead of approximately

$$A_{12(3)} = \frac{3h}{4\pi} \int_0^\infty \frac{[\varepsilon_3(i\omega) - \varepsilon_1(i\omega)][\varepsilon_3(i\omega) - \varepsilon_2(i\omega)]}{[\varepsilon_3(i\omega) + \varepsilon_1(i\omega)][\varepsilon_3(i\omega) + \varepsilon_2(i\omega)]} d\omega \quad (9)$$

The difference between (5) and (9) is typical. Equation (9) requires integration of the complex permittivity excesses ($\hat{\varepsilon}_3 - \hat{\varepsilon}_1$, etc.) over all frequencies. Replacement of $\hat{\varepsilon}_j(\omega)$ (complex permittivity as a function of frequency) by $\varepsilon_j(i\omega)$ (real permittivities as functions of imaginary frequencies) is just a mathematical trick to simplify the equations. The occurrence of Planck’s constant in (9) reflects the quantummechanical nature of the derivation. Interaction of two flat plates (as in thin films) or closely related geometries (two crossed cylinders of sufficiently large radii of curvature as in the surface force apparatus) allows experimental verification. For many systems, nowadays reliable Hamaker constants with experimental values close to the Lifshits predictions are available, with Hamaker-de Boer computations mostly off by not more than 10–15% [15–17].

With the above in mind, let us now consider the nanolimit. It is obvious that when particles become very small they may no longer be considered macroscopic, but it is not so obvious to tell below which size deviations start to occur. The problem mainly resides in the size needed to fully develop the fluctuation waves for the various wavelengths, which is system-specific. The trend is that the Lifshits-equivalent of the Hamaker constant decreases, but as it does so to different extents for different wavelengths the way in which G decreases with h will also be affected. Here is a pabulum for theoretical research.

However, at the same time the Hamaker-de Boer approach becomes better because the assumption of additivity becomes less restrictive for assemblies of fewer molecules. Reconsidering (5), it has two virtues which may be beneficial for the

present purpose. The first is that its radius dependence is likely comprehensive and correct. At low h ($h \ll a, s \rightarrow 2$) $U(h) \rightarrow -Aa/12h$, as also found by Lifshits, whereas for long distance $U(r) \sim r^{-6}$ just as in (1) and (2). So, the equation has the proper limiting behaviour. The second is that of scale-invariance: reduction of r and a by the same factor does not affect $U(h)$, so the equation is valid for billiard balls and nanoparticles alike, although the Hamaker constant may alter when a becomes very small. In fact, in the extreme limit of particles consisting of only one atom or molecule, the prefactor containing the Hamaker constant should simply reduce to the corresponding β of van der Waals’ equation.

5. Electrostatic interaction

Qualitatively and semi-qualitatively the interaction between colloidal particles and nanoparticles is identical, but details remain to be solved. For dispersions in a liquid medium the principles are as follows [16].

1. For electrostatic interaction, the particles must carry an electric double layer. The origin of these double layers is always of a non-electrostatic, or chemical, nature [10].

2. As a whole, electric double layers are electroneutral: surface charge and countercharge are equal in magnitude, but opposite in sign. Electroneutrality persists when particles interact.

3. The way in which the countercharge is distributed is of crucial relevance for interaction; it is governed by chemical, electrical and entropical forces. For particles in isolation the distribution is such that the Gibbs energy of the double layer is a minimum at given p, T and solution composition, particularly the electrolyte and charge-determining electrolyte concentrations.

4. In practice, double layers consist of three parts: a surface charge σ^0 , a Stern charge σ^i and a diffuse charge, σ^d . Mostly σ^d is relatively small, but as the diffuse charge extends far into the solution, its role in interaction dominates. For isolated particles $\sigma^d \approx \zeta$.

5. When two particles approach each other the double layers interact, charge- and potential distributions change. When the Gibbs energy of the pair exceeds that of the sum of the Gibbs energies for two particles far apart work must be done to reduce the distance h , i.e. the particles repel each other. In the opposite situation attraction prevails.

6. Two identical double layers always repel each other, but two double layers with the same charge sign but significant differences in magnitude repulsion at large h may at short h be followed by attraction because of induction. Interaction between identical double layers is called homo-interaction, that between different double layers hetero-interaction.

7. The adjustment of charge- and potential distributions upon overlap is known as regulation. In the literature models have been developed in which some parameters are fixed but others remained free to regulate. This point takes us to the present state of affairs.

Historically speaking DLVO theory is the mother (or father) of colloid stability theory. DLVO stands for Deryagin (in

English and French often transcribed as Derjaguin), Landau, Verwey and Overbeek who two-by-two developed the theory independently during the second world war. This theory is very restrictive because it only considers diffuse double layers with ψ^d assumed constant and σ^d allowed to regulate upon interaction. Notwithstanding these severe limitations the theory has served well as a first step towards understanding interaction. One of the items that could be explained semiquantitatively was the Schulze-Hardy rule i.e. the very strong decrease of the critical coagulation concentration (c.c.c.) with the valency of the counterion. As far as the present author is aware this rule has not yet been systematically investigated for charge-stabilized nanoparticles.

After DLVO a plethora of improvements has been proposed and elaborated, many of these just cosmetic. Recently, we have developed a comprehensive theory, called DLVOE theory, which accounts for Stern layers, regulation of σ^0 , σ^i and σ^d and which also covers hetero-interaction so that curves with repulsive and attractive sections can also be predicted [19]. Parameters include the pK 's for the surface charging process, specific adsorption (Gibbs) energy of counterions and capacitances of the inner and outer parts of the Stern layers. Numerical results are available for interaction Gibbs energies, interaction forces, charge- and potential distributions, all as a function of h .

For the time being this is the most advanced and comprehensive model, but it has only been elaborated for flat plates. What is then the state-of-affairs for spherical particles, in particular for very small spheres? Briefly, this issue is not yet satisfactorily elaborated, but there are some approximations that may serve us well in specific cases. Let us review this.

For flat plates the Stern layer and diffuse layer are mathematically relatively easily described. The potential in the diffuse part obeys one-dimensional Gouy-Chapman statistics, also for two double layers in overlap. The ensuing Gibbs energy of interaction can for purely diffuse layers under the conditions of either ψ^d or σ^d constant be rigorously formulated in terms of Bessel functions. Analytical formulas are also available for the situation of weak overlap (particles not too close to each other) when the linear superposition approximation (LSA, midway potential is the sum of the potentials of the two particles far apart) holds. As these equations are not needed for our present purpose we shall not give these, but note that, notwithstanding the neglect of Stern layers and absence of regulation of σ^0 and σ^i they appear to be acceptable approximations in experiments (thin film studies and the surface force apparatus). Examples of such equations can be found in the appendix to [16].

The classical trick to arrive at equations for spheres, cylinders, etc. is to consider the spherical object to consist of parallel disks of narrow width dx , between which the flat symmetry equation holds. Summing all these disk-interactions and taking the limit for $dx \rightarrow 0$ results in an integration. For two spheres of identical size a

$$G(h) = -\pi a \int_h^\infty G_a(x) dx \quad (10)$$

if $G_a(x)$ is the Gibbs energy per unit area for flat plates, a distance x apart. As before, h is the shortest distance between the two spheres. Equation (10) is known as the Deryagin approximation after its originator who proposed it as long ago as 1934. For the interaction between two identical spheres, assuming the double layers to be diffuse with $\psi^d \sim \zeta$ constant, application of the Deryagin equation leads to

$$G(h) = \frac{64\pi a c R T}{\kappa^2} \tanh^2 \left(\frac{z y^d}{4} \right) \ln(1 + e^{-\kappa h}) \quad (11)$$

where c is the electrolyte concentration, z the valency of the (z - z) electrolyte and κ the reciprocal Debye length. The equation is valid for $\kappa h \geq 2$, becoming increasingly poorer for lower κh . Equation (11) is widely applied, far beyond its range of applicability in studies involving many interacting particles per unit volume and then found to work reasonably well, for instance in interpreting the structure factor of static light scattering. Most likely in such interpretations only the outer part of the diffuse double layer plays a role, which is not very sensitive to the inner layer structure and its regulation.

By its very nature, the Deryagin approximation works only for large κa , implying that it becomes increasingly defective for smaller particles. For nanoparticles κa is large only if κ is large, i.e. if the salt concentration is high. In 10^{-1} M of an (1-1) electrolyte $\kappa \approx 1 \text{ nm}^{-1}$ so for $a = 10 \text{ nm}$ $\kappa a \approx 10$ and (11) applies. However, in 10^{-3} M of the same electrolyte $\kappa \approx 1$ and the condition is no longer fulfilled. For nanoscience it is important to know what the low-size deviations of the Deryagin approximation are. For a thorough theoretical analysis of this, see Carnie et al. [20] and for an experimental (SFM) investigation see Todd and Eppell [21]. Perhaps it is fair to state that there is not yet a general analytical equation for the low κa situation.

Two remarks can be made. The first is that for spherical geometry the Debye-Hückel approximation (replace $\exp(-zy^d)$ by the first two terms of its series expansion) is relatively better than for flat plates. The reason is that the field strength decays more rapidly with distance from the surface (the lines of force become radial). At low ψ^d the hyperbolic tangents may be replaced by their argument ($\tanh hx = x$). If we have a spherical particle with a Stern layer of thickness d which does not substantially change by regulation (weak overlap), (11) may be replaced by

$$G(r) = 2\pi\epsilon_0\epsilon a(\psi^d)^2 \ln \left(1 + e^{-\kappa[r-2(a+d)]} \right) \quad (12)$$

where r is the distance between the centres, and $\psi^d \approx \zeta$. Secondly, for non-aqueous media of very low dielectric permittivity $\kappa \rightarrow 0$. Verwey and Overbeek showed that in that case

$$G(r) = \frac{4\pi\epsilon_0\epsilon a^2(\psi^d)^2}{r} \quad (13)$$

It is readily recognized that (13) is essentially Coulomb's law ($u(r) = Q^2/4\pi\epsilon_0\epsilon r$, where Q is the total charge; $\psi(r) = Q^2/4\pi\epsilon_0\epsilon r$, applied to the surface, $r = a$ and ψ^0 becoming equal to ψ^d or ζ because the potential decay is so slow that these potentials become indistinguishable). The $\kappa \rightarrow 0$ case

implies absence of screening. As the redistribution of counterions upon overlap also vanishes the entropic contribution to $G(r)$ also disappears, so that the Gibbs energy reduces to an energy.

Finally, in the limiting case that there are so few charges on the particle surface that it is no longer allowed to assume charges and potentials to be smeared out, a situation arises in which approaching particles may attract or repel. A kind of statistical averaging will take place in which attractive configurations prevail over the repulsive ones, comparable to the interaction between two free dipoles according to Keesom. Most likely the overall effect will be attractive but with a decay function $\exp(-2\kappa h)$ instead of $\exp(-\kappa h)$.

Obviously in this field there is room for much more challenging theoretical and experimental work.

6. Steric interactions

Steric interactions refer to the influence of added macromolecules on colloid stability. The mechanisms come in a variety of forms, depending on the nature of the macromolecule and its interaction with the particle and, therefore we suffice by briefly ticking off the main trends. Many of these are qualitatively and semiquantitatively identical between colloids and nanoparticles. For recent reviews see Fler et al. [22] and Currie et al. [23].

The first distinction is between adsorbing and non-adsorbing polymers. In the latter case around each particle a zone devoid of polymer develops, the depletion zone. Overlap of depletion zones gives more space for the polymers, is therefore entropically favourable and hence leads to depletion flocculation. It is a weak phenomenon in the sense that its Gibbs energy is much less than that of adsorbing polymers when the first polymers completely cover the particle surface and when this layer repels the free polymer in solution (good solvent quality). So, depletion flocculation takes place as a secondary phenomenon: it can for instance be detected by rheology.

As to adsorbing macromolecules, distinction can be made between uncharged polymers and polyelectrolytes. (We shall not consider even more complex macromolecules such as proteins). Adsorption of polymers is entropically unfavourable because the number of available conformations in the adsorbed state is much less than in the free state. Therefore, a minimum critical segment adsorption (Gibbs) energy is required for attachment. Once this threshold is surpassed the binding is very strong, because so many segments can attach. However, polymers rarely adsorb completely flat: that would again be entropically very unfavourable. So they form, besides *trains* (a few attached segments in series) *loops* and *tails*. Typically, most of the adsorbed weight is in the loops; only a few percent is in the tails, but this fraction dominates the interaction because it protrudes farthest into the solution. It is also typical that a large fraction of an adsorbed polymer is still in contact with the solvent. For that reason the *solvent quality* plays an important role, the poorer it is, the easier it is to form loops, and the higher the adsorbed amount. All of this is also valid for nanoparticles. As a trend, for fully polymer-covered parti-

cles, displaying no desorption upon particle approach (i.e. non-regulating layers in this respect) the interaction is attractive in a poor solvent and repulsive in a good one.

Polymer adsorption displays a number of dynamic idiosyncracies. One is a consequence of the (usual) heterodispersity. The smaller molecules adsorb faster but the bigger ones adsorb more strongly, slowly replacing the former group. As a result polymer adsorption takes a long time to come to equilibrium, although not-equilibrated adsorbates can already act as potent stabilizers. Pressurization of polymer-protected (nano or colloidal) particles must ultimately lead to desorption, and subsequent destabilization. This is the reason for poor shelf stability of many paints.

In order to better control the properties of attached polymers, many studies are being devoted to end-grafted (tethered) chains, leading to brushes or “mushroom”-shaped attached polymers.

The difference between colloids and nanoparticles is mostly a matter of relative sizes of particle and polymer. For colloids and larger macrobodies mostly $a \gg a_g$ (the radius of gyration of the polymer), but for nanoparticles this is no longer necessarily the case. Situations can occur where the more appropriate picture is that of particles adsorbed onto polymer coils. For chains tethered on nanoparticles the brushes can develop better.

Polyelectrolyte adsorption and the ensuing influence on stability is a story on its own. We suffice by making a few notes.

(i) Attachment of polyelectrolytes to surfaces is not a purely electrostatic effect; besides this there is the same specific adsorption of segments by “chemical” forces, say by hydrophobic binding. The two come on top of each other, they may amplify or oppose each other.

(ii) Electrolytes now play a role: they screen the electric interactions, both the attractive and the repulsive ones. For very high salt concentrations the polyelectrolyte behaves as an uncharged polymer.

(iii) Adsorbed polyelectrolytes form very thin layers because the interchain repulsion inhibits loop formation. Typically, plateau adsorptions of polymers amount to a few mg m^{-2} whereas for polyelectrolytes it is rather a few tenths of a mg m^{-2} .

(iv) The trend is that long-distance polyelectrolyte stabilization is of an electrostatic nature whereas at shorter distances steric elements and partial desorption (regulation) also plays a role. Sometimes this interaction is called electrosteric interaction.

(v) As compared with uncharged polymers, for nanoparticles situations where $a < a_g$ occur more frequently because polyelectrolyte coils are strongly swollen. Cases of nanoparticles captured in a maze of polyelectrolyte are not rare.

These few lines may indicate that, just as for purely electrostatic interaction this matter offers several interesting challenges.

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