

Colloidal cluster phases, gelation and nuclear matter

J Groenewold¹ and W K Kegel²

¹ Polymer Materials and Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

² van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Research Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

E-mail: j.groenewold@tmw.tudelft.nl

Received 6 April 2004

Published 8 October 2004

Online at stacks.iop.org/JPhysCM/16/S4877

doi:10.1088/0953-8984/16/42/006

Abstract

The combination of short-range attractions and long-range repulsions can lead to interesting clustering phenomena. In particular there are strong indications that the colloidal cluster phase is in fact a manifestation of such a competition. Here we compute the stability boundary of the cluster phase by invoking counter-ion condensation. It is found that a condensation catastrophe leading to an infinite cluster sets in if the level of charge on the colloid is too low.

The same ingredients leading to the cluster phase are found in nuclear physics: strong short-range attractions due to nuclear force and weak long-range Coulomb repulsions. We will show explicitly here the equivalence of a semi-empirical mass formula for the binding energy of the nucleus and the free energy of a cluster in a colloidal cluster phase. This identification enables an exploitation of theoretical results from nuclear physics to the colloidal domain and, perhaps, the construction of a colloidal system mimicking various aspects of nuclear matter.

1. Introduction

Recently we investigated theoretically the possibility of equilibrium cluster phases for weakly charged colloids in apolar solvents [1]. Next to the weak Coulomb repulsions the requirements cluster-phase formation are: (1) negligible screening by added electrolyte—as is the case for apolar solvents—and (2) short-range attractions to induce clustering. Simultaneously but independently a colloidal cluster phase was experimentally observed under similar conditions [2] as considered in our analysis. This experimental system consisted of colloids with polymer induced depletion attractions. The density matching solvent used in [2] is now known to provoke the PMMA colloids to have a positive charge [3], although the charging mechanism is somewhat enigmatic. A more detailed study and explicit verification of the theoretical clustering laws in the same colloidal system are being published elsewhere in

this issue [4]. Also very recently a small angle neutron scattering study by Stradner and Schurtenberger [5] shows that lysozyme proteins obey similar clustering laws. In this context let us note that the model proposed in [1] is not restricted to apolar solvents. The restriction to apolar solvents was made to direct attention to the type of system where the cluster phase was most likely to occur in our view. It is encouraging to see that the cluster phase also manifests itself in aqueous media which can be expected, provided screening is sufficiently absent.

The behaviour of colloidal systems in many ways resembles that of (simple) atomic and molecular systems [6]. However, contrary to the situation in molecular systems, the interaction potential between colloidal particles (being essentially a potential of mean force) can in principle be adjusted by choosing proper solvent(s) [6] or adding polymers [7]. It has been shown, for example [8], that under appropriate conditions colloidal systems behave as hard spheres. It is also well known that the addition of inert polymer induces (short) range attractions [7]. The ramifications of those two features of the colloidal interaction already generate much complexity, and there has been limited interest to investigate the effect of charge on this *particular* system. In general the role of charge in colloidal systems has been extensively studied in the past [9] and present. Of interest here are unscreened Coulomb interactions which, without short-range attraction, can lead to Wigner crystallization [3, 10]. Also there is fairly recent but largely controversial work, suggesting the existence of attractions between like charged colloids [11]. For monovalent counter-ions such attractions are highly unlikely as has been demonstrated in [12]. In that work it was demonstrated that the apparent attractive instabilities are a spurious result of the linearization of the Poisson–Boltzmann equation. To avoid this controversy we assume that the short-range attractions between the colloids are due to dispersion (van der Waals) attractions, or induced by addition of polymer.

In [1] we implicitly assumed a low degree of ionic dissociation, a property that is present in weakly polar solvents. However, at the same time, weakly polar solvents do not favour ionic dissociation and the levels of charging are expected to be low. Let us however recall that some of the free energy differences under investigation in the colloidal hard sphere phase diagram are of the order of $10^{-4} k_B T$ per particle [13]. It is clear that even a tiny amount of charge can significantly disturb statistics based on such energy scales. Moreover, in a cluster phase we find that a small amount of charge in combination with short-range attractions can dominate as the variable limiting the cluster size.

The main ingredient in the model for colloidal cluster phases is a competition between short-range attraction and long-range repulsion. The attractive force can be classical van der Waals attraction [14] or depletion attraction [15]. The long-range repulsion is caused by (screened) Coulomb interactions. At first sight, it may come as a surprise that these are similar forces to the ones that play key roles in the classical theory of colloid stability [9] (DLVO theory). This theory predicts either stable dispersions of colloid monomers or macroscopic aggregates, and no finite-size equilibrium clusters. However, in our treatment colloidal particles are dispersed in solvents of low dielectric constant and carry a small (self-consistent) charge. The combination of (small) charge and low screening by the medium leads to long-ranged electrostatic repulsion (relative to the scale of a colloid). In contrast, DLVO theory considers colloids in media with relatively large ionic strengths. The ions screen the Coulomb force, with the consequence that either monomers or infinite aggregates minimize the potential energy of the system. In our analysis of the cluster phase we invoked a capillarity approximation, in which the cluster is treated as a drop of uniform matter. This approximation holds for large clusters. In this picture the incentive for cluster growth is the excess energy of the particles on the surface, and it is controlled by the surface tension parameter. The stabilizing factor stopping the cluster growth comes from the long-ranged Coulomb repulsions [1].

Given the ingredients leading to a colloidal cluster phase (see above) one can observe a similarity with classical models for the atomic nucleus. There one finds a competition between the attractive strong forces and the repulsive Coulomb forces. This similarity is remarkable as the energy scales are separated by many orders of magnitude (~ 100 meV for the colloid binding energy versus ~ 20 MeV for the nucleonic binding energy); at the same time there is a large difference in length scale (10^{-15} m for the nucleon radius versus 10^{-6} – 10^{-8} m for the colloidal dimension). So in addition to the similarity with atomic or molecular systems there is a possibility for colloids to serve as a model system for nuclear matter. To illustrate this we shall show that the minimization of the mass formula leading to the most stable isotope is equivalent to our treatment in [1] leading to the optimal cluster size—but this size is now a function of variables such as the dielectric constant of the solvent, ionic strength, temperature, etc.

Before proceeding we wish to emphasize that although similarities are expected, we are aware that nuclear matter and colloidal clusters are not profoundly equivalent. The most important difference lies in the quantum mechanical character of nuclear matter. For example, the fermionic nature of the nucleon leads to a transition to a neutron liquid at very high densities. Such a transition (upon increasing the density) from an inhomogeneous system, i.e. nuclear matter in coexistence with a neutron gas, to more homogeneous distribution of matter, i.e. the neutron liquid, is most definitely not expected in the classical colloidal system.

We wish to emphasize the similarity between the colloidal cluster phase and nuclear matter. This will be done by identifying the semi-empirical mass formula for the binding energies in the nucleus with the cluster free energy for a spherical cluster in a cluster phase. Next to this stimulating equivalence we will discuss counter-ion induced gelation of the colloidal cluster phase. This gelation scheme is markedly different from vitrification in short-ranged attractive and hard-sphere repulsive systems.

2. Classical nucleus

The crudest approach imaginable to describe the atomic nucleus involves a surface tension and Coulombic repulsions. Let us recall the semi-empirical mass formula for a nucleus of atomic number Z and mass number A , which can be found in any introductory text on nuclear physics, e.g. [16]:

$$\frac{\mathcal{E}_{\text{bind}}}{A} = -a_{\text{vol}} + a_{\text{surf}} A^{-1/3} + a_{\text{sym}} \left(1 - \frac{Z}{2A}\right)^2 + a_{\text{coul}} \frac{Z^2}{A^{4/3}}. \quad (1)$$

On the left-hand side one finds the total binding energy per nucleon, where $\mathcal{E}_{\text{bind}}$ is the total binding energy. On the right-hand side we neglected the pairing energy terms, which are relevant for the smaller nuclei. The first term is the so-called volume term that sets the energy scale and is a constant contribution to the binding energy per nucleon. Being constant, this term does not play a role for the size and charge of the nucleus. The second—surface—term gauges the portion of strong interaction that is missing at the surface of the nucleus. The symmetry term stems from the fermionic nature of the nucleon and is related to the possibility of electron capture:



In this reaction a proton, p , and an electron e^- recombine into a neutron n while emitting a neutrino. This reaction allows for a change of the relative number of protons in nuclei. Accordingly, at higher temperature, when the energy barriers are lower, the nucleus can adapt itself to a size dictated by equation (1). Let us go back to the origin of the symmetry term.

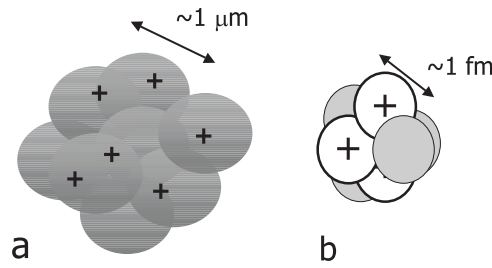


Figure 1. Colloidal cluster (a) and the nucleus (b). In the colloidal cluster the charge per colloid is fluctuating. The charge per nucleon is one elementary charge (proton) or none (neutron).

In order for the nucleons to be at their lowest possible Fermi level, an equal partition between protons and neutrons is required. This is reflected by the third term on the right-hand side of equation (1) which is minimal for $Z = A/2$. (In fact this term is the result of an expansion of the nuclear matter equation of state in the limit of weak deviations of proton density: $Z - A/2 \ll A$.) Finally in equation (1) there is the repulsive Coulomb term which disfavours the proportionality of protons in large nuclei. Minimization of equation (1) with respect to Z at fixed A gives the optimum charge of a nucleus of mass A . The resulting curve of this exercise follows the actual average isotope values rather well especially for the heavier elements.

Minimization of the binding energy per nucleon with respect to A and Z gives the optimum nucleus. Experiment shows that ^{56}Fe is the most stable isotope, but due to the approximate nature of equation (1) minimization yields an isotope close to this. At the high densities of nuclear matter ($>10^6 \text{ g cm}^{-3}$) to be found in neutron stars [22], the electron energy of the electrons becomes comparable to the binding energy of the nucleons. At this point electron capture as in equation (2) sets in, reflected by a decrease in a_{sym} being the coefficient of the symmetry term in equation (1). As a consequence the size of the most stable isotope is predicted to increase. Later, we shall see that this situation is qualitatively similar to the decreased dissociation of counter-ions upon increasing the number density of colloidal particles and thus forming larger equilibrium clusters.

3. Colloidal cluster

In the previous section we discussed aspects of the nucleus to be compared with a charged colloidal cluster. To pursue this comparison, let us replace a nucleon (proton or neutron) with a charged colloid. Similarly to the electron capture as in equation (2) one may consider a counter-ion condensation event in the case of weakly charged colloids:



C^n here stands for a colloid of charge $+n$ and ci^- for a negatively charged counter-ion. (Of course the charge signs of the colloid and counter-ion can be reversed.) Note that the difference with equation (2) is that for the colloids one can easily have many charges per colloid whereas the maximum for a nucleon clearly is one elementary charge; see figure 1. It turns out that this difference does not spoil the analogy as long as a coarse-grained description can be used, i.e. the case for large nuclei.

In [1] we also considered cluster shapes other than spherical. It was concluded in [1] that the most favourable shape was disc-like. This calculation contained an error and the conclusion is subject to doubt. A more accurate analysis will probably give spherical shapes as the most favourable one, consistent with results from nuclear physics. A precise analysis

of the preferred cluster shape is, however, postponed. For now we assume the clusters to be spherical, which is probably accurate and does not alter the results qualitatively anyway. Let us now write the free energy per unit volume of a spherical cluster with radius R as derived in [1] in a slightly more general way:

$$f_{\text{cluster}}(R, \rho) = f_0 + \frac{3\gamma}{R} + \frac{4\pi}{5} Q \rho^2 R^2 + 2\rho[\ln(\rho/\rho_0) - 1]. \quad (4)$$

Alongside the dependence on R there is the coarse-grained charge density ρ which is the total cluster charge divided by the total volume of the (spherical) cluster. The first term on the right-hand side is a constant contribution per particle, and it can be related to an aggregation energy ϵ of a pair wise interaction between two particles in contact: $f_0 = -q\epsilon/2v$, where q is an effective aggregation number and v the volume per particle in a cluster. The second term on the right-hand side is the same surface term which can be found in equation (1), and it is related to the missing inter-colloidal attractions for particles located at the cluster surface. The surface tension γ is related to the strength of the attractive interaction ϵ by $\gamma = f\epsilon/s$, where s is the area occupied by the particle at the cluster surface, and f the effective number of interaction contacts that are missed at the cluster surface. The second term is the capacitive energy for a homogeneously charged sphere, in other words the repulsive Coulomb term. In this term one finds the Bjerrum length Q defined as the distance for which the interaction between two elementary charges equals kT . (At room temperature one has $Q = 56 \text{ nm}/\epsilon$, with ϵ the relative dielectric constant of the medium. Generally the dielectric constant of the solvent and the cluster are unequal, and there is an issue concerning the interpolation, i.e. what is the effective value of ϵ . Here we assume the dielectric constants to be equal, and we postpone discussion about the more general case.) The last term in equation (4) can also be viewed as a general, charge-generating term. This term is governed by the bare charge density ρ_0 which will be the charge density in the absence of Coulombic repulsions: when $Q = 0$ the minimum of $f_{\text{cluster}}(R, \rho)$ with respect to ρ is located at ρ_0 . In terms of the site binding model discussed in [1], where it is the sum of the combinatorial entropy of the dissociating ions and the translational entropy of the released counter-ions in the absence of impurity electrolyte,

$$\rho_0^2 \simeq \frac{e^{-Q/b}\sigma}{rb^3\phi}. \quad (5)$$

Here ϕ is the overall volume fraction of colloid and b is the distance of closest approach between a counter-ion and a charge on the colloid surface (typically a few ångströms). Further, there is the colloid radius r and the areal density of chargeable groups on the colloidal surface σ . In fact $kT Q/b$ is a dissociation energy of an ion pair located at the colloidal surface.

In equation (4) there is a competition between the surface tension term (favouring large clusters) and the Coulomb term (penalizing large clusters). Another determinant for the cluster size is the charge density of the cluster which is governed by the last term in equation (4). The dependence on volume fraction of the bare charge density is of interest as this implies a growth of the cluster size upon adding particles.

4. Equivalence of colloidal cluster with nucleus

Having described the cluster free energy and the necessary energetics of the atomic nucleus we can now try to establish the formal connection between the two models. Comparing the structure of the cluster free energy equation (3) with the mass formula equation (1) we note that only the charge-generating term differs in analytic structure from the symmetry term in equation (1) which is the charge-generating term for the nucleus. Note that the latter is a result from a Taylor expansion of the energy around symmetric nuclear matter. A form valid

for a broader range of A and Z is found in a seminal paper of Baym *et al* [17]. Now one can analogously expand the entropic charge-generating term in equation (3)—a much easier task—to obtain exactly the same structure as in equation (1). We expand around the bare charge density: $2\rho[\ln(\rho/\rho_0) - 1] \simeq -2\rho_0 + \rho_0^{-1}(\rho_0 - \rho)^2$. Within this approximation the semi-empirical mass formula equation (1) and the colloidal cluster free energy equation (4) are identical if we make the following identifications:

$$\begin{aligned} A &\rightarrow 4\pi R^3/3v \\ Z &\rightarrow 8\pi R^3\rho/3v\rho_0 \\ a_{\text{vol}} &\rightarrow -f_0v + 2\rho_0v \\ a_{\text{surf}} &\rightarrow 4.84\gamma v^{2/3} \\ a_{\text{sym}} &\rightarrow kT\rho_0v \\ a_{\text{coul}} &\rightarrow 0.48kTQ\rho_0^2v^{5/3}. \end{aligned}$$

Here v is the occupied volume of a particle in the cluster. The prefactors in front of the identifications of a_{surf} and a_{coul} are approximate values for the case of spherical clusters. In these identifications the first is to relate the aggregation number with the mass number A , so a nucleon is simply identified with a particle in the cluster. The identification of the atomic number Z with the total cluster charge in units of bare charge per particle ρ_0v reflects the fact that the role of elementary charge is taken over by ρ_0v . Further, the energy scale is set by a_{vol} which has as a colloidal equivalent: $-f_0v$ modified by the counter-ion entropy $2\rho_0v$. (Actually this modification is not present in the mass formula due to the definition of the reference state, i.e. the state for which a_{vol} can be theoretically determined. This state is known as idealized nuclear matter: very large ($\rightarrow\infty$) number of nucleons, equal number of neutrons and protons, and the Coulomb interaction being switched off.) By necessity one has that the energy scales by a_{surf} and $\gamma v^{2/3}$ should be comparable to their ‘volume’ counterparts. The charge-generating term a_{sym} must be identified by the charge per particle, and the Coulomb term is given by a simple rescaling of the nucleon radius into the colloid radius, and the elementary charge into the elementary colloid charge, ρ_0v .

Let us see how the numerical values of the coefficients can compare. Typical values for the nuclear coefficients are [18] $a_{\text{vol}} = 15.75$, $a_{\text{surf}} = 17.8$, $a_{\text{sym}} = 23.7$ and $a_{\text{coul}} = 0.71$ MeV. Then, given these energy scales, we can deduce what the colloidal parameters should be to find a cluster with the same aggregation number as the most stable isotope ^{56}Fe . Such a colloidal cluster should be formed when one has $v^{1/3}/Q \simeq 102\gamma v^{2/3}/kT$. Since by necessity one has $\gamma v^{2/3} > kT$, a mimic of ^{56}Fe can be achieved only if the particle diameter, which is close to $v^{1/3}$, exceeds the Bjerrum length by a few hundred times. This is the case, for instance, with colloids of one micron diameter in a solvent with relative dielectric constant of 10. Note that it is a necessary condition but not a sufficient one, because the charge density has to be tuned by changing the volume fraction or temperature. From these estimations it seems possible to mimic the values of the nuclear coefficients.

5. Gelation

In certain colloidal systems low density gels are observed [19]. (The packing fractions are well below the typical repulsive glass limit, i.e. $\phi = 0.58$.) Simulations on systems of exclusively attractive hard spheres with a short-range attraction and implicit *reversible* bonds [20] do not show such low density gels. By incorporating long-range Coulombic repulsions there is a clear possibility of finding the phenomenon in simulation [21]. At the same time the incorporation of Coulomb interactions gives the possibility of finding low-density gels with reversible bonding.

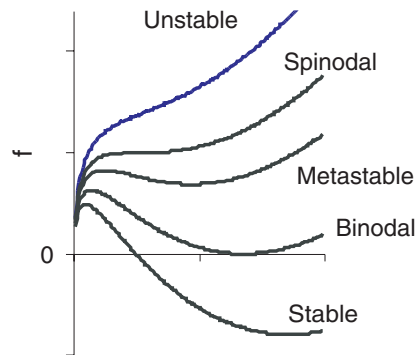


Figure 2. Excess free energy of the free energy per particle in a cluster as a function of the charge density ρ . The different curves correspond to different values of the parameter $\rho_0 \gamma^{-2} Q^{-1}$. The curves show three regimes: stable, metastable and unstable clusters. The point $\rho = 0$ corresponds to an ‘infinite’ cluster

(This figure is in colour only in the electronic version)

As such the gel is an equilibrium structure with voids stabilized by Coulomb repulsions. We will come back to this in the discussion.

Here we will concentrate on an important instability of the cluster phase related to counterion condensation. The instability is driven by the following mechanism: if the clusters are very large their surface or ζ potential grows. If this potential exceeds several kT then counterions are drawn to the cluster, and the effective charge density of the cluster will be lowered. Then due to this lower charge density the cluster can grow larger, see equation (6), and more counter-ions are drawn in. This process can continue indefinitely if the aggregation is strong enough, thus forming an infinite cluster. Below we will show this instability to occur within the assumptions of our model.

Equation (4) can be minimized with respect to the cluster radius, resulting in

$$R^3 = \frac{15\pi}{8} \frac{\gamma}{Q\rho^2}. \quad (6)$$

This reflects the intuition that a low charge density cluster can grow larger. Inserting this optimum radius in the free energy expression (3) one finds

$$f(\rho) = c \gamma^{2/3} Q^{1/3} \rho^{2/3} + 2\rho[\ln(\rho/\rho_0) - 1]. \quad (7)$$

For spherical clusters the constant is given by $c = 5.34$. In the free energy equation (7) we have two terms remaining. The first term on the right-hand side is the combined Coulomb and surface term, the second the charge generating entropy. The Coulomb/surface term is unstable with respect to the charge density and the entropic term has a stabilizing effect. The relative importance of the terms determines the stability of the system. The free energy equation (7) is graphically represented in figure 2. One finds for increasing values of the parameter $\rho_0 \gamma^{-2} Q^{-1}$ a regime of unstable, metastable and stable clusters, respectively. In the unstable regime there are no local minima, and the free energy is minimized for zero charge density, $\rho = 0$, which corresponds to an infinite cluster by equation (6). Passage to this infinite cluster should be observable as some kind of clustering catastrophe. At first this catastrophe will manifest itself as phase separation, of which the dense phase is expected to be gel-like.

In the metastable regime a local minimum emerges in the free energy, yet the absolute minimum still corresponds to the infinite cluster. In the metastable state a cluster phase may nucleate to form an infinite cluster. The unstable and metastable regimes are demarcated by a

spinodal. For higher charge densities the local minimum turns into an absolute minimum. In this stable regime the finite cluster is stable with respect to the infinite cluster, and gelation will not occur based on this simple free energy in an average sense equation (7). The metastable and stable regimes are demarcated by a binodal. In terms of our model parameters the binodal and spinodal are given by

$$\rho_0 = \begin{cases} 4.21\gamma^2 Q & \text{spinodal} \\ 5.22\gamma^2 Q & \text{binodal.} \end{cases} \quad (8)$$

Note that the parameters driving the instability influence cluster growth qualitatively in the same way: large surface tension, low charge density and large Bjerrum length favour the instability expressed in equation (8) and lead to larger clusters as can be seen from equation (6). In terms of short-ranged attractive potential well depth ϵ ($\gamma \sim \epsilon$) and the charge density in equation (5) the spinodal scales as

$$\epsilon_{\text{gel}} \sim \phi^{-1/4}. \quad (9)$$

Generally we will find that the clusters grow as one approaches the instability boundary. The maximum size of a cluster R_{max} is found at the spinodal:

$$R_{\text{max}} \simeq \frac{2.4}{\gamma Q}. \quad (10)$$

Again the prefactor is an approximation valid for spherical clusters. In fact we do not expect this prefactor to be right due to the approximations made (see discussion). In this expression the bare charge density has been eliminated by combining equations (6) and (8). This is an interesting elimination as the charge density generally is difficult to determine. The expression predicts that the size of the cluster at the gel line is independent of the volume fraction. Also there is no divergence of the size, but instead one finds a discontinuity of the value from equation (10) to an ‘infinite’ cluster. We can rewrite equation (10) in terms of the cluster aggregation number n_{max} : $n_{\text{max}} \simeq vQ^{-3}\epsilon^{-3}$, where we recall that the sticking energy is ϵ and v is the volume per particle in the cluster. From this it is seen that large aggregation numbers can be obtained only if the particle diameter is larger than the Bjerrum length. This reflects the fact that large Bjerrum lengths stimulate counter-ion condensation and thus inhibit larger clusters.

6. Discussion and conclusion

The colloidal cluster phase was observed experimentally by Segre [2]. Simultaneously and independently we proposed the possibility of such phases as a result of short-range attractions and long-range repulsions. Later experimental results [4] seem to support our theoretical ideas on the cluster phase, and they have been a strong stimulus to continue our investigations. In this paper we presented the computation of a stability boundary for a cluster phase as a new contribution to the subject. It is clear that there are many points to be improved upon. For this let us recall that the results in the section on gelation have been derived under the following assumptions: (1) spherical clusters, (2) low volume fractions, (3) homogeneous distribution of counter-ions and cluster charge, (4) neglect of inter-cluster interactions, and (5) equal dielectric constant of cluster and solvent. It must be noted that we cannot neglect the third condition close to the gel line. The condition of spherical clusters is also debatable but the assumptions (2) and (4) are in principle feasible by limiting to low volume fractions. Also (5) is a restriction that can be satisfied in principle, but it would be useful to find the general case. We do not expect the results expressed in equations (8) and (10) to be qualitatively modified by a more accurate treatment of the problem, in particular by taking the ionic distributions into account,

both of the charge density on the clusters and that of the counter-ions in solution. We do expect, however, a modification of the prefactors.

We hope to have shown that the similarity of the colloidal cluster phase with the classical picture of the nucleus is more than superficial. In fact we have been able to show that—within approximation—the semi-empirical mass formula for the nuclear binding energy is equivalent to the free energy of a cluster in our model of the cluster phase. The relationship between the two fields at such a simple level is appealing, and we can hope to find guidance and inspiration from the advances made in nuclear physics. It is interesting to speculate about the equivalent of gelation in the nuclear context. It has been pointed out in the context of neutron stars, [17], for densities of the order of nuclear matter (10^{14} g cm⁻³), that inverse structures can be formed. An elaboration of these ideas have been reviewed in [22], where one finds a discussion on nuclear tubes, sheets and bubbles very similar to the ones found for other branches of soft condensed matter, in particular in block copolymer systems [23]. A nuclear bubble phase refers to a continuous background of weakly charged nuclear matter with equilibrium bubbles containing electrons and a gas of free neutrons. We think that it is an interesting challenge both theoretically and experimentally to see if such phases exist in the colloidal context. In particular can the ‘infinite’ cluster contain ‘bubbles’ of solvent and counter-ions? Note that in the past such structures have been observed in dilute de-ionized colloidal dispersions [24]. A theory describing this phenomenon, e.g. [25], uses the linear Poisson–Boltzmann, without invoking explicit attractions. Unfortunately, the linearization of the Poisson–Boltzmann equation is known to generate spurious instabilities [12]. We have some hope that the colloidal equivalent of the nuclear bubble phase is exemplified by the voids observed by Ise [24]. The most serious reservation we have lies in identifying the origin of the short-ranged attraction in this dilute colloidal system.

Acknowledgments

We would like to acknowledge Helen Sedgwick and Wilson Poon for sharing their views on the cluster phase, and are grateful for their interest in our work; Peter Schurtenberger for discussions on protein clustering; Emanuela Zaccarelli and Francesco Sciortino for stimulating discussions on colloidal gelation and long-range interaction. Also we are grateful to Gert Aarts and Achim Schwenk for correcting some of the terminology, and a referee for very constructive comments. JG acknowledges the Dutch Polymer Institute for financial support.

References

- [1] Groenewold J and Kegel W K 2001 *J. Phys. Chem. B* **205** 11702
- [2] Segre P N, Prasad V, Schofield A B and Weitz D A 2001 *Phys. Rev. Lett.* **86** 6042
- [3] Yethiraj A and van Blaaderen A 2003 *Nature* **421** 531
- [4] Sedgwick H, Egelhaaf S U and Poon W C K 2004 *J. Phys.: Condens. Matter* **16** S4913
- [5] Stradner A and Schurtenberger P 2004 submitted
- [6] Vrij A 1983 *Faraday Discuss. Chem. Soc.* **76** 19
- [7] Vrij A 1976 *Pure Appl. Chem.* **48** 471
- [8] Pusey P N and van Megen W 1986 *Nature* **320** 340
- [9] Verwey E J W and Overbeek J T G 1999 *Theory of Stability of Lyophobic Colloids* (New York: Dover)
- [10] Van Winkle D H and Murray C A 1988 *J. Chem. Phys.* **89** 3885
- [11] van Roij R and Hansen J-P 1997 *Phys. Rev. Lett.* **79** 3082
- [12] Tamashiro M N and Schiessel H 2003 *J. Chem. Phys.* **119** 1855
- [13] Frenkel D and Ladd A J C 1984 *J. Chem. Phys.* **81** 3188
- [14] Israelachvili J 1992 *Intermolecular and Surface Forces* 2nd edn (San Diego, CA: Academic)
- [15] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255

-
- [16] Burcham W E 1971 *Nuclear Physics: an Introduction* (London: Longman Group Ltd)
 - [17] Baym G, Bethe H A and Pethick C J 1971 *Nucl. Phys. A* **175** 225
 - [18] Moskowski S A 1957 *Handbuch der Physik* vol 39 (Berlin: Springer)
 - [19] Pham K N *et al* 2002 *Science* **269** 104
 - [20] Zaccarelli E, Sciortino F, Buldyrev S V and Tartaglia P 2003 *Preprint* cond-mat/0310765
 - [21] Sciortino F, Mossa S, Zaccarelli E and Tartaglia P 2003 *Preprint* cond-mat/0312161
 - [22] Haensel P 2001 *Physics of Neutron Star Interiors* ed D Blaschke, N K Glendenning and A Sedrakian (Heidelberg: Springer)
 - [23] Leibler L 1980 *Macromolecules* **13** 1602
 - [24] Yoshida H, Ise N and Hashimoto T 1995 *J. Chem. Phys.* **103** 10146
 - [25] Warren P B 2000 *J. Chem. Phys.* **112** 4683