# Electrophoresis in Charge-Stabilized Colloidal Cluster Phases

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ABSTRACT: The reversible properties of cluster phases have been described by theories that invoke Coulomb interactions as a stabilizing mechanism. What is lacking so far is direct measurement of these charges. This contribution aims at predicting what to expect if electrophoresis measurements were to be performed on these systems. As a result, we get a picture that exhibits several interesting features: (1) The existence of monomers and clusters lead to distinctly different mobilities (zeta potentials) in a single sample. (2) Strong dependence of the mobilities on particle volume fraction. It is our aim that the theory outlined in this paper may serve as a guideline to interpret the expectedly "messy" electrophoretic measurements.
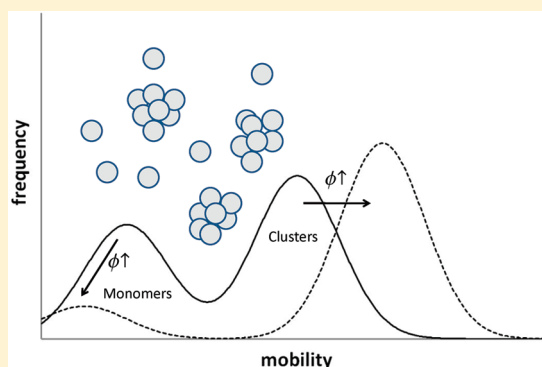
INTRODUCTION

The combination of short-ranged attractive interactions and long-ranged (Coulombic) repulsions have been identified as basic ingredients for the existence of large and thermodynamically stable clusters of colloidal particles.[1,2] Before and after this theoretical analysis, a number of experimental realizations have been identified.[3−5] At the same time, the role of charge in apolar solvents regained interest in the community of fundamental colloid science.[6] In addition to colloidal systems in apolar solvents, a cluster phase was also observed in a deionized protein suspension.[5] Lu et al.[7] have shown that not every apparently stable cluster in a colloidal system results from long-range Coulomb repulsions. From a technological point of view, the subject of charged colloids in apolar solvents is relevant for a number of key suspension applications:[8] electrophoretic displays (E-books), toners, and the design of photonic crystals. In all of these areas a precise knowledge of what causes the charging of the particles, what the effect is of short-range attractions, and what the role is of an external electric field on such suspensions is still largely unexplored. With this in mind, it is our aim to initiate the use of electrophoresis measurement as a way to obtain more insight in such systems. Obviously, the charge or mobility of clusters could determined by electrophoresis.[9] However, cluster phases are generally quite polydisperse and next to clusters (coexisting) monomers are also found to exist. Also the determination of electrophoretic mobility in nonaqueous solvents is challenging.[10] In this contribution, the properties of the monomers (electrophoretic mobility and concentration) will be analyzed. At the same time, both hydrodynamic and Coulombic interactions between clusters and/or monomers can be expected. Ignoring these interactions we hope to provide sufficient theoretical predictions in this paper that will enable to make headway in interpreting expectedly "messy" electrophoresis measurements in the limit of sufficiently low volume fraction.

MODEL

Consider a system with noninteracting clusters coexisting with monomers. Within our description, the monomers will be included explicitly since it is our aim to derive an expression for the coexisting monomer concentration. For simplicity, we will consider the clusters to contain the same number of particles n and the particles in the clusters will be in a unique state that has a (free) energy f_n Thus, f_n is the free energy per particle of a cluster of size n, where n has yet to be determined by minimization. To neglect the cluster polydispersity can be justified to a degree by noting that the cluster size distribution is expected to be peaked around an average value [1]. The predictions for the scaling mobility peak position with volume fraction is expected to be described by the mobility of a typical (or average) cluster. Invoking polydispersity may improve the predictions but leads to too much complexity at this stage.

Denoting the total number of clusters with N_{cl} and the number of monomers N_{mon} and the respective volume fractions with ϕ_{mon} and ϕ_{cl} the free energy of the total system can be written as

$$F_{tot}(n, N, N_{mon}) = N_{mon} \ln\left(\frac{N_{mon}v_n}{Ve}\right) + N_{cl} \ln\left(\frac{N_{cl}v_n}{Ve}\right) + N_{cl}nf_n \quad (1)$$

In this expression, e is the base for the natural logarithm, such that $\ln(e) = 1$. It should be noted that in this expression the quantity volume v_n is related to the entropic length scale. The

entropic length scale is discussed by Reiss[11] in the context of micelles in microemulsions. For micelles, this length scale is taken to be of molecular range. In this colloidal context, it is probably more appropriate to relate the entropic length scale to the interparticle interaction range. The entropic length scale is the result of a course graining procedure, and it is out of scope here to obtain a general expression for it. Since we are interested only in the scaling of the critical cluster concentration, it has been decided to ignore this complication and to leave an explicit estimate of v_n to future research. This expression has to be minimized with respect to N_{mon} under the constraint that the total number of particles N is conserved

$$N = N_{mon} + nN_{cl} \qquad (2)$$

To find the optimal cluster size we will minimize the total free energy with respect to n

$$\frac{\partial F_{tot}}{\partial n} = 0 \qquad (3)$$

Because the clusters are not interacting by assumption, the condition for the total free energy minimum coincides with minimization of the cluster free energy per particle with respect to the number of particles in a single cluster

$$\frac{\partial f}{\partial n} = 0 \qquad (4)$$

To find the monomer fraction that coincides with the clusters, it suffices to minimize the free energy with respect to the number of monomers in the system

$$\frac{\partial F_{tot}}{\partial N_{mon}} = 0 \qquad (5)$$

This minimization results in an expression for the fraction of free monomers coexisting with the clusters. If one assumes that the volume fraction of monomers is much smaller than the fraction of clusters, the expression for the monomer concentration is particularly simple:

$$\ln\left(\frac{N_{mon}v_n}{V}\right) = f_* \qquad (6)$$

The quantity f_* is the free energy per particle in the cluster evaluated for the optimum cluster size. This is an expression akin to one for the critical micelle concentration, where the free surfactant concentration is given by the Boltzmann factor of the free energy of condensation in the micelle. In order to proceed it is required to have an expression for f_n, the free energy of a particle in an n-cluster. We will essentially use the same model as in refs 1 and 12 but provide a bit more detail. First, the free energy is written as a part related to the short-range attraction and a electrostatic part f_{es}

$$f_n = p(n)\varepsilon + f_{es} \qquad (7)$$

Here, ε is the energy gain per bond in the cluster and $p(n)$ is the number of bonds contained in a cluster. The function $p(n)$ is approximated via a capillary approximation where the number of missing bonds on the surface are counted

$$p(n) = p_\infty - p_s\frac{3v}{sR} + \cdots \qquad (8)$$

The first term on the right is the number of contacts associated as if all particles are located in the bulk of the cluster. Thus p_∞ is

the average number of contacts per bulk particle. In case of an hexagonal packing p_∞ is equal to 6. The second term is related to the missing bonds on the surface. p_s is the number of missing bonds per particle on the surface. R is the radius of the cluster, s is the surface occupied by a surface particle, and v is the volume occupied of a particle in the cluster. The second term is related to an effective surface energy via

$$\gamma = \frac{p_s\varepsilon}{s} \qquad (9)$$

The electrostatic free energy per particle f_{es} is estimated with the Coulomb energy of a uniformly charged sphere with an effective dielectric constant ε_c immersed in dielectric with a dielectric constant ε_s with the aid of basic electrostatic calculation.[13] Note that this is a more general case compared to ref 1 where the dielectric constant of cluster and solvent was taken to be the same. The charge density of the sphere (cluster) is denoted by ρ. At this point, it is more convenient to use the assumption of a spherical cluster and use the cluster radius R instead of the number of particles in a cluster. The electrostatic energy is now expressed as

$$\frac{f_{es}}{v} = \frac{2\pi^2}{3}\left(1 + \frac{\varepsilon_s}{5\varepsilon_c}\right)\lambda_B R^2\rho^2 \qquad (10)$$

Here v is the volume occupied by a particle in the cluster. The Bjerrum length λ_B is related to the pure solvent.[1] Note that the correction due to a difference in dielectric constant between cluster and solvent is small in most practical cases. Now the total free energy per particle can be written as follows

$$f = \varepsilon p_\infty + \frac{3v\gamma}{R} + Kv\lambda_B\rho^2R^2 \qquad (11)$$

with $K = [(2\pi^2)/3](1 + (\varepsilon_s/5))$. Now the total free energy is ready to be minimized with respect to the cluster size R, resulting in

$$R_* = K'\left(\frac{\gamma}{\lambda_B\rho^2}\right)^{1/3} \qquad (12)$$

In this expression, the prefactor in front of the right-hand side can be expressed as $K' = \{[9/(4\pi^2)][(5\varepsilon_s)/(5\varepsilon_s + \varepsilon_p)]\}^{1/3}$ At this point the equilibrium cluster size can be reinserted to get the free energy corresponding to the optimum. The optimum free energy can be used to get an expression for the critcal monomer concentration

$$\ln \phi_{mon} = \varepsilon p_\infty + \frac{5}{2}\frac{\gamma v}{R_*} \qquad (13)$$

In the cluster phase, the cluster size generally increases with volume fraction.[1,5] This has as a consequence that the concentration of free monomer actually decreases as the volume fraction increases. This behavior is markedly different from how the coexisting monomer concentration for surfactants behaves. In such systems, usually the free surfactant concentration increases (slightly) with volume fraction, whereas here we expect a sharp decrease of the free colloid concentration with volume fraction The verbal rationalization of this remarkable behavior lies in the fact that as the clusters grow in size, the free energy per particle in the cluster is actually decreasing due to the decreasing surface to volume ratio. As a consequence the energy gap between a free monomer and a monomer condensed in the cluster increases, which is reflected by a lower free monomer concentration. Actually, it is the strong size dependence with volume fraction that underlies

the difference with microemulsions where the size of the micelles is almost constant. Recently, we have seen some experimental results on a density matched PMMA cluster phase that point in the direction of a decreasing monomer concentration upon increasing volume fraction, yet a systematic study has not been performed yet.

■ CLUSTER MOBILITY

The relevant limit in for electrophoretic mobility of the cluster phase is expected to be the Hueckel[14] limit. We emphasized above that a cluster phase has to satisfy the condition that the Debye screening length is larger than the cluster size. Within this same limit the Hueckel approximation is operative for electrophoretic mobility

$$\mu_{\text{cluster}} = \frac{Ze}{6\pi\eta R} \tag{14}$$

Here Z is the total number of elementary charges on a cluster and η is the solvent viscosity. This expression can be rewritten in terms of the charge density ρ. The Hueckel limit can be obtained by balancing the electrostatic force on a particle with the Stokes friction of a sphere. This can be done only if the backflow or retardation force corresponding to the diffuse double layer can be neglected. The neglect of the backflow can be justified if the Debye screening length exceeds the particle radius, that is, $\kappa R < 1$. To proceed, note that the total charge within a cluster is written as $Z = 4\pi\rho R^3/3$ Next, ρ can be eliminated in terms of the particle radius via eq 12 ultimately resulting in

$$\mu_{\text{cluster}} = K''\frac{ek_{\text{B}}T}{\eta}\frac{\gamma}{\lambda_{\text{B}}}R^{1/2} \tag{15}$$

The prefactor K'' is equal to $K'' = \{[1/(3\pi)][(5\varepsilon_s)/(5\varepsilon_s + \varepsilon_p)]\}^{1/2}$. An attractive feature of this result is that it is independent of the particular charging model. In principle, now the surface tension can be obtained through a linear fit of cluster mobility versus the square root of the cluster size.

■ MONOMER MOBILITY

The mobility of a free monomer should be also in the Hueckel limit as the monomers are smaller than the clusters. So for the monomers the same basic expression eq 14 applies. Instead of the cluster radius one should invoke the particle radius a (which is constant) and the particle charge per particle z, which is expected to vary with concentration. In the cluster phase one expects that the charge per particle is independent of whether the particle exists as a monomer or resides in a cluster. So, consistent with this assumption, the monomer charge can be written as $z = 4pi\rho a^3/3$ and after elimination of the charge density via eq 12, the monomer mobility can be expressed in terms of the coexisting cluster size R. The result is then

$$\mu_{\text{monomer}} \simeq \frac{ekT}{\eta}\left(\frac{\gamma a^4}{\lambda_{\text{B}}}\right)^{1/2} R^{-3/2} \tag{16}$$

So one finds that the mobility of the monomers decrease as the clusters grow in size. Interestingly, the clusters themselves are expected to get a higher mobility as they grow in size.
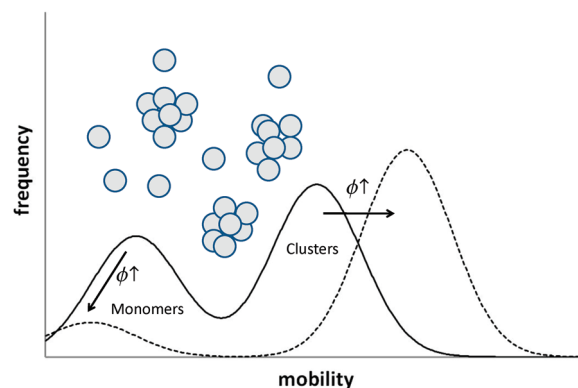
Figure 1. This figure depicts an impression of the cluster phase exhibiting clusters and monomers. In the accompanying graph, a sketch of the anticipated mobility spectrum is shown. The spectrum may show two peaks associated with monomers and clusters respectively. The trend with concentration is that the monomer peak will decrease in intensity and will shift to lower mobility, while the cluster peak will increase in intensity while it shifts to higher mobility values. Please note it is quite possible that in a real mobility measurement of the monomer and cluster peak cannot be separated.

■ FULL MOBILITY SPECTRUM

By aid of dynamic light scattering combined with laser Doppler electrophoresis measurement,[9] effective size distributions and mobility distributions of a suspension can be obtained in a relatively straightforward way. On the basis of the preceding discussion the following features are being expected in a mobility histogram: (1) The existence of two peaks, which should be assigned to monomers and clusters respectively. The clusters will have the higher mobility compared to the monomers. (2) Monomer mobility; average value and signal intensity decreases upon increasing volume fraction. (3) Cluster mobility; average value increases upon increasing volume fraction (Figure 1). The claims on the volume fraction dependence are based on a charge model that regards the particles essentially as a weak salt. This model leads to an inverse square root dependence of the charge per particle $z \sim \phi^{-1/2}$. Within the same charging model the following scaling laws with volume fraction are expected

$$\begin{aligned}
\mu_{\text{monomer}} &\sim \phi^{-1/2} \\
\mu_{\text{cluster}} &\sim \phi^{1/6} \\
R_* &\sim \phi^{1/3} \\
\ln(\phi_{\text{monomer}}) &\sim \phi^{-1/3}
\end{aligned} \tag{17}$$

At this point it is hard to predict whether the monomer and cluster peak are separable. This depends on polydispersity, measurement details, and some specific suspension parameters. Since the scattering is proportional to the square of the particle or cluster volume it is likely that the monomer peak will be overwhelmed by the cluster peak. However, if the peaks are distinguishable the trends above can be checked.

■ CONCLUDING REMARKS

This paper presents some new predictions regarding electrophoretic properties of a colloidal cluster phase. It may be possible to find two peaks in the electrophoretic mobility spectrum, that is, one peak associated to monomers and another peak to the clusters. Please note that it remains to be seen whether these

7266

dx.doi.org/10.1021/jp1097603 |*J. Phys. Chem. B* 2011, 115, 7264–7267

peaks can be distinghuised in a set of experimental data. This paper is meant to be a guideline to interpret electrophoretic mobility data in a cluster phase. Underlying the mobility spectrum we identified three quantities for which theoretical expressions are being derived. These are (1) electrophoretic mobility of the individual monomers, (2) electrophoretic mobility of the clusters, and (3) the actual volume fraction of monomers. This last quantity is determined via the assumption that the cluster phase is a truly thermodynamic phase with sufficient escape and adsorption of particles from and onto the clusters. Perhaps electrophoretic light scattering is not a sufficiently powerful technique to determine cluster- and monomer mobility simultaneously. Perhaps confocal microscopy could provide the means to establish the electrophoretic properties of monomers and clusters.[15] The main assumption that has been made to obtain the results is that the cluster phase is dilute. Dilute means that the clusters are not interacting, not hydrodynamically nor via direct (Coulomb) interactions. Another requirement is that the interaction between the charges on a cluster are weak such that the charge per particle can be assumed independent of the state of aggregation.[1] Within the dilute approximation, the relatively simple Hückel limit can be applied to the clusters in the suspension. Electrophoretic measurements of a colloidal cluster phase may be messy but could provide complementary evidence for the role of charge in the formation of clusters. The main finding is that under neglect of cluster—cluster interactions that the cluster mobility increases upon increasing cluster size. Another result that has been derived in this paper is that the concentration of free monomers in a cluster phase is actually a decreasing function of the total volume fraction. Another expectation is related to the polydispersity in size and electrophoretic mobility. In our model of the cluster phase, both the charge and the size of a cluster are fluctuating. Because the combination of charge and size determines the mobility, it is expected that the fluctuations in the mobility are larger than the fluctuations in size.

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7267

dx.doi.org/10.1021/jp1097603 |*J. Phys. Chem. B* 2011, 115, 7264–7267