Anomalously Large Equilibrium Clusters of Colloids[†]

Jan Groenewold* and Willem K. Kegel

Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received: May 1, 2001

We propose a mechanism for mesophase separation in a system of aggregating colloids. Conditions are outlined under which colloids can form equilibrium clusters with very large sizes, i.e., aggregation numbers of a thousand or more. The driving force for clustering is a short range attractive interaction which will be treated within a capillarity approximation. The stabilizing mechanism is a small amount of charge per particle. Under the appropriate conditions these charges will interact with unscreened Coulomb potentials and, consequently, prevent large-scale phase separation.

1. Introduction

When colloids have attractive interactions of sufficient strength, i.e., some k_BT per particle, aggregation can be expected. This aggregation can occur in a wide variety of shapes and time scales, depending on the size of the colloids and the strength of their interaction. Irreversible aggregation has been studied in ref 1 where the clustering is described by Smoluchowski kinetics. So-called reversible aggregation has been tackled within the Russian school.[2] The aggregation described in that work takes into account that clustered particles can rearrange or evaporate from the cluster. However, the final (equilibrium) state always consists of an infinitely large aggregate, and thus, the evaporation is an intermediate process. The kind of aggregation that is the subject of this paper is such that the final state of aggregation consists of equilibrium clusters. There is continuous evaporation from and condensation onto clusters but there is no growth into a single, infinite, cluster. To get this situation, a stabilizing mechanism must be present. Molecular aggregation into micelles is an example where large aggregates are stabilized by entropy.[3,4] The aggregating particles are in this case small anisotropic molecules. In this paper, we will deal with the situation where these are colloidal particles. This implies of course longer equilibration times.

The stabilization mechanism in this paper is the effect of a small amount of charge on each aggregating particle. To get the most effective stabilization, electrostatic screening must be minimized. We will therefore focus on apolar or weakly polar solvents, because then the concentration of charges other than the counterions from the particles is low. At the same time, the degree of dissociation of the surface charges on the particles is also small. We will see that under appropriate conditions this charge, although small, is sufficient to stabilize clusters that have extremely large aggregation numbers. We note that similar ingredients are used in the classical liquid droplet model from nuclear physics,[5] though the emphasis there is more on dynamics and fluctuations. In turn, many features of this model go back to the analysis of Rayleigh.[6] The same model is used in atomic and molecular physics, see, e.g., ref 7. In colloidal aggregation, the role of charges is particularly interesting as the charge on the particle emerges from an association−dissociation equilibrium. Under the conditions used in this paper, the equilibrium changes with the volume fraction of colloid and sometimes with the degree of clustering (counterion condensation). This results in a dependence of cluster-size upon volume fraction, which will be one of the salient features presented in this paper.

The paper is organized as follows: In section 2, the charge mechanism on the particle surface is modeled via a site-binding model. Section 3 presents the general framework to describe the equilibrium clustering. Here, the charging mechanism of section 2 and the attractions between the particles are combined. The next section, Section 4 treats the case where the particles cluster into large spherical clusters. Then we discuss aggregation into disk shaped clusters (section 5) and rod-shaped clusters (section 6), respectively. In section 7, some experimental work of what could be a manifestation of the mechanism proposed in this paper is discussed. The last section is devoted to a discussion of the approximations made.

2. Site-Binding Model

We will be dealing with the aggregation of colloidal particles in apolar solvents. To stabilize large sized clusters, we require a small amount of charge on each particle. The conditions under which these charges emerge are outlined in this section.

To generate charges on colloids, one requires the presence of ionic bonds. Usually these are located on the particle surface. In Figure 1a, we show a schematic picture of this. If the distance between the opposite charges is b, the energy required to dissociate this ion pair is

$$\Delta\epsilon = \frac{Q}{b} \tag{1}$$

We use units $k_B\,T$ (T temperature and k_B Boltzmann's constant) for $\Delta\epsilon$. Q is the Bjerrum length, given by $Q = e^2/4\pi\epsilon_0\epsilon_r k_B T$, where e is the elementary charge, ϵ_0 is the dielectric permittivity of vacuum, and ϵ_r is the relative dielectric constant of the solvent. At room-temperature we find

$$Q = \frac{56}{\epsilon_r}\,\text{nm} \tag{2}$$

So in a solvent like benzene ($\epsilon_r = 2.3$) and a separation b of

---

[†] Part of the special issue "Howard Reiss Festschrift".

* To whom correspondence should be addressed.

10.1021/jp011646w CCC: $20.00

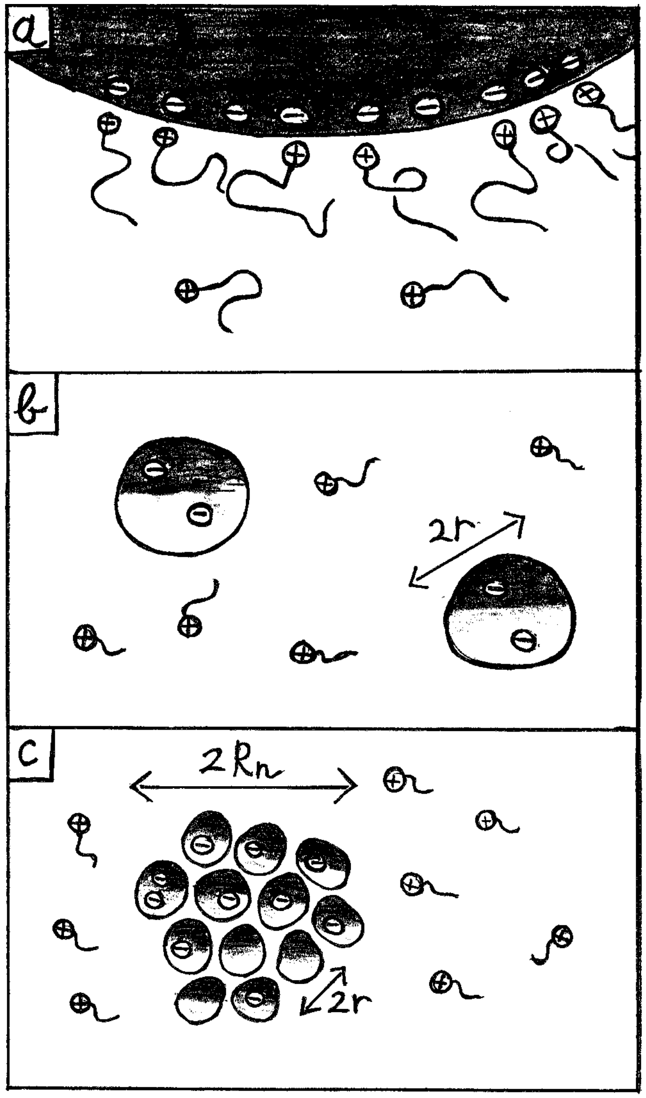

Figure 1. (a) Charging mechanism on a particle surface. For entropic reasons, a small fraction of the ion pairs dissociate (see eq 3). On a larger scale, particles are either in (b) a monomer state or (c) an aggregated state. In the latter case, eq 44 constitutes a model that predicts the charge on the cluster.

0.1 nm, we find a dissociation energy of $243k_BT$. This energy is comparable to that of a strong covalent bond. Under these circumstances, one expects no charge effects. We note however that with a variety of special stabilizers significant amounts of charge can be generated on colloidal surfaces even in benzene. In somewhat less apolar solvents (say with $\epsilon_r = 10$) and with slightly larger separations, $b = 0.2$ nm,[9] one finds significantly lower dissociation energies, i.e., $28k_BT$. This is an intriguing number in a colloidal context. As we shall see later, an energy like this can give a 50 nm colloidal particle sufficient charge to stabilize large clusters. The charge will be treated as an additional degree of freedom. The long ranged nature of the Coulomb interaction will cause interactions between all particles in one cluster.

In any event, with dissociation energies such as this, we can safely assume only a small fraction of the bonds to be dissociated. In the model described below, entropy will give the colloids their charge, and this means that we must have sufficient dissociable sites or ionic bonds present at the surface of the particle.

Consider a single spherical particle (radius r) carrying a charge z. The counterions are dispersed in the suspending fluid. For a depiction of this situation, see Figure 1b. The counterions are drawn as surfactants because this is often the case in apolar media, see ref 8, but is not a necessary requirement here. Let us write the number of dissociable sites on the surface by σs, where s is the total surface of the particle and σ is the areal number density of sites. The free energy due to the charge is written as a site-binding model:

$$f_{\text{charge}}(z) = z\Delta\epsilon + \frac{1}{2}\frac{Q}{r}z^2 + z\ln(z/\sigma s) + z\ln(n_b b^3) \qquad (3)$$

In the above expression, the first terms on the right-hand side is simply the energy to independently dissociate z sites, each with an energy $\Delta\epsilon$ given by eq 1. The second term represents the interaction between the charges on the particle. It is given by simply adding the Coulomb interactions between the charges on the surface. Note that by writing this term we have neglected the effect of screening by the counterions in the solvent. In more technical terms, we use the linearized Poisson–Boltzmann equation and assume the effective screening-length to be much larger than the linear size of the cluster. The third term represents the combinatorial entropy of dissociating z out of σs sites under the assumption that $z \ll \sigma s$. The fourth term represents the gain in translational entropy upon dissociation. Here n_b is the number density of counterions in the bulk. b is a confinement length, the typical distance under which the ions are considered to be a pair. For convenience, we choose this length to be equal to the distance of closest approach. Equation 3 constitutes a rather primitive version of Bjerrum's theory of ionic dissociation[10] in combination with the more general site binding model,[11] adapted to this particular context.

If the particles cluster, we still expect them to carry charge such as depicted in Figure 1a. The free energy due to a total charge, Z, on a spherical cluster of n such particles is quite similar to eq 3. If we assume the charge to be homogeneously distributed throughout the sphere, we get

$$f_{\text{charge}}(n, Z) = Z\Delta\epsilon + \frac{3}{4}\frac{Q}{R_n}Z^2 + Z\ln(Z/n\sigma s) + Z\ln(n_b b^3) \qquad (4)$$

Note the following differences: In the second term, we now have the cluster radius R_n which is assumed to be significantly larger than the radius of the individual particles r. The prefactor of this term is now $^3/_4$ instead of $^1/_2$. This stems from the fact that the charge now also resides in the interior of the sphere and not exclusively on the surface. In the third term, a trivial increase in dissociable sites is taken into account.

3. General Clustering Model

We will now consider an ensemble of clusters characterized by $\rho_n(Z)$, which is the number density of clusters with an aggregation number n and a total charge Z. We write the total free energy per unit volume as follows:

$$\frac{F}{Vk_BT} = \sum_{n,Z} \rho_n(Z)[\ln(\rho_n(Z)l^3) - 1 + f_n(Z)] \qquad (5)$$

The first term between the square brackets represents the entropy associated with the distribution $\rho_n(Z)$. The magnitude of the length scale l is subject to debate, and we have no intent to dwell on it too long. Naturally we will take this length to be of the order of the size of the primary particle, respecting, in this way, Reiss et al.[12] For convenience, we subtracted a constant equal to one from the logarithm; it can be absorbed, if one wishes, in the logarithm by redefining l.

The free energy of a cluster is denoted by $f_n(Z)$ and is assumed to be composed of a part that is due to dispersion attractions, $f_{\mathrm{disp}}(n)$, and a part due to the charge on the cluster, $f_{\mathrm{charge}}(n, Z)$:

$$f_n(Z) = f_{\mathrm{disp}}(n) + f_{\mathrm{charge}}(n, Z) \tag{6}$$

Note that we neglected direct interactions between clusters by writing $f_n(Z)$ to be independent of the cluster distribution.

For the dispersion energy of the cluster, we use a simple model. We assume that particles in the interior of the cluster have an energy $-\epsilon$ and write the dispersion energy of the total cluster as

$$f_{\mathrm{disp}}(n) = -\epsilon n + \gamma A_{\mathrm{n}} \tag{7}$$

The second term on the right-hand side represents the energy that the particles on the surface are "missing" and is written as the product of a surface tension γ and the area of the cluster A_n. Note that γ can only be thought of in a macroscopic sense when the charges are absent. What is meant here is the part of the excess free energy that is due to the short-range dispersion attractions only. The surface tension γ is scaled by $k_{\mathrm{B}}T$ just as $f_n(Z)$ and ϵ. Generally, we assume the attractions between the particles to be short ranged. The term dispersion attraction is actually too narrow, as any other short-range attraction will do. For instance, polymer mediated depletion attractions or attractions between possible steric polymer layers. As long as it is short-ranged, the description by eq 7 is accurate enough for our purposes. By counting the number of contacts that a particle misses at the surface, the following approximate relation can be written for γ:

$$\gamma \simeq \frac{\epsilon}{s} \tag{8}$$

Here s is the total surface of the particle as in eq 3. Now, to have a significant amount of aggregation even without charges, one needs cohesive energies of, say, $\epsilon = 5$. This must be kept in mind when γ is estimated.

The charge-dependent part of f_n is given by eq 3. At this point, we have to specify the value of the bulk density n_{b} of counterions. In apolar solvents, the concentration of free charges other than the counterions is very low because of the high dissociation energies (see eq 2). We therefore assume the bulk density n_{b} to be solely determined by the ions that have dissociated from the surface sites:

$$n_{\mathrm{b}} = \sum_{n,Z} Z\rho_n(Z) \tag{9}$$

This equation constitutes a coupling between the degree of dissociation and the density of particles. Naturally, the total volume fraction ϕ of colloids in the system is fixed and must be treated as a constraint:

$$\phi = \sum_{n,Z} n\upsilon\rho_n(Z) \tag{10}$$

where υ is the volume per particle.

To proceed further, we will make a substantial simplification. The cluster distribution is assumed to be sharply peaked around one single aggregation number. In other words, we assume the system to be monodisperse. In the Appendix, it is shown that under these conditions we can neglect the translational entropy of the cluster. Also, the charge on the average cluster is assumed to fluctuate little. Therefore, we will write

$$\frac{F}{Vk_{\mathrm{B}}T} \simeq \frac{\phi}{\upsilon n} f_n(Z) \tag{11}$$

Here Z is the value for which $f_{\mathrm{charge}}(n, Z)$ is minimal. See the Appendix for a justification of eq 11. Also in the Appendix, one can find the conditions for size and charge monodispersity. In short, these are (1) large aggregation numbers, $n \gg 1$, and (2) large total charge on a cluster, $Z \gg 1$. We further note that if we find clusters of considerable size within this approach, they will also be found when we include fluctuations. This is due to the fact that entropy tends to stabilize large clusters, see refs 3 and 4. Therefore, to analyze the approximation, eq 11 is a good starting point to predict equilibrium clustering.

Instead of the total charge on a cluster Z, we now take the charge per particle z (compare eqs 3 and 4):

$$Z = nz \tag{12}$$

In the approximation of monodisperse charge and size distribution, the bulk density of counterions is given by $n_{\mathrm{b}} = \phi z/\upsilon$. The charge dependent part of the free energy of a cluster is now

$$f_{\mathrm{charge}}(n, nz) = nz\left[\Delta\epsilon + \ln\left(\frac{z^2\phi b^3}{\sigma s \upsilon}\right) + g\frac{Qnz}{R_n}\right] \tag{13}$$

The prefactor of the Coulomb term, i.e., $^3/_4$ for homogeneously charged spheres, is generalized to g in order to apply this to shapes other than spherical. The optimum charge per particle can be found by minimization, with respect to z.[13] We will assume the last term on the right-hand side, the Coulomb interaction term, to be small compared to the entropic terms:

$$z = z_0 + \delta z \tag{14}$$

Here z_0 is the value that minimizes eq 13 for $Q = 0$. The correction due to the Coulomb interaction is denoted by δz. Carrying out the minimization we find

$$z_0^{\,2} = \frac{\upsilon\sigma s}{b^3 \mathrm{e}^{\Delta\epsilon+2}}\frac{1}{\phi} \tag{15}$$

We explicitly see here that the charge per particle depends on volume fraction. This is caused by the increase in translational entropy of the dissociated ions upon diluting the system. For the correction δz, we find to linear order in Q/R_n:

$$\frac{\delta z}{z_0} \simeq -g\frac{Q\, n\, z_0}{R_{\mathrm{n}}} \tag{16}$$

$$\equiv -\frac{\zeta}{2} \tag{17}$$

This equation defines the ζ potential. If it is too high, the charge per particle will depend on the aggregation number. In other words, counterions will condense on the surfaces upon aggregation. If this condensation effect is too strong, simultaneous aggregation and charge condensation will take place and large aggregates might become unstable to further growth. Equivalently, at high ζ potentials, the interaction between the counterions and the surface charge can no longer be neglected. In the following, we will be somewhat easy on the condition of low ζ potential and allow for potentials of $\zeta = 2$. Other studies on the linearization of the Poisson−Boltzmann equation support to take this liberty.[14] The error made by eqs 15 and 16 can be circumvented by numerically minimizing eq 13. The counterion condensation is then taken into account implicitly in a somewhat simplified way. This will be done in section 7.

The free energy of a cluster due to the charge in the approximation of low ζ potential can be written as

$$f_{\text{charge}}(n) \simeq g\frac{{z_0}^2 n^2}{R_n} - 2nz_0 \tag{18}$$

We have inserted the minimizing charge z, and therefore, the only remaining dependence is on the aggregation number n. The optimum number n can now be determined by minimizing the total free energy per unit volume. If we can neglect the translational entropy of a cluster, which we can if the clusters are large enough, we may just as well minimize the free energy per particle in a cluster, f_n/n (see the Appendix).

The second term on the right-hand side of eq 18 represents the counterion condensation and works stabilizing with respect to fluctuations in volume fraction as will be shown in section 8. This term enters the free energy per particle as a constant and will therefore not influence the average aggregation number. Note that we can be sure that the stabilizing second term dominates the first as long as $\zeta \leq 1$, see eq 16.

4. Aggregation into Spherical Clusters

We now assume that particles of fairly general shape, each having an effective volume v, aggregate into large spherical clusters of radius R. The aggregation number is related to the cluster size via

$$n = \frac{4\pi R^3}{3v} \tag{19}$$

The charge dependent part of the free energy per cluster (for low ζ) is

$$f_{\text{charge}} = \frac{3Qn^2}{4R}{z_0}^2 - 2z_0 n \tag{20}$$

see eq 13. The energy due to dispersion interactions, eq 7, is

$$f_{\text{disp}} = -\epsilon n + 4\pi\gamma R^2 \tag{21}$$

Therefore the free energy per particle in a cluster written as a function of cluster radius R is

$$\frac{f_{\text{n}}}{n} = \frac{\pi {z_0}^2 Q}{v}R^2 + \frac{3\gamma v}{R} \tag{22}$$

where we omitted constant terms. This can be minimized to get the equilibrium aggregation number n_*:

$$n_* = \frac{2\gamma v}{Q{z_0}^2} \tag{23}$$

$$= \frac{1}{162\pi^2}\frac{\zeta_*^6}{vQ^3\gamma^3} \tag{24}$$

Note the small prefactor when n_* is written as a function of ζ potential. The dependence on Bjerrum length Q suggests that the clusters will be larger in more polar solvents. However, we must bear in mind that in more polar solvents there is more electrostatic screening due to ions other than the counterions. This destabilizes large clusters to further growth. The dependence on the ζ potential is strong so if we allow for $\zeta = 2$, we can indeed find large equilibrium clusters.

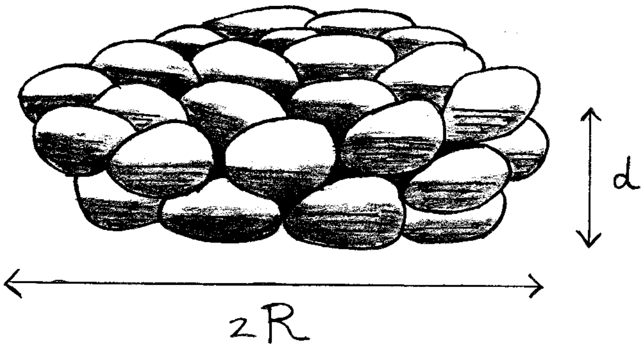

Figure 2. Particles may aggregate in a disk type shape such as the one here.

Interestingly, we find a dependence on volume fraction without invoking the translational entropy of the clusters. Because the charge per particle depends on volume fraction, see eq 15, we get the following dependence of size on volume fraction:

$$R_* \sim \phi^{1/3} \tag{25}$$

Another quantity of interest is the free energy per particle evaluated at optimum size and charge:

$$\frac{f_{\text{n}*}}{n_*} + \epsilon - 2z_0 = 5.76(\gamma v {z_0}^2 Q)^{1/3} \tag{26}$$

This enables us to compare with aggregation into shapes other than spherical. The exact prefactor is given by $(243\pi/4)^{1/3}$. Because there are more terms in the free energy than surface tension, the aggregation in a spherical shape is no longer obvious. In fact, the sphere, though favorable for the dispersion energy, is not so favorable for the coulomb energy because charges are packed relatively close together. The next sections are concerned with aggregation in disk-shaped and cylindrically shaped clusters.

5. Aggregation in Disk-Shaped Clusters

Assume the particles aggregate into a disklike shape as depicted in Figure 2. We will model this cluster as a disk with radius R and thickness d. The free energy of a cluster, up to linear terms in n, is

$$f_n = g\frac{QZ^2}{R} + \gamma(\pi R^2 + 2\pi R d) \tag{27}$$

Here $Z = nz_0$ as we assumed the ζ potential to be low. The prefactor of the Coulomb term is determined for high aspect ratio and homogeneously charged disks by numerical integration; it is approximately: $g \simeq 0.850$. We may omit terms linear in the aggregation number in eq 27, as these terms are irrelevant in the determination of the optimum size.

The aggregation number is related to the dimensions of the disk by

$$n = \frac{\pi R^2 d}{v} \tag{28}$$

The free energy per particle (up to a constant) in a cluster in terms of d and R is

$$\frac{f_n}{n} = g\frac{\pi Q {z_0}^2}{v} Rd + \gamma v\left(\frac{2}{R} + \frac{1}{d}\right) \tag{29}$$

By minimization with respect to R and d, we find a constant value of R/d:

$$\left(\frac{R}{d}\right)_* = 2 \tag{30}$$

This corresponds to an aspect ration of 4. Note that this is not very large so corrections due to finite aspect ratio are probably important. The approximation of high aspect ratio overestimates the Coulombic energy, so we expect the true aspect ratio to be somewhat smaller than that in eq 30, and also the energy per particle is expected to be smaller than the one given below in eq 33. The minimizing aggregation number is

$$n_* = \frac{2\gamma v}{g{z_0}^2 Q} \tag{31}$$

$$= \frac{1}{128\pi^2 g^3}\frac{{\zeta_*}^6}{vQ^3\gamma^3} \tag{32}$$

The similarity with the spherical case is large except for the prefactors. This is related to the constancy of aspect ratio, i.e., no independent length scale enters the problem. The free energy per particle in an optimum cluster is

$$\frac{f_{n*}}{n_*} + \epsilon - 2z_0 = 5.24(\gamma v {z_0}^2 Q)^{1/3} \tag{33}$$

The exact prefactor is given by $(54\pi g)^{1/3}$. By comparing prefactors in the free energy expressions for disk (eq 33) and sphere (eq 26) we see that the disk is the preferred shape.

6. Aggregation in Cylindrical Clusters

Consider aggregation in cylindrical shape. It has a length, L, which is assumed to be much larger than the diameter D. The free energy of a cluster like this is written as

$$f_n = \frac{QZ^2}{L}\ln\left(\frac{L}{D}\right) + \gamma\left(\frac{\pi D^2}{4} + \pi LD\right) \tag{34}$$

The first term on the right-hand side is the Coulomb energy of a slender rod on which the charges are distributed homogeneously. Within the logarithm, there should be a constant of order unity, which we will ignore. The error we make by doing this is of the same order of the error we generate by the approximations made in this section. Same as for the disks, we ignore terms linear in n.

The aggregation number is related to the dimensions of the cylinder:

$$n = \frac{\pi D^2 L}{4v} \tag{35}$$

The free energy per particle in a cluster in terms of L and D is (up to a constant)

$$\frac{f_n}{n} = \frac{\pi Q{z_0}^2}{v} D^2 \ln(L/D) + \gamma v\left(\frac{1}{L} + \frac{2}{D}\right) \tag{36}$$

Note the weak dependence of the Coulomb energy on the cylinder length. Minimizing with respect to D gives the following relation between the length and diameter:

$$D^3 = \frac{v^2\gamma}{\pi Q{z_0}^2}\frac{1}{\ln(L/D)} \tag{37}$$

In terms of the ζ potential, this is

$$D = \frac{1}{\pi Q\gamma \ln(L/D)}\zeta^2 \tag{38}$$

with the ζ potential given by

$$\zeta = \frac{\pi Q z_0 D^2}{v}\ln(L/D) \tag{39}$$

We see from eq 37 that the diameter is a very weak function of the rod length. If, in addition, we minimize with respect to L, no minimum can be found. To analyze the trend, we evaluate the free energy of a cluster for values of D and L satisfying eq 37. We can now write the free energy per particle in a way that it only depends on the aspect ratio:

$$\frac{f_{n_*}}{n_*} + \epsilon - 2z_0 = C(L/D)(\gamma v{z_0}^2 Q)^{1/3} \tag{40}$$

where C depends weakly on the aspect ratio $C(x) = 1.46(3 + 1/x)\ln(x)^{1/3}$. It varies slowly; for $L/D = 2$, we have $C = 5.29$, and for $L/D = 8$, $C = 6.28$. We find that $C(x)$ has a minimum around $x = 1$. Therefore, aggregation into cylinders is not favorable compared to aggregation into spheres.

A charming exception occurs if the aggregating particles themselves are slender rods that form bundles with a diameter smaller than the rod length. In this case, L should not be taken as a variable but taken equal to the length of an individual rod. Equation 37 for the diameter for the bunch can then readily be used. For work on the aggregation of rods with purely attractive forces, see ref 15.

7. Comparison with Experiment

From the clustering into spheres or disks, we find for the equilibrium radius

$$R_* \simeq K\left(\frac{\gamma v b^3 e^{\Delta\epsilon}}{Q\sigma s}\right)^{1/3}\phi^{1/3} \tag{41}$$

The constant K has a different value for disks, $K = 2.23$, and for spheres, $K = 1.52$. Buitenhuis et al.[16] made a study of the clustering of sterically stabilized Boehmite rods in the solvent ortho-dichlorobenzene ($\epsilon_r = 10.12$), i.e., a Bjerrum length, Q, of 5.1 nm. The rods have a diameter of 15 nm and a length of 75 nm, where we have included a steric layer of 2 nm. Light scattering on this system revealed the presence of structures of typically one μm in diameter. This points to very large aggregation numbers. The main focus in ref 16 was characterization of these clusters, but no attempt was made in modeling them. A frequent and often justified thought in systems such as these is that these large clusters are not in equilibrium but that their growth is kinetically hindered. However, the suspensions were stable for weeks. On this time-scale, even the larger clusters can collide, and therefore, a stabilizing mechanism must be at play. This is very likely to be charge, especially because the stabilizer used in ref 16 is anchored to the surface via ionic bonds.[8,17]

Before applying the theory developed in this paper to the findings in ref 16, we will discuss another alternative. This is the classical picture that has emerged in the synthesis of inorganic colloids. In this picture, a colloid is formed by *irreversible* aggregation of small primary particles. At a certain point, the charge of the aggregate is so high that a collision of two such aggregates does not lead to a larger aggregate. This is different from the mechanism suggested in this paper, which is fully equilibrium. We note that in ref 16 the clusters are observed to coexist with a substantial fraction of single rods (monomers) being inconsistent with the alternative clustering scenario described above.

Measurements of the Guinier radius in this system can be fitted with

$$R_* \simeq 1.4\phi^{1/3}\mu\text{m} \tag{42}$$

The raw data are $\phi = 0.007\,55$ and $R_g = 350$ nm, $\phi = 0.03$ and $R_g = 450$ nm and $\phi = 0.3$ and $R_g = 980$ nm. So the number of points is limited, but the variation in volume fraction is considerable. We will see if these trends can be explained with reasonable parameter values.

We will assume disklike aggregates. As stated, the diameter $\delta = 15$ nm and the length $l = 75$ nm. The surface tension γ is taken to be ϵ/s, see eq 8, with $\epsilon = 7.5$. Note that we cannot go too much lower with this value because, in that case, the whole driving force for aggregation, i.e., the dispersion interaction, is too weak. We assume the stabilizer to be grafted with an areal density of 0.15/nm^2, so the number of dissociable sites per particle is 675. We take for the confinement length $b = 0.18$ nm. Inserting these values in eq 41 and comparing with the experimental prefactor from eq 42, we can get a value for the dissociation energy: $\Delta\epsilon = 29$. This corresponds to an effective separation of 0.18 nm, see eq 1. This is a very reasonable value. Furthermore, we do not get, within reasonable bounds, very different values for the effective separation. Unfortunately, the ζ potentials we get with these parameters are too high; we get $\zeta \simeq 11.3\ \phi^{1/6}$. So it varies between 5 for the most dilute sample and 9 for $\phi = 0.3$. This is way beyond the limit of what we can reasonably accept being a low ζ potential, and thus, the approximation of constant charge per particle is not valid. This approximation has been used to derive eq 41, so we must solve the problem without it. This is most conveniently done numerically and is outlined in the following.

At high ζ potentials, the effect of counterion condensation must be included. A way to deal with this is to solve the Poisson−Boltzmann equation in a cell model.[14] Here we do not consider the full spatial problem; the effect of counterion condensation is taken into account by numerically minimizing eq 13 with respect to the charge per particle z. We no longer assume the Coulomb term to be small. What we find is qualitatively the same trends as described by eq 41, yet the prefactors are modified. The charge per particle is now depending on the aggregation number. A further minimization of eq 6 with respect to the aggregation number gives the cluster radius. This can be repeated for different volume fractions, and an example that fits the Buitenhuis data can be found in Figure 3a. The parameters that we used were the same as above, except the effective separation between paired ions, b, was taken to be 0.134 nm to fit the data. This corresponds to dissociation energies of $37k_BT$, which is significantly higher than the value without counterion condensation ($\epsilon = 29$). The result of the minimization is very sensitive to the effective separation, b. The other unknowns, i.e., the surface tension and number of chargeable groups σs, have a very limited impact.

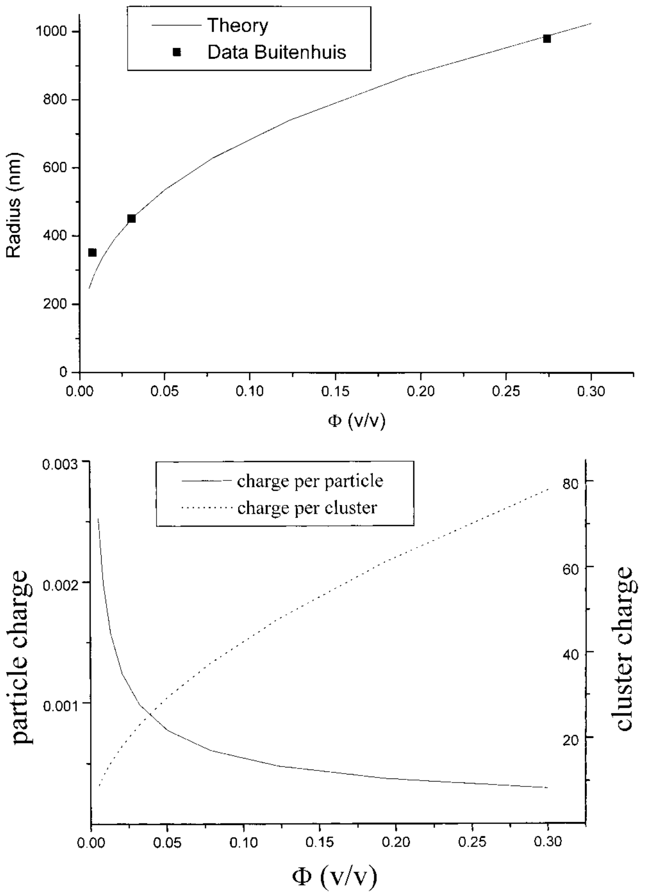

Figure 3. (a) Data from ref 16 are plotted. The line is the result of a numerical minimization eq 11. (b) The number of elementary charges per particle and cluster. Note the low value of the former.

8. Discussion

This paper has been focused on the calculation of equilibrium clusters. The cluster size and charge per particle were found to depend on volume fraction. The free energy depends on the volume fraction via these quantities, and one may ask what the stability with respect to variations in overall volume fraction is. To do this, we combine eqs 11, 18, 23, and 15 to get

$$\frac{F}{Vk_BT} \sim \phi^{2/3} - \phi^{-1/2} \tag{43}$$

The prefactors are neglected here. From the discussion below eq 18, we recall that the first term on the right-hand side in eq 43, which is destabilizing, is smaller than the stabilizing second term as long as the ζ potential is smaller than one. However, eq 18, and thus eq 43 also, is derived under the same condition of low ζ. In fact, as soon as counterion condensation becomes important ($\zeta \simeq 1$), the destabilizing term is suppressed and stability is ensured longer than expected when the counterion condensation is neglected.

The effect of counterion condensation was treated in a rather nonsophisticated way. Minimizing the full eq 13 captures the essence of the counterion condensation without invoking too much complexity, yet we are aware that doing this gives some error. Calculation of the correct ionic density profiles outside and *inside* the cluster is expected to alter the distance b by a factor comparable to the one that was seen in section 7, i.e., between $b = 1.8$ (without counterion condensation) and $b = 1.34$ (with condensation).

The Buitenhuis data could be fitted with a surface tension $\gamma = 0.001\,67$ nm^{-2} which corresponds to values of the aggregation energy per particle $\epsilon = 7.5$ by eq 8. The corresponding volume fraction of monomers is then approximately $\phi_{\mathrm{monomer}} \simeq \exp(-\epsilon + 2)$. We subtracted 2 from the cohesive energy to account for the orientational degrees of freedom that are lost upon aggregation. For our choice of ϵ, we get $\phi_{\mathrm{monomer}} = 0.0041$. So, as long as we have volume fractions higher than this, we can assume that all of the particles are contained in the clusters. Experimentally, half the fraction of the sample with total volume fraction 0.755% has been observed to consist of monomers.

The monodispersity is easily checked with the aid of eq A.9 from the Appendix. With the value for the surface tension and the aggregation numbers involved, we find that $\delta n^2 \ll n_*^2$. The neglect of charge fluctuations can be justified by looking at Figure 3b where we plotted both the charge per particle and the total charge on the cluster as a function of volume fraction. We see that the amount of charge per particle is very small, i.e., about one thousandth of an elementary charge;[18] therefore, at first sight, it is expected that fluctuations will play a considerable role. However, the number of particles in the aggregate is so large that the total charge on the cluster is much larger than unity. From eq A.9, we then see that the fluctuations in total charge on the cluster is relatively small.

Although the combination of electrostatic repulsion and dispersion attraction is classical in colloid science, we feel that we have added something new here, mainly because the focus was on equilibrium clustering of very large aggregates. For this, one needs long screening lengths, which can be realized in solvents with a low dielectric constant. In that case, electrolyte concentrations are low. However, if the dielectric constant is too low, the colloids themselves cannot attain significant charge to stabilize clusters. Intermediate dielectric constants of about 10 are suitable, as we have seen from the example. The number of charges per particle is then low enough to let the clusters grow sufficiently but large enough to prevent large scale phase separation. In ref 19, we see another example of the effect of charge in apolar solvents. In this work, the influence on the conductivity of inverse micellar solutions due to charge fluctuations on the micelles is investigated.

Somewhat peculiar is that the disk shaped aggregate (section 5) is more stable than both the rod-shape (section 6) and the sphere (section 4). If we compare different shapes with equal volumes, we have the dispersion energy: rod > disk > sphere. The coulomb energy though follows the opposite sequence: sphere > disk > rod. Therefore, the disk-shape is a compromise between coulomb and dispersion energy. In this light it seems plausible that this structure turns out to be the most favorable. We hope for some experimental evidence that shows the existence of these disk-shaped aggregates. However, the difference in prefactor of the free energy per particle in a disk-shaped and spherical cluster is only small.

Acknowledgment. Discussions with Dr. Dam of Papyron B. V. on charging mechanisms have been of great value. We are grateful to Profs. Philipse and Vrij for sharing their knowledge on charged colloids in organic solvents. We both owe Prof. Howard Reiss a great deal. First of all his enthusiasm has infected both of us. We still marvel at his lack of fear for jet lags, at his views on the Human Condition and at his deep and broad knowledge of the complex field of Physical Chemistry. Due to him, we both miss sunny California. He often told us about finding a pot of gold by boldly going where no one's gone before; and then, having found this treasure, not knowing what to do with it. In fact, Prof. Reiss has shown us that he darn well knows what to do with a pot of gold. And for sure, with all respect for his scientific trophies, his greatest treasure is, if we may say so, his lovely wife Phyllis.

Appendix

Charge and Number Fluctuations. Minimizing eq 5 with respect to the cluster distribution $\rho_n(Z)$ subject to the constraint eq 10 gives

$$\rho_n(Z) = l^{-3} \mathrm{e}^{-f_n(Z) + \mu n} \tag{A.1}$$

Here, μ is the chemical potential (scaled by $k_{\mathrm{B}}T$) fixing the overall volume fraction. The corresponding grand canonical free energy, $\Omega = F - k_{\mathrm{B}}T\mu\phi V/v$, is given by

$$\frac{\Omega}{Vk_{\mathrm{B}}T} = -l^{-3} \sum_{Z,n} \mathrm{e}^{-f_n(Z) + \mu n} \tag{A.2}$$

The charge Z_n that maximizes the exponent in eq A.2 for each n satisfies

$$\frac{\partial f_n(Z)}{\partial Z}\Big|_{Z=Z_n} = 0 \qquad f_n \equiv f_n(Z_n) \tag{A.3}$$

We can replace the sum over Z in the free energy eq A.2 by the largest term given by eq A.3. The remaining sum over n can also be approximated by finding the largest term. The n corresponding to the largest term is denoted by n_* and is given by

$$\frac{\partial f_n}{\partial n}\Big|_{n=n_*} = \mu \tag{A.4}$$

Within this approximation of negligible fluctuation in both charge and aggregation number, we get for the constraint from eq 10

$$\mu n_* \simeq f_{n_*} + \ln(\phi v / n_* l^3) \tag{A.5}$$

Suppose the cluster energy f_{n_*} is large compared to the translational entropy of the cluster; that is

$$|\mu n_*| \gg |\ln(\phi v / n_* l^3)| \tag{A.6}$$

Now combining eqs A.4, A.5, and A.6 gives

$$\frac{\partial (f_n/n)}{\partial n}\Big|_{n=n_*} \simeq 0 \tag{A.7}$$

In other words, if fluctuations in aggregation number can be neglected, minimizing the total free energy is equivalent to minimizing the cluster energy per particle. Let us now estimate the size of the fluctuations in charge and aggregation number by expanding the exponent in eq A.2 around the optimum values up to quadratic order

$$\Delta f_n(Z) = \left[\frac{3}{4}\frac{Q}{R_n} + \frac{1}{Z}\right]\delta Z^2 - \left[\frac{2}{n} + \frac{QZ}{2R_n}\right]\delta Z\,\delta n + \left[\frac{2}{3}\frac{QZ^2}{R_n n^2} + \frac{Z}{n^2} + \frac{\gamma R_n^{\,2}}{n^2}\right]\delta n^2 \tag{A.8}$$

Here we defined $\Delta f_n(Z) = f_n(Z) - f_{n_*}(Z_{n_*})$, $\delta n = n - n_*$, and $\delta Z = Z - Z_{n_*}$. Note that in this expression we left out the suffixes of Z and n for aesthetic reasons. The fluctuations in both charge and aggregation number can be shown to remain within the bounds indicated below:

$$\delta Z^2 \leq 1/Z \quad \delta n^2 \leq \frac{n^2}{Z + 4\pi\gamma R_n{}^2/9} \tag{A.9}$$

References and Notes

(1) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability Lyophobic Colloids*; Elsevier: New York, 1948; Chapter 8.

(2) Derjaguin, B. V. *Theory of Stability of Colloids and Thin Films*, Transl. from Russian; Consultants Bureau: New York, 1989; Chapter 11 by V. M. Muller.

(3) Reiss, H.; *J. Colloid Interface Sci.* **1975**, *53*, 61.

(4) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc. Far. Trans. 2* **1976**, *72*, 1525.

(5) Bohr, A.; Mottelson, B. R. *Nuclear Structure, Vol. II Nuclear Deformations*; W. A. Benjamin: Reading, MA, 1975; Appendix 6A.

(6) Rayleigh, J. W. S. *Theory of Sound*; MacMillan, London 1877.

(7) Amusia, M. Y.; Kornyushin, Y. *Contemp. Phys.* **2000**, *41*, 219.

(8) Fowkes, F. M.; et al. In *Colloids and Surfaces in Reprographic Technology ACS Symp. Ser. 200*; Hair, M., Croucher, M. D., Eds.; American Chemical Society: Washington DC, 1982; Chapter 15.

(9) If the polarizability of the particle is higher than the solvent, one gets higher effective separations b than the real distance of closest approach. This is an image charge effect: crudely speaking, we get $b/b_0 = 1 + \chi(\epsilon_r{}^{(\mathrm{part})} - \epsilon_r)/(\epsilon_r{}^{(\mathrm{part})} + \epsilon_r)$ with $\epsilon_r{}^{(\mathrm{part})}$ the relative dielectric constant of the particle b_0 the real distance between the ion pair and χ is a constant of order unity that depends on the positioning of the ions.

(10) Bjerrum, N. *Mater. Fys. Medd. K. Dan. Vidensk. Selsk.* **1926**, *7*.

(11) Hunter, R. J. *Zeta potential in colloid science*; Academic Press: London, 1981.

(12) Reiss, H.; Kegel, W. K.; Groenewold, J. *Ber. Buns. Ges., Phys. Chem.* **1996**, *100*, 279.

(13) The minimization of eq 13 with respect to the charge z is equivalent to equating the chemical potential of free counterions in the solvent to the chemical potential of ions adsorbed on the surface. These are respectively (for $Q = 0$) $\mu_{\mathrm{free}} = \mu^{(0)} + \ln(\rho_b b^3) + 1 + \Delta\epsilon$ and $\mu_{\mathrm{ads}} = \mu^{(0)} - \ln(z/\sigma s) - 1$.

(14) Alexander, S.; et al. *J. Chem. Phys.* **1984**, *80*, 5776.

(15) van der Schoot, P. *J. Phys. Chem*. **1992**, *96*, 6083.

(16) Buitenhuis, J.; Dhont, J. K. G.; Lekkerkerker, H. N. W. *Macromolecules* **1994**, *27*, 7267.

(17) Dam, R. Private comminucation.

(18) This can be interpreted by thinking of the particle being charged with one charge only a thousandth of the time

(19) Eicke, H. F.; Borkovec, M.; Das-Gupta, B. *J. Phys. Chem.* **1989**, *93*, 314.