Mesoscopic theory for size- and charge-asymmetric ionic systems: I. The case of extreme asymmetry

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Mesoscopic theory for size- and charge-asymmetric ionic systems: I. The case of extreme asymmetry

A Ciach[1], W T Góźdź[1] and G Stell[2]

[1] Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland
[2] Department of Chemistry, State University of New York, Stony Brook, NY 11 794-3400, USA

Abstract

A mesoscopic theory for the primitive model of ionic systems is developed for arbitrary size, $\lambda = \sigma_+/\sigma_-$, and charge, $Z = e_+/|e_-|$, asymmetry. Our theory is an extension of the theory that we developed earlier for the restricted primitive model. The case of extreme asymmetries $\lambda \to \infty$ and $Z \to \infty$ is studied in some detail in a mean field approximation. The phase diagram and correlation functions are obtained in the asymptotic regime $\lambda \to \infty$ and $Z \to \infty$, and for infinite dilution of the larger ions (volume fraction $n_p \sim 1/Z$ or less). We find a coexistence between a very dilute 'gas' phase and a crystalline phase in which the macroions form a bcc structure with the lattice constant $\approx 3.6\sigma_+$. Such coexistence was observed experimentally in deionized aqueous solutions of highly charged colloidal particles.

1. Introduction

For many years, theoretical studies of phase behaviour in ionic solutions have been focused mainly on the special case of the restricted primitive model (RPM), in which half of the equal-sized charged hard spheres carry positive charge and half carry negative charge of equal magnitude, with the ions assumed to be dissolved in a structureless solvent [1–4]. Even the simplest real ionic solutions have some degree of size asymmetry, but with some notable exceptions [5–7] a common tacit assumption has been that the effects of weak and moderate asymmetry in both size and charge is not important to phase behaviour. Recently, the size- and charge-asymmetric case has drawn increasing attention [8–19]. Most extensions beyond the RPM are based either on the Debye–Hückel theory and Poisson–Boltzmann equation, or on the mean spherical approximation. These theories [15–19] as well as simulations [8–14], are typically limited to the case of small differences in sizes and charges. Only in very recent simulations have moderate [12] and large [13, 14] asymmetries been studied. Moreover, these theories are all 'classical' (i.e., mean field-like), and none of them are designed to describe the special Ising-like behaviour that is known to characterize the primitive model in its critical region. The development of a theory that does describe that behaviour was sketched by one of us in [20] and further developed in [21] and [22]. A field-theoretic method that also yields the

correct Ising-like behaviour was given by Ciach and Stell in [23] and further developed in our subsequent papers [24–27]. The mesoscopic theory described in this paper is an extension of the theory given there, and reduces to it when applied to the restricted primitive model.

In the case of extreme asymmetry (charge and diameter ratios between the two kinds of ions tend to infinity) the PM potentials describe highly charged colloidal particles suspended in a structureless solvent containing one kind of counterions and no coions. The physical properties of such a system are significantly different to those of the usual electrolytes. Highly asymmetric systems exhibit an interesting phase behaviour which is neither fully described nor understood, but it is clearly quite different to that of the RPM. In particular, formation of a colloidal bcc crystal with large interparticle separation coexisting with voids [28–32], various crystals formed by oppositely charged colloidal particles [33], and other anomalies [32, 34, 35] have been observed. The experimental findings suggest the existence of effective attractions between like-charged macroions as a possible explanation of the observed phase behaviour. The classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [36, 37], however, predicts purely repulsive interactions between the like-charged colloids. In recent approaches geometrical effects, as well as fluctuations and correlations are included [38, 39, 39–45]. The approaches are based e.g. on integral equations [40, 41], density functionals [39, 44, 45], and variational methods [38]. The effective attractions appear in a modified DLVO theory [46], and will also result from the explicit inclusion of various effects, such as 'charge regulation' [40], excluded volume ('Coulomb depletion') [43], metastable states [42] etc. On the other hand, 'volume terms' considered in [47] lead to a phase separation for purely repulsive interactions. Some of the above-mentioned works are questioned by authors of the other papers. In particular, the modification of the DLVO theory developed in [46] was criticized on theoretical grounds in [48, 49]. Because many experimental observations were interpreted [31, 32] in terms of the modified DLVO potential [46], the question of the phase behaviour of the highly charged colloidal systems is very controversial. The controversies are also associated with contradictory experimental results for the same systems. For example, in [50] gas–liquid-type separation was reported and explained on the basis of the modified DLVO potential [46]. The experiments for the same system were repeated in [51]. No such transition was observed in an absence of transport processes. It goes beyond the scope of our paper to discuss the above-mentioned approaches and experiments in more detail; extensive lists of recent works and discussions can be found in [38, 39, 45, 52]. The void–bcc crystal coexistence was observed experimentally in several systems with different sizes and charges of the particles [28–31], and different experimental techniques were used. However, such a transition has not been predicted theoretically, and the issue is still controversial. In theoretical approaches to colloidal systems one typically assumes extreme size asymmetry between the macroions and microions, and the methods differ from those developed for the RPM or for the PM with a small asymmetry.

In principle it should be possible to analyse the evolution of phase diagrams when the size and charge ratios increase from unity to infinity. To achieve this goal one needs a theory applicable to arbitrary size and charge asymmetries for the PM potentials. Within the context of Ornstein–Zernike formalism, one can go quite far in obtaining the general structure of such a theory, from which a number of important general results follow, such as the relation between the charge–charge and density–density correlation lengths, which shows that they must diverge together in the asymmetric case [7]. However, quantitative results for the thermodynamics and structure of systems of asymmetric ions are very sensitive to approximations and assumptions [15–17, 38, 39]. In fact one often needs to know the results to make proper assumptions, i.e. to identify the physical effects that have to be explicitly taken into account (association [15], 'border zone' [16] and cluster [17] formation, 'charge regulation' [40], 'Coulomb depletion' [43], 'volume terms' [47] etc). Recently developed field

theory for asymmetric ions, based on the Hubbard–Stratonovich transform [53–55], is elegant and in principle exact. In practice, however, the phase equilibria and correlation functions can be obtained by using different approximate methods. In [53] the size of ions is taken into account through the single cut-off in the Fourier space. Since in ionic systems the dominant fluctuations are short-range charge-density waves [56], the short-distance properties of the system are important, and this approximation may lead to inaccurate results. Moreover, the effect of size asymmetry cannot be studied in the theory with a single microscopic length. In [55] the hard spheres are taken into account more directly, and the charges are smeared inside the spheres to regulate the Coulomb potential. Formal expressions and relations are derived for arbitrary asymmetry, but in the general case they are very complex (and depend on the smearing function) and the author restricts the analysis of the thermodynamics and structure to the case of equally sized ions. Reliable theory allowing for a determination, with a reasonable effort, of phase equilibria and structure in the case of arbitrary asymmetry between the ions has not been developed yet. Therefore the crossover between the case of full symmetry and the case of extreme asymmetry is an essentially unexplored problem. The PM in the crossover region might be an appropriate model for ionic liquids, and it certainly deserves attention.

In a tractable theory simplifying assumptions and approximations are unavoidable. The key issue is to identify the degrees of freedom relevant for phase transitions and critical phenomena (i.e. along the spinodal lines), and to develop a theory which takes them into account correctly, with the irrelevant degrees of freedom treated in an approximate way. In order to describe phase transitions where ordering occurs at the length scales large compared to molecular sizes, a coarse-graining procedure, leading to the Landau–Ginzburg–Wilson (LGW) approach, has been introduced. The basic assumption of the LGW theory is that for macroscopic phase separation the short-wavelength fluctuations, and hence the precise form of correlations at distances $r \approx \sigma$ are irrelevant. In the case of simple fluids a correlation function can be thought of as being the sum of two pieces—the piece that is on the scale of the distance between particles plus the piece that is on the scale of the correlation length, which is arbitrarily large close to the spinodal, and it is only the latter piece that determines universality class and critical exponents. One can neglect the short-range behaviour of correlation as long as one is in a critical region (but only then).

In the coarse-grained description one considers deviations from random distributions of molecules, and it is important to include the dominant, most probable fluctuations. In simple fluids these correspond to macroscopic separation, i.e. to fluctuations with the wavenumber $k \rightarrow 0$ in the Fourier representation. Because like-charged ions repel, and oppositely charged ions attract each other, in ionic systems charge-ordered clusters, where positive- and negative-charge ions are the nearest neighbours, are observed in real space [12, 57]. In the Fourier representation the dominant fluctuations are charge-density waves [23, 56]. Thus, the fluctuations associated with charge ordering in periodic structures should be included in the coarse-grained description.

The idea of coarse graining was successfully extended by Brazovskii [58] and others to soft-matter systems (liquid crystals, microemulsions, diblock copolymers), where microphase separation occurs, i.e. periodic phases with a mesoscopic period of density oscillations may become stable. A mesoscopic period means a period of order of several molecular diameters or larger. In this case one expects that the phase equilibria should be qualitatively correctly described, provided that the fluctuations on the length scale corresponding to the ordering are included. Again, the correlation function consists of a short-distance piece and of the piece that oscillates on the mesoscopic scale and decays on the scale of the correlation length, which is arbitrarily large close to the spinodal. It is the latter piece that determines the phase transitions, as in simple fluids. The separation into the short- and long-distance pieces of the correlation

function can be conveniently done by a pole analysis in the complex Fourier space [20, 59–61]. The dominant pole (or a pair of complex conjugate poles) with the smallest imaginary part determines the asymptotic large-distance behaviour. It turns out that this dominant pole (or a pair of poles) describes quite correctly the correlation function down to the second maximum for short-range [59] and for Coulombic interactions [60–62]. In the coarse-grained mesoscopic theories the remaining poles of the correlation functions are neglected. Note, however, that down to the second maximum in the correlation functions the neglected poles lead to a small correction to the correlation function, and the results of the Landau-type, mesoscopic theories work well for such distances, although for distances $r \leqslant \sigma$ they are meaningless. To conclude, if one is interested in the vicinity of the spinodal line and in the large-distance part of the correlation functions (but only then), and one wants to take into account the possibility of ordering at distances corresponding to the second maximum of the correlation function or larger, one can consider the mesoscopic Landau–Brazovskii theory.

Here we propose to extend the mesoscopic field theory introduced for the RPM in [23] to the case of arbitrary size and charge asymmetry. The results of our field theory agree with simulations [63–67] in continuum-space RPM [24, 26], on the sc and the fcc lattices [26, 68], and on finely discretized versions of the former [26, 27], and also in the presence of additional short-range attractive [69] and repulsive [26, 68] interactions. Moreover, the electrostatic free energy has a correct behaviour for low densities, and the exact result in the Debye–Hückel limit is correctly reproduced [25]. So far no example of qualitatively wrong predictions of the mesoscopic theory has been found, although in some cases (including the RPM in continuum space) the effect of fluctuations has to be properly taken into account [26, 27, 68]; this can be done systematically in the perturbation theory. Foundations of the mesoscopic theory do not depend on the symmetry properties between the ionic species. On the basis of the results obtained for different extensions of the RPM one can hope that an extension to the case of arbitrary asymmetry will also result in a predictive theory yielding correct results on a semiquantitative level.

In this work we introduce the general framework of the mesoscopic theory for the PM (section 2). Next, in section 3, we focus on the case of extreme asymmetry, which turns out to be particularly simple. We find the phase behaviour and compare it with experimental results for highly charged colloidal particles in salt-free water [28, 32, 35]. We find good agreement with experimental results on a semiquantitative level. We also derive the correlation functions for extremely asymmetric case and show their forms for various thermodynamic states. We obtain monotonic decay of correlations for very dilute system, and results consistent with electric double-layer formation for less dilute systems. Near the transition to the bcc structure the double layer becomes denser and thinner. We find a pronounced maximum of the colloid correlation function at distances that agree with experimentally observed ordering [32]. At such distances the clouds of counterions around the particles do not overlap. Our results indicate that the theory developed for arbitrary asymmetry leads to qualitatively correct predictions in two opposite limiting cases—fully symmetric (RPM) [23–26, 68] and extremely asymmetric. Hence, we can expect qualitatively correct results in the crossover region as well. The results in the case of arbitrary asymmetry will be described elsewhere.

2. Mesoscopic theory for the PM

2.1. Coarse-graining procedure

We consider the PM electrolytes with the diameter and charge ratio between the large and small ions

$$\sigma_+/\sigma_- = \lambda \qquad \text{and} \qquad e_+/|e_-| = Z \tag{1}$$

respectively (without a loss of generality we assume $e_- = -|e_-|$, $e_+ = |e_+|$). For $Z = \lambda = 1$ the model reduces to the RPM, and for $Z, \lambda \to \infty$ the model describes highly charged colloid particles and point-like counterions with a small charge. In the PM the interaction potential of a pair $\alpha, \beta = \pm$ is infinite for distances smaller than the sum of radii,

$$\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2, \tag{2}$$

i.e. we assume hard-core repulsions. The electrostatic potential $V_{\alpha\beta}(\mathbf{r}_1 - \mathbf{r}_2)$ between the pair of ions α, β is

$$V_{\alpha\beta}(r) = \frac{e_\alpha e_\beta}{Dr}\theta(r - \sigma_{\alpha\beta}), \tag{3}$$

where D is the dielectric constant of the solvent (water). The θ-functions above exclude the contributions to the electrostatic energy coming from overlapping hard spheres.

In our field-theoretic, coarse-grained approach, we consider local instantaneous densities of the ionic species, $\rho_\alpha(\mathbf{r})$, i.e. we specify the numbers of ions of both kinds per mesoscopic volume $d\mathbf{r}$. For given densities $\rho_\alpha(\mathbf{r})$ precise positions of the ions can be different, and the probability density p that the local densities assume a particular form $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$ is given by

$$p[\rho_\alpha(\mathbf{r})] = \Xi^{-1} \int_{\mathcal{S}_p} e^{-\beta E(\mathcal{S}_p)}, \tag{4}$$

where $\beta = (kT)^{-1}$, and where T and k are temperature and the Boltzmann constant respectively. By $\int_{\mathcal{S}_p}$ we denote an integral over all microscopic states $\mathcal{S}_p$ compatible with the chosen densities $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$, and by $E(\mathcal{S}_p)$ we denote the energy of the corresponding microstate. The energy of the microstate $\mathcal{S}_p$ can be written in the form $E(\mathcal{S}_p) = U[\rho_+, \rho_-] + \Delta E_p(\mathcal{S}_p)$, where $U[\rho_+, \rho_-] = \int_{\mathcal{S}_p} E(\mathcal{S}_p)/\mathcal{N}$ is the mean energy for fixed densities $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$, and $\mathcal{N} = \int_{\mathcal{S}_p}$ is the number of all microscopic states compatible with $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$. We assume that for all microscopic states compatible with the given local densities the energy of the whole system is approximately the same, so that $\beta\Delta E_p(\mathcal{S}_p) \ll 1$. Hence,

$$e^{-\beta E(\mathcal{S}_p)} = e^{-\beta U[\rho_+, \rho_-]}\left[1 - \beta\Delta E_p(\mathcal{S}_p) + \tfrac{1}{2}(\beta\Delta E_p(\mathcal{S}_p))^2 + \cdots\right], \tag{5}$$

and the probability (4) can be written in the form

$$p = \Xi^{-1} e^{-\beta U[\rho_+, \rho_-]}\left[\mathcal{N} + \text{corr}\right]. \tag{6}$$

The correction term is proportional to $\int_{\mathcal{S}_p}(\beta\Delta E_p)^2 \ll \mathcal{N}$ and will be neglected. Finally, we assume that for particular fields $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$ the electrostatic energy is given by

$$U[\rho_+, \rho_-] = \tfrac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2\, \rho_\alpha(\mathbf{r}_1)V_{\alpha\beta}(\mathbf{r}_1 - \mathbf{r}_2)\rho_\beta(\mathbf{r}_2), \tag{7}$$

where the summation convention for Greek indices is used. The fields $\rho_\alpha(\mathbf{r})$ for which $U \to \infty$ occur with the probability $p \to 0$. Hence, in macroscopic regions the charge neutrality condition

$$\int d\mathbf{r}\rho_+(\mathbf{r})e_+ = \int d\mathbf{r}\rho_-(\mathbf{r})|e_-| \tag{8}$$

must be obeyed. One can easily verify that when (8) is satisfied for uniform fields $\rho_\alpha(\mathbf{r}) = $ const, then $U[\rho_+, \rho_-] = 0$. Due to thermal motion the charge neutrality can be violated in mesoscopic regions containing a small number of ions. The energy (7) associated with local deviations from the charge neutrality remains finite.

When $\Delta E(\mathcal{S}_p)$ can be neglected (i.e. for all microscopic states compatible with $\rho_\alpha(\mathbf{r})$ the energy is approximately the same), we can use the Boltzmann formula $\mathcal{N} = \exp(\beta T S)$, where by S we denote entropy. In an open system the probability is also proportional to the activities

$\exp[\beta(\mu_+ N_+ + \mu_- N_-)]$, where $N_\alpha = \int d\mathbf{r}\, \rho_\alpha(\mathbf{r})$ is the number of ions of the species α, and the chemical potentials μ_α are not independent—they have to be consistent with the requirement of the charge neutrality (8). The above discussion shows that the local instantaneous densities assume the form $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$ with the probability density given by

$$p = \Xi^{-1} \exp(-\beta \Omega^{MF}[\rho_+, \rho_-]), \tag{9}$$

where $\Omega^{MF}[\rho_+, \rho_-]$ is the grand potential in the system where the local concentrations of the two ionic species are constrained to be $\rho_+(\mathbf{r})$, $\rho_-(\mathbf{r})$. Next we assume that the entropy is determined by the hard-core reference system with the Helmholtz free energy $F_h = -TS$, and $\Omega^{MF}[\rho_+, \rho_-]$ is assumed to have the form

$$\Omega^{MF}[\rho_+, \rho_-] = F_h[\rho_+, \rho_-] + U[\rho_+, \rho_-] - \int d\mathbf{r}\mu_\alpha \rho_\alpha(\mathbf{r}). \tag{10}$$

For the reference system we assume the local density approximation $F_h[\rho_+, \rho_-] = \int d\mathbf{r}\, f_h(\rho_+(\mathbf{r}), \rho_-(\mathbf{r}))$. The f_h consists of the ideal-gas contribution plus the excess free-energy density of hard spheres with different diameters f_h^{ex}. For example, the Percus–Yevick approximation for hard-sphere mixtures [70] can be adopted. Because of the above assumption, packing effects of hard spheres cannot be described in our theory, and in the present form it is not applicable to very high densities. In principle, extensions beyond the local density approximation are also possible.

In the field theory introduced above the physical quantities are obtained by averaging over all fields ρ_+, ρ_- with the Boltzmann factor (9). The average densities and the correlation function are respectively given by

$$\langle \rho_\alpha(\mathbf{r}) \rangle = \Xi^{-1} \int D\rho_+ \int D\rho_- e^{-\beta \Omega^{MF}[\rho_+, \rho_-]} \rho_\alpha(\mathbf{r}) \tag{11}$$

and

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \langle \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') \rangle - \langle \rho_\alpha(\mathbf{r}) \rangle \langle \rho_\beta(\mathbf{r}') \rangle \tag{12}$$

with

$$\langle \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') \rangle = \Xi^{-1} \int D\rho_+ \int D\rho_- e^{-\beta \Omega^{MF}[\rho_+, \rho_-]} \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}'), \tag{13}$$

and

$$\Xi = \int D\rho_+ \int D\rho_- e^{-\beta \Omega^{MF}[\rho_+, \rho_-]}. \tag{14}$$

The grand potential Ω is

$$-\beta \Omega = \log \Xi. \tag{15}$$

In practice we are not able to evaluate the functional integrals in equations (11), (13) and (14), and we need to make approximations. In the simplest, mean field (MF) approximation the average values of the local densities are approximated by their most probable values, $\rho_{0\alpha}$, and the grand thermodynamic potential is approximated by the minimum of $\Omega^{MF}[\rho_+, \rho_-]$ at $\rho_\alpha = \rho_{0\alpha}$.

As convenient thermodynamic variables we choose dimensionless number density of all ionic species, s, and dimensionless temperature $T^* = 1/\beta^*$, where

$$s = \frac{\pi}{6}(\rho_{0+}^* + \rho_{0-}^*), \qquad \beta^* = \beta \frac{e_+|e_-|}{D\sigma_{+-}}, \tag{16}$$

and

$$\rho_\alpha^* = \sigma_{+-}^3 \rho_\alpha. \tag{17}$$

Here and below as a length unit we choose σ_{+-}. Because of the charge neutrality,

$$\rho_{0-}^* = Z\rho_{0+}^*, \tag{18}$$

the volume fraction of ionic species is

$$\zeta = \frac{\pi}{6}(\rho_{0+}\sigma_+^3 + \rho_{0-}\sigma_-^3) = \frac{2^3(\lambda^3 + Z)}{(1+\lambda)^3(1+Z)}s. \tag{19}$$

Let us study the form of Ω^{MF} in more detail. For small deviations $\Delta\rho_\alpha^*(\mathbf{r}) = \rho_\alpha^*(\mathbf{r}) - \rho_{0\alpha}^*$ of the local densities from their most probable values the grand potential (10) can be expanded about its value Ω_0^{MF} at the minimum,

$$\Delta\Omega^{\mathrm{MF}} = \Omega^{\mathrm{MF}} - \Omega_0^{\mathrm{MF}} = \Omega_2^{\mathrm{MF}} + \Omega_{\mathrm{int}}^{\mathrm{MF}}. \tag{20}$$

Here Ω_2^{MF} denotes the Gaussian part of the functional. In the Fourier representation we have

$$\beta\Omega_2^{\mathrm{MF}} = \tfrac{1}{2}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\Delta\tilde{\rho}_\alpha^*(-\mathbf{k})\tilde{C}_{\alpha\beta}^0(\mathbf{k})\Delta\tilde{\rho}_\beta^*(\mathbf{k}) \tag{21}$$

where $\Delta\tilde{\rho}_\alpha^*(\mathbf{k})$ is the Fourier transform of $\Delta\rho_\alpha^*(\mathbf{r})$, and the wavenumbers are in σ_{+-}^{-1} units. The second functional derivatives of Ω^{MF}, $\tilde{C}_{\alpha\beta}^0(\mathbf{k})$, consist of two terms,

$$\tilde{C}_{\alpha\beta}^0(\mathbf{k}) = a_{\alpha\beta} + \beta\tilde{V}_{\alpha\beta}(k). \tag{22}$$

The first term is given by the corresponding second derivative of βf_{h} taken at $\rho_\alpha^* = \rho_{0\alpha}^*$. The second term in $\tilde{C}_{\alpha\beta}^0(\mathbf{k})$ is the Fourier transform of the potential (3), and we find

$$\beta\tilde{V}_{\alpha\beta}(k) = \frac{e_\alpha e_\beta}{e_+|e_-|}\frac{4\pi\cos(kr_{\alpha\beta})}{k^2}\beta^*, \tag{23}$$

where $r_{\alpha\beta} = \sigma_{\alpha\beta}/\sigma_{+-}$. The remaining part of the functional has the expansion

$$\beta\Omega_{\mathrm{int}}^{\mathrm{MF}} = \int \mathrm{d}\mathbf{r}\left[\frac{a_{\alpha\beta\gamma}}{3!}\Delta\rho_\alpha^*(\mathbf{r})\Delta\rho_\beta^*(\mathbf{r})\Delta\rho_\gamma^*(\mathbf{r}) + \frac{a_{\alpha\beta\gamma\delta}}{4!}\Delta\rho_\alpha^*(\mathbf{r})\Delta\rho_\beta^*(\mathbf{r})\Delta\rho_\gamma^*(\mathbf{r})\Delta\rho_\delta^*(\mathbf{r})\right] + \cdots, \tag{24}$$

where

$$a_{\alpha\beta\gamma} = \frac{\partial a_{\alpha\beta}}{\partial\rho_\gamma^*} \qquad \text{and} \qquad a_{\alpha\beta\gamma\delta} = \frac{\partial a_{\alpha\beta\gamma}}{\partial\rho_\delta^*}, \tag{25}$$

and the derivatives are taken at $\rho_\alpha^* = \rho_{0\alpha}^*$. For pair potentials and for the local density approximation for the reference system, $\Omega_{\mathrm{int}}^{\mathrm{MF}}$ is strictly local. The explicit forms of the coefficients depend on the reference system.

2.2. Phase transitions

Let us focus on the boundary of stability of the uniform phase. The uniform phase is unstable with respect to fluctuations $\tilde{\rho}_\alpha^*(\mathbf{k})$ when the second functional derivative of Ω^{MF} is not positive definite, i.e. $\det\tilde{C}_{\alpha\beta}^0(k) < 0$. The temperature at the instability with respect to the $\mathbf{k}$-mode is thus given by

$$\det\tilde{C}_{\alpha\beta}^0(\mathbf{k}) = 0. \tag{26}$$

Boundary of stability with respect to the deviations $\Delta\rho_\alpha^* \propto \cos(\mathbf{r}\cdot\mathbf{k})$ from the densities $\rho_{0\alpha}^*$ corresponds to $\mathbf{k} = \mathbf{k}_b$ such that the equation (26) is satisfied first when the temperature is

decreased. For fixed $\rho_{0\alpha}^*$ the boundary of stability is thus given by the maximum of $T^*(\mathbf{k})$ obtained from (26), therefore $\mathbf{k}_b$ can be determined from the equations

$$\frac{\partial(\det \tilde{C}_{\alpha\beta}^0(k_i))}{\partial k_i} = 0. \tag{27}$$

Solutions of the set of equations (26) and (27) give both, the wavevector of the critical fluctuations $\mathbf{k}_b$, and the spinodal line in the phase space (s, T^*). For temperatures higher than at the spinodal line the randomly chosen instantaneous local densities are most probably uniform. For lower temperatures, however, the randomly chosen instantaneous densities most probably have a form of planar waves with the wavevector $\mathbf{k}_b$, or of linear combinations of such waves with different orientations of the wavevectors. The amplitudes of the density waves of the ionic species and the order of the associated phase transition depend on the form of Ω_{int}. In the next section we shall find the phase transition in the case of extreme asymmetry in MF.

2.3. Correlation functions

Let us consider the structure of the disordered phase, i.e. the correlation functions for the density deviations from $\rho_{0\alpha}^*$. In our mesoscopic theory, especially in the local density approximation, the correlation functions defined in equation (13) are meaningful for distances larger than $\sigma_{\alpha\beta}$, and in principle we can only expect a semiquantitative agreement with results of exact theories or simulations for large distances. The pole analysis of the correlation functions in the Fourier representation shows that in the mesoscopic theory for the RPM only the dominant poles, characterizing the long-distance behaviour, are present [61]. On the other hand, the dominant poles yield quite accurate results down to the second maximum of the correlation functions [60, 62], and for such distances we can expect semiquantitatively correct results in the colloid limit as well. However, the functional integrals in equation (13) cannot be calculated exactly. In practice we are able to calculate $G_{\alpha\beta}(r)$ in a perturbation expansion in $\gamma_{2n,m}$. In the Gaussian approximation, $\Delta\Omega^{\text{MF}} = \Omega_2^{\text{MF}}$, i.e. with the term $\Omega_{\text{int}}^{\text{MF}}$ in equation (20) neglected, the correlation functions (13) can be easily calculated by inverting the matrix of second functional derivatives of Ω^{MF}. In the Fourier representation we have thus

$$\tilde{G}_{\alpha\beta}^0(\mathbf{k}) = \left[\tilde{\mathbf{C}}^0(\mathbf{k})\right]_{\alpha\beta}^{-1}. \tag{28}$$

The functions analogous to pair distribution functions are related to $G_{\alpha\beta}$ (equation (13)) by

$$g_{\alpha\beta}(r) = \frac{G_{\alpha\beta}(r)}{\rho_{0\alpha}^* \rho_{0\beta}^*} - \frac{\delta(\mathbf{r})\delta_{\alpha\beta}^{Kr}}{\rho_{0\alpha}^*} + 1. \tag{29}$$

Beyond the Gaussian approximation we expect corrections to the correlation functions. Their relevance in different thermodynamic states will be studied in future works.

3. Case of extreme asymmetry

The above model can be applied to a suspension of highly charged colloid particles in a (salt-free) solvent containing one kind of point-like counterions. In the case of extreme asymmetry the reference system corresponds to a mixture of hard spheres and point-like species, with the densities constrained according to equation (18). For $\lambda \to \infty$ the volume fraction ζ reduces to the volume fraction n_p of the large species, and in the asymptotic regime $Z \to \infty$ (such that $Z/\lambda^3 \to 0$) we obtain (see (19), (18) and (16)),

$$\zeta = n_p = 8s/Z. \tag{30}$$

Hence, finite values of the number density, $s = O(Z^0)$, correspond to infinite dilution of hard spheres for $Z \to \infty$. At infinite dilution a hard-sphere system can be approximated by an ideal gas. The smaller ions are point-like in the limit $\lambda \to \infty$, and also behave as an ideal gas. Thus, for $\lambda, Z \to \infty$ we can assume that the reference system is just a mixture of ideal gases. For a mixture of ideal gases $a_{\alpha\beta} = \delta_{\alpha\beta}^{Kr}/\rho_{0\alpha}^*$, and from equations (16) and (18) we obtain

$$a_{--} = \frac{1}{\rho_{0-}^*} = \frac{\pi}{6s}, \qquad a_{++} = \frac{1}{\rho_{0+}^*} = \frac{\pi}{6s}Z, \qquad a_{+-} = 0. \tag{31}$$

Strictly speaking, in our analysis we assume that $\lambda \to \infty$ first, and next we consider the asymptotic behaviour of $Z \to \infty$ with $s = O(Z^0)$. The above asymptotic behaviour will be referred to as the colloid limit. From equation (23) we easily find that in the colloid limit the electrostatic potentials are

$$\beta \tilde{V}_{++}(k) = O(Z), \qquad \beta \tilde{V}_{+-}(k) = O(Z^0), \qquad \beta \tilde{V}_{--}(k) = O(Z^{-1}). \tag{32}$$

Hence, in the colloid limit we obtain

$$\tilde{C}_{++}(k) = Z\tilde{C}_p(k), \qquad \tilde{C}_{+-}(k) = \beta \tilde{V}_{+-}(k) = O(Z^0), \qquad \tilde{C}_{--}(k) = \frac{\pi}{6s} + O(Z^{-1}) \tag{33}$$

and in turn

$$\det \tilde{C}_{\alpha\beta}(k) = Z\frac{\pi}{6s}\tilde{C}_p(k) + O(1), \tag{34}$$

where

$$\tilde{C}_p(k) = \frac{\pi}{6}\left[\frac{1}{s} + \frac{24\cos(2k)}{k^2}\beta^*\right]. \tag{35}$$

3.1. Stability of the disordered phase

Instability of the disordered phase, in general given in equation (26), for $Z \gg 1$ is equivalent to

$$\left[\tilde{C}_p(k)\frac{\pi}{6s} + O(Z^{-1})\right] = 0, \tag{36}$$

and for $Z \to \infty$ the latter equation is satisfied when $\tilde{C}_p = 0$. From equation (33) we obtain that if $\tilde{C}_p = 0$, then $\tilde{C}_{++}(k) = 0$ for arbitrarily large Z. This means that in the considered asymptotic regime of $Z \to \infty$ and $n_p = O(Z^{-1})$, the fluctuations $\Delta\tilde{\rho}_+(\mathbf{k})$ can destabilize the uniform phase. The line of instability of the uniform phase with respect to these fluctuations, given by (26) and (27), assumes the form

$$\tilde{C}_p(k) = 0 = \partial\tilde{C}_p(k)/\partial k. \tag{37}$$

The spinodal line is given by the explicit expression

$$T_b^*(s) = -\frac{24\cos(2k_b)}{k_b^2}s, \qquad \tan(2k_b) = \frac{1}{k_b}, \tag{38}$$

and we find $k_b \approx 1.23$ in σ_{+-}^{-1} units.

In order to determine the phase transition associated with the spinodal (38), let us consider the asymptotic behaviour of Ω_{int} (equation (20)) for $Z \to \infty$ with $s = O(Z^0)$ and $\lambda \to \infty$. For the reference system corresponding to a mixture of ideal gases the only nonvanishing coefficients in equation (20) are (see equation (31))

$$a_{\alpha\alpha\alpha} = -\frac{1}{\rho_{0\alpha}^{*2}}, \qquad a_{\alpha\alpha\alpha\alpha} = \frac{2}{\rho_{0\alpha}^{*3}}. \tag{39}$$

After using equations (16) and (18) we obtain

$$\beta \Delta \Omega^{\mathrm{MF}} = \frac{Z}{2} \int_{\mathbf{k}} \Delta \tilde{\rho}_+^*(\mathbf{k}) \tilde{C}_p(k) \Delta \tilde{\rho}_+^*(-\mathbf{k})$$
$$+ \int_{\mathbf{r}} \left[\frac{Z^2 A_3}{3!} \Delta \rho_+^{*3}(\mathbf{r}) + \frac{Z^3 A_4}{4!} \Delta \rho_+^{*4}(\mathbf{r}) + \cdots \right] + \mathrm{O}(Z^0), \tag{40}$$

where

$$A_3 = -\left(\frac{\pi}{6s} \right)^2, \qquad A_4 = 2 \left(\frac{\pi}{6s} \right)^3, \tag{41}$$

and by $\mathrm{O}(Z^0)$ we denote all remaining contributions to $\Delta \Omega^{\mathrm{MF}}$ with the integrands that remain finite or tend to zero for $Z \to \infty$. All integrands proportional to $\Delta \rho_-^*$ turn out to be $\mathrm{O}(Z^0)$. For $Z \to \infty$ we neglect such terms compared to those given in equation (40). Note that we again come to the conclusion that the phase transition in the colloid limit is determined only by the macroion-density fluctuations. In the second step we rescale the field, $\Delta \tilde{\rho}_+^* = \tilde{\psi}/Z$, and the functional, $\Delta \Omega[\Delta \tilde{\rho}_+, \Delta \tilde{\rho}_-] = \Omega_r[\tilde{\psi}]/Z$, and we obtain

$$\beta \Omega_r[\tilde{\psi}] = \tfrac{1}{2} \int_{\mathbf{k}} \tilde{\psi}(\mathbf{k}) \tilde{C}_p(k) \tilde{\psi}(-\mathbf{k})$$
$$+ \frac{A_3}{3!} \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} \int_{\mathbf{k}_3} \delta \left(\sum_i^3 \mathbf{k}_i \right) \prod_i^3 \tilde{\psi}(\mathbf{k}_i)$$
$$+ \frac{A_4}{4!} \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} \int_{\mathbf{k}_3} \int_{\mathbf{k}_4} \delta \left(\sum_i^4 \mathbf{k}_i \right) \prod_i^4 \tilde{\psi}(\mathbf{k}_i), \tag{42}$$

where we truncated the expansion in the field at the fourth-order term. Because the cubic term is present, the transition to the phase with periodic ordering of the particles is first order in the MF. A similar functional was already studied by Leibler in the context of block copolymers [71], and we can directly use his results. In order to find the stable structure one considers ψ of a form of linear superpositions of n planar waves with the wavevectors $\mathbf{k}_b^j$ having different orientations (with $j = 1, \ldots, n$ and $|\mathbf{k}_b^j| = k_b$),

$$\tilde{\psi}(\mathbf{k}) = \frac{\Phi}{\sqrt{n}} \sum_j^n \left[\delta(\mathbf{k} - \mathbf{k}_b^j) w_n + \delta(\mathbf{k} + \mathbf{k}_b^j) w_n^* \right], \tag{43}$$

where w_n, w_n^* are complex conjugate and $w_n w_n^* = 1$. For $\tilde{\psi}(\mathbf{k})$ of the form (43) the functional Ω_r (42) per volume V can be written as

$$\beta \Omega_r / V = \tilde{C}_p(k_b) \Phi^2 - \alpha_3 \Phi^3 + \alpha_4 \Phi^4, \tag{44}$$

where the geometric factors α_j depend on n and have been found in [71] for several structures. For metastable structures Ω_r assumes local minima,

$$\partial \beta \Omega_r / \partial \Phi = 0, \tag{45}$$

and the stable structure corresponds to the global minimum. At the coexistence of the disordered phase with the periodic structure

$$\beta \Omega_r = 0, \tag{46}$$

and the actual phase transition occurs when the above equation is satisfied for this phase which corresponds to the global minimum of $\beta \Omega_r$; another words, for the phase which becomes stable, equation (46) is satisfied at the highest temperature. From (44), (45) and (46) we obtain the transition line as $\tilde{C}_p(k_b) = \alpha_3^2/(4\alpha_4)$. From the results of [71] it follows that in MF the
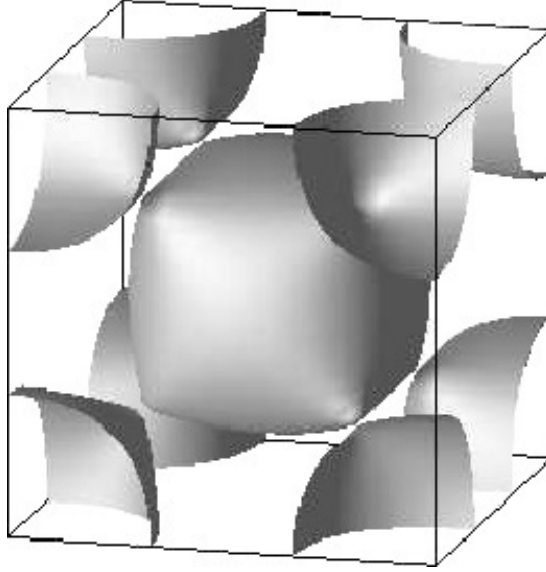
Figure 1. The surface $\Delta\rho_+(x, y, z) = 0$, separating the regions of enhanced and depleted density of particles. $\Delta\rho_+(x, y, z) > 0$ inside the droplets. The cubic unit cell with the lattice constant $a = 2\sqrt{2}\pi/q_b$ is shown.

disordered fluid coexists with the bcc crystalline structure if $A_3 \neq 0$. In the bcc arrangement of colloids the wavevectors $\mathbf{k}_b^j$ form edges of a regular tetrahedron, and for our particular case $\alpha_3 = 4A_3/(3\sqrt{6})$ and $\alpha_4 = 5A_4/8$ [71]. The above results and equations (35) and (41) enable us to obtain the explicit expression for the transition line in MF

$$T^* = -1.063 \frac{24\cos(2k_b)}{k_b^2} s \approx 13.1s \approx 1.64 Z n_\mathrm{p}. \tag{47}$$

The transition line (47) is valid only for $n_\mathrm{p} = \mathrm{O}(1/Z)$, because our asymptotic analysis here is restricted to $s = \mathrm{O}(Z^0)$.

In the colloid limit it is more convenient to use $\sigma_+ = 2\sigma_{+-}$ as a length unit, and σ_+^{-1} as a wavelength unit. To avoid confusion, the wavenumbers in σ_+^{-1} units will be denoted by q. In real space the field (43) in the case of the bcc structure is for $\mathbf{r} = (x, y, z)$ in suitably chosen coordinate frame given by

$$\Delta\rho_+(x, y, z) \propto \psi(x, y, z) \propto \cos\left(\frac{q_b(x+y)}{\sqrt{2}}\right)$$
$$+ \cos\left(\frac{q_b(x+z)}{\sqrt{2}}\right) + \cos\left(\frac{q_b(y+z)}{\sqrt{2}}\right)$$
$$+ \cos\left(\frac{q_b(x-y)}{\sqrt{2}}\right) + \cos\left(\frac{q_b(x-z)}{\sqrt{2}}\right) + \cos\left(\frac{q_b(y-z)}{\sqrt{2}}\right). \tag{48}$$

In figure 1 the surface $\Delta\rho_+(x, y, z) = 0$ is shown. This surface separates the regions with the particle density exceeding the average value from the regions of depleted particle density. From (48) we see that the lattice constant a of the bcc structure is related to the critical wavenumber q_b by $a = 2\sqrt{2}\pi/q_b \approx 3.6$ in σ_+ units. The distance between nearest neighbours (nn) in the bcc crystal is $\sqrt{6}\pi/q_b \approx 3.12\sigma_+$.

Let us focus on the two-phase region in the (n_p, T^*) phase diagram. The gas-side boundary of the two-phase region is given by the line (47). Let us determine the other boundary of the

Table 1. Experimental results obtained in [28–30] for three colloidal systems, and predictions of the theory developed in this work, for the same systems as in experiments. σ_+ and Z denote the particle diameter and valency respectively. T^*, $\bar{n}_p$ and a_{nn} denote the reduced temperature (equation (16)), the average volume fraction in the sample and the measured nearest-neighbour distance in the bcc crystal respectively. Finally, $3.12\sigma_+$ and n_p (gas) denote the calculated nn distance in the bcc phase at the coexistence with the gas phase and the particle volume fraction in the gas coexisting with the crystal respectively. The distance is given in nanometres (nm), the remaining quantities are dimensionless. In [28–30] temperature is $\sim$20–30 °C and salt concentration is negligible. In our theory no salt is present. For the system SS23, [28] the data for $\bar{n}_p$ and a_{nn} are taken from the plot in figure 2, and are not precise. For the system G5401 the data are taken from table II in [28], and correspond to the smallest and the largest volume fraction that was investigated. In table II, [28], $a_{nn}(\bar{n}_p)$ is a monotonically decreasing function.

System	σ_+	Z	T^*	$\bar{n}_p$	a_{nn}	$3.12\sigma_+$	n_p (gas)
SS23 [28]	302	1.5×10^5	1.46	1×10^{-2}	1000	942	5.9×10^{-6}
SS23 [28]	302	1.5×10^5	1.46	2×10^{-2}	750	942	5.9×10^{-6}
G5401 [28]	419	2.5×10^5	1.2	7.5×10^{-3}	1260 ± 70	1307	2.9×10^{-6}
G5401 [28]	419	2.5×10^5	1.2	11.2×10^{-2}	710 ± 60	1307	2.9×10^{-6}
Ref. [30]	112	5.7×10^5	0.15	2.5×10^{-2}	329	349	1.56×10^{-7}
Ref. [29]	112	5.7×10^5	0.15	3.8×10^{-2}	260	349	1.56×10^{-7}

two-phase region (located at the higher densities). Note first that there are two particles per cubic cell in the bcc structure. Moreover, the lattice constant at the coexistence with the gas phase is $a \approx 3.6\sigma_+$. Thus, the particle volume fraction in the bcc crystal is

$$n_p^{bcc} = 2\frac{\frac{\pi}{6}\sigma_+^3}{(3.6\sigma_+)^3} \approx 0.022. \tag{49}$$

The particle volume fraction at the coexistence is independent of T^*, and the two-phase boundary on the bcc side is given by the vertical line $n_p = 0.022$.

In table 1, several typical experimental results [28–30] for large σ_+ and large Z are compared with our theoretical predictions. We compare the experimentally observed nn distance a_{nn} in the ordered phase with our prediction $a_{nn} \approx 3.12\sigma_+$. We also quote the average particle volume fraction, $\bar{n}_p$ [28–30], which should be compared with $n_p^{bcc} \approx 0.022$. Note, however that at the coexistence with the gas phase $\bar{n}_p$ is expected to be smaller than n_p^{bcc}, because of the presence of gas-occupied regions in the experimental vessels. On the other hand, in the single-crystal samples $\bar{n}_p$ can be larger than at the coexistence with the gas phase. Accordingly, in the single-crystal phase off the phase boundary, a_{nn} should be smaller than at the coexistence. The more the experimental volume fraction increases, compared to the corresponding value at the phase coexistence, the larger should be the difference between the measured a_{nn} and its value at the coexistence with the gas phase. As far as we know, the particle volume fraction in the crystal phase at the coexistence with the gas phase has not been determined experimentally.

Let us first focus on the systems such that $\bar{n}_p \leqslant 0.022$. In table 1 we can see quite good agreement between the predicted ($3.12\sigma_+$) and measured (a_{nn}) values of the nn distance. For $\bar{n}_p > 0.022$ we see that $3.12\sigma_+ - a_{nn} > 0$ and increases for increasing value of $\bar{n}_p - 0.022$, as expected. The above observations indicate that in the experiments $n_p^{bcc} \approx 0.02$, and that $a_{nn} \approx 3\sigma_+$.

The above behaviour is not confirmed by simulations [12–14], where gas–liquid-type separation with a critical point, rather than crystallization, has been observed. However, in [12–14] the size and/or charge asymmetry is two–three orders of magnitude smaller than in experiments.

The asymptotic theory described above is strictly valid only in the colloid limit ($\lambda \to \infty$ first and next the asymptotic behaviour for $Z \to \infty$ with $n_p \sim 1/Z$ or smaller is considered). Beyond the colloid limit the full set of equations (26) have to be solved. Since there are two eigenmodes in the general case, both eigenvalues can vanish, leading to two spinodal lines associated with two phase transitions. As will be shown in [72], the other spinodal is associated with a gas–liquid separation. Beyond MF the crystallization may be pre-empted by the gas–liquid separation, as is the case for the RPM [24, 26, 68]. The latter transition corresponds to vanishingly low values of n_p and T^* in the limit $Z, \lambda \to \infty$, therefore only the crystallization survives in the colloid limit. Thus, although predictions of our theory in the colloid limit disagree with the results of simulations (obtained beyond that limit) it is plausible that the results of the full theory will agree with simulations for appropriate values of the asymmetry parameters and for the corresponding regions in the phase diagram (n_p, T^*). It is worth noting that in snapshots shown in [12] clusters separated by 'voids' are clearly distinguishable.

3.2. Gaussian correlation functions

For temperatures lower than that given in equation (47) the periodic structure is stable. This suggests effective attractions between like-charged macroions at the distances $r \sim 3\sigma_+$, at least near the transition to the crystalline phase. In fact already the experimental discovery of void–crystal coexistence and other anomalies [32] inspired a debate on the origin of the effective attraction between like-charged particles [32, 38, 40, 42, 43, 47].

In the mesoscopic theory instead of effective interactions between the macroions in the uniform phase we consider the correlation function $G_{++}(\mathbf{r}_1 - \mathbf{r}_2)$ defined in equation (12), and related to the pair correlation function according to equation (29). Maxima of $G_{++}(\mathbf{r}_1 - \mathbf{r}_2)$ indicate increased probability of finding a pair of colloid particles at the corresponding positions. In the lowest order, Gaussian approximation (neglected Ω_{int} in equation (20)) the correlation functions are given in equation (28), and in the colloid limit (i.e. for $n_p \sim 1/Z$ and $\lambda, Z \to \infty$) we find

$$\tilde{G}_{++}(q) = \frac{T^*}{4Z}\left[S + \frac{4\pi \cos q}{q^2}\right]^{-1},\tag{50}$$

$$\tilde{G}_{--}(q) = \frac{6s}{\pi} - \frac{4\pi}{Sq^2}\left(1 - \frac{4\pi \sin^2(q/2)}{Sq^2}\right)\tilde{G}_{++}(q)\tag{51}$$

and

$$\tilde{G}_{+-}(q) = \frac{4\pi \cos(q/2)}{Sq^2}\tilde{G}_{++}(q),\tag{52}$$

where

$$S = \pi T^*/(24s),\tag{53}$$

and terms $O(Z^{-2})$ have been neglected. Note that the q-dependent parts of the correlation functions are all of the same order $O(Z^{-1})$. The q-dependent parts of the functions (50)–(52) multiplied by $4Z\beta^*$ are independent of Z, and depend on the thermodynamic state only through S. In the colloid limit the functions $4Z\beta^* G_{\alpha\beta}$ assume universal shapes along the straight lines (53) in the phase diagram (s, T^*), at least in the Gaussian approximation.

From the above result and from equation (18) it follows that for $s = O(Z^0)$ the corresponding g-functions (equation (29)) are $\tilde{g}_{++} = O(Z)$, $\tilde{g}_{+-} = O(Z^0)$ and $\tilde{g}_{--} = O(Z^{-1})$. Note the strong dependence of these functions on the charge asymmetry resulting from the difference in the number densities in the charge-neutral system.

In real-space representation $G_{\alpha\beta}(r)$ can be obtained by residue method [60, 61]. All the functions have the same denominator, hence the same poles determine the decay lengths and (where applicable) the period of damped oscillations. The form of $\tilde{G}_{++}(q)$ is similar to the form of charge-density correlation function in the RPM, and the latter was studied in [61]. From the results of [61] it follows that for $S > S_K \approx 11.8$, where $S = S_K$ is known as the Kirkwood line [60], there are two imaginary poles ia_1 and ia_2 in the upper half of the complex plane, and

$$rG_{\alpha\beta}(r) = A^{(1)}_{\alpha\beta}e^{-a_1 r} + A^{(2)}_{\alpha\beta}e^{-a_2 r}. \tag{54}$$

For $S < S_K$ there are two conjugate complex poles, $q_1 = \alpha_1 + i\alpha_0$ and $q_2 = -q_1^*$ with $\alpha_0 > 0$, and [61]

$$rG_{\alpha\beta}(r) = \mathcal{A}_{\alpha\beta}\sin(\alpha_1 r + \theta)e^{-\alpha_0 r}. \tag{55}$$

The poles can only be found numerically, except near the spinodal line [61]. Following the analysis of [61] we find the characteristic lengths and the amplitudes. The correlation functions $4Z\beta^* G_{\alpha\beta}$ are shown in figures 2–4 for three different regimes. In figure 2 we show the correlation function above the Kirkwood line, i.e. for very dilute systems or for very high temperatures. Figure 3 corresponds to $S < S_K$, i.e. to denser system and/or lower temperatures, but far from the phase coexistence. Finally, in figure 4 we show the correlation functions at the coexistence with the bcc crystal.

From equation (54) it follows that for $r \gg a_2^{-1}$ (where $a_2 > a_1$ and the numbers are well separated) we recover the well known Yukawa-type decay of correlations (see figure 2), expected for very dilute systems. In this regime the effective interactions between the like-charged ions are purely repulsive, as in the DLVO theory and in the mean spherical approximation [73–75].

In figure 3 we see a qualitative change in the shape of the correlation functions, which in this part of the phase diagram exhibit oscillatory decay (55). Let us first analyse $4Z\beta^* G_{+-}(r)$ and $4Z\beta^* G_{--}(r)$. The $4Z\beta^* G_{+-}(r)$ assumes a maximum for $r \approx \sigma_+/2$ and then decreases rather slowly for increasing r. For $2\sigma_+ < r < 3\sigma_+4$, $Z\beta^* G_{+-}(r)$ is negative, and assumes a minimum for $r \approx 2.5\sigma_+$. At the same time $4Z\beta^* G_{--}(r) > 0$ for $1.5\sigma_+ < r < 3\sigma_+$, and assumes a positive maximum for $r \approx 1.8\sigma_+$. This means that the counterions are preferably separated by distances $1.5\sigma_+ < r < 3\sigma_+$, i.e. when there is more than enough room for a colloid particle to be located between them. The behaviour of the two correlation functions suggests a tendency for ordering in a structure where a diffuse cloud of counterions is formed around the colloid particle. The cloud of counterions extends to the distance from the centre of the colloid $r \approx 2\sigma_+$. For the distance from the centre of the colloid particle $r > 2\sigma_+$ the density of the counterions is depleted compared to ρ^*_{0-}. Let us turn to the $4Z\beta^* G_{++}(r)$. It assumes a positive maximum at $r \approx 3\sigma_+$, indicating preferable location of the corresponding pair of ions at such distances, consistent with formation of the cloud of counterions between them. Note that the clouds surrounding the two colloid particles separated by $r \approx 3\sigma_+$ overlap weakly in a small region around half the distance between the particles. The maximum of $4Z\beta^* G_{++}(r)$ in figure 3 is only slightly larger than zero, and the tendency of the colloids to be separated by such a distance is very weak.

Let us finally analyse the correlations in the uniform phase at the coexistence with the bcc crystal. Note first that the phase coexistence (47) occurs quite close to the spinodal line (38), where the amplitudes of the correlation functions diverge, and for $S \to S_b^+$ behave as $\sim (S - S_b)^{-1/2}$ in the Gaussian approximation [61] (S is defined in equation (53), and $S_b = \pi T_b^*/(24s)$). Thus, the amplitudes of the correlation functions are large at the coexistence with the crystal, and the fluid phase is strongly structured. To investigate this structure in more detail, consider first $4Z\beta^* G_{+-}(r)$ and $4Z\beta^* G_{--}(r)$. We find a rather large value of
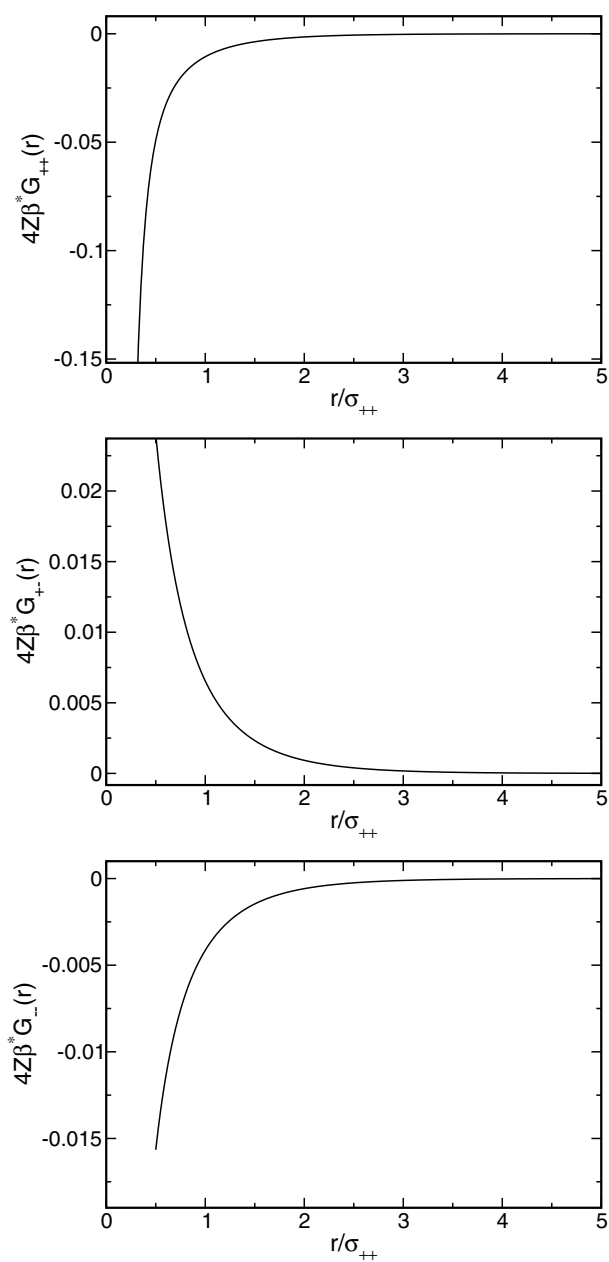
Figure 2. Correlation functions $4Z\beta^* G_{\alpha\beta}(r)$ (dimensionless) in the uniform phase for $S = 15$, i.e. for very strong dilutions. The inverse decay lengths in equation (54) are $a_1 = 1.265$ and $a_2 = 3.19$. Distance is in units of the particle diameter. As discussed in section 2.3, results of the mesoscopic theory for $r \leqslant \sigma$ are not expected to be correct.

$4Z\beta^* G_{+-}(r)$ for $r \approx \sigma_+/2$, namely $4Z\beta^* G_{+-}(\sigma_{+-}) \approx 0.737$, and a rather fast decay of $G_{+-}(r)$ for increasing r; $4Z\beta^* G_{+-}(r) < 0$ for $1.2\sigma_+ < r < 2.5\sigma_+$. The counterion correlation function $4Z\beta^* G_{--}(r)$ assumes a maximum for $r \approx \sigma_+$, i.e. when the counterions are located at the opposite sides of the colloid–particle surface. From the above observations
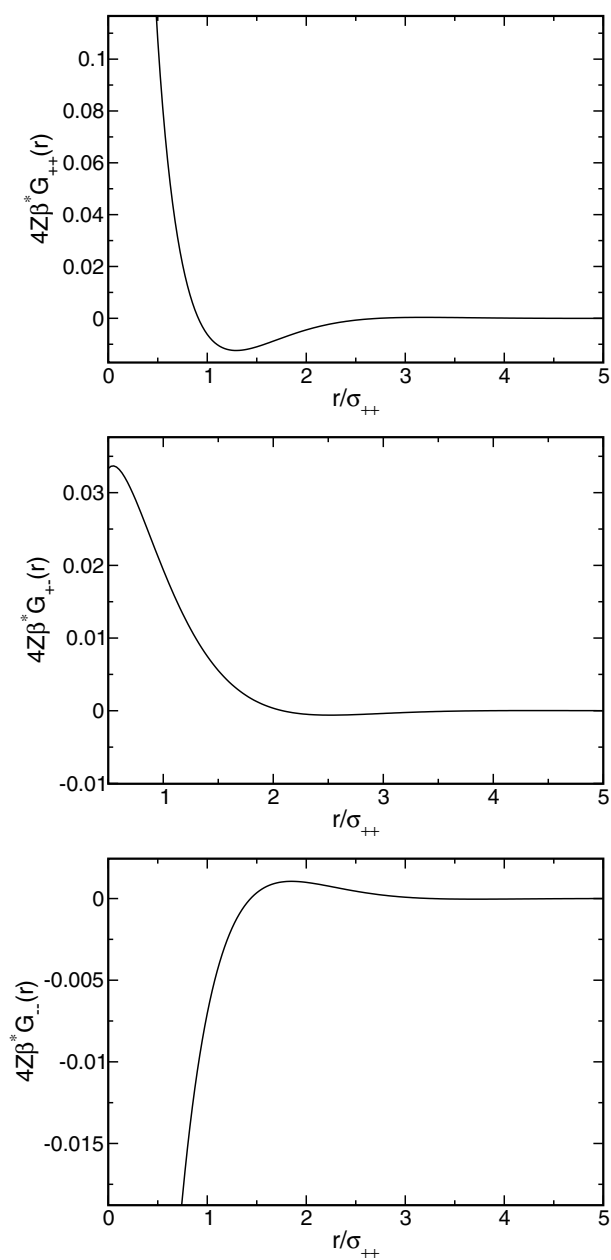
Figure 3. Correlation functions $4Z\beta^* G_{\alpha\beta}(r)$ (dimensionless) for $S = 5$, i.e. in the uniform phase at larger densities, but still far from the transition to the bcc crystal. The characteristic lengths in equation (55) are $\alpha_0 = 1.45$ and $\alpha_1 = 1.72$. Distance is in units of the particle diameter. As discussed in section 2.3, results of the mesoscopic theory for $r \leqslant \sigma$ are not expected to be correct.

we can deduce that the cloud of counterions becomes much denser and thinner, and is closely attached to the particles. Consider now $4Z\beta^* G_{++}(r)$. A positive value of $4Z\beta^* G_{++}(\sigma_+)$ suggests effective attraction between the like-charged macroions at the distance of the closest approach. Similar result was also found in [12]. This can only be possible if the point-like
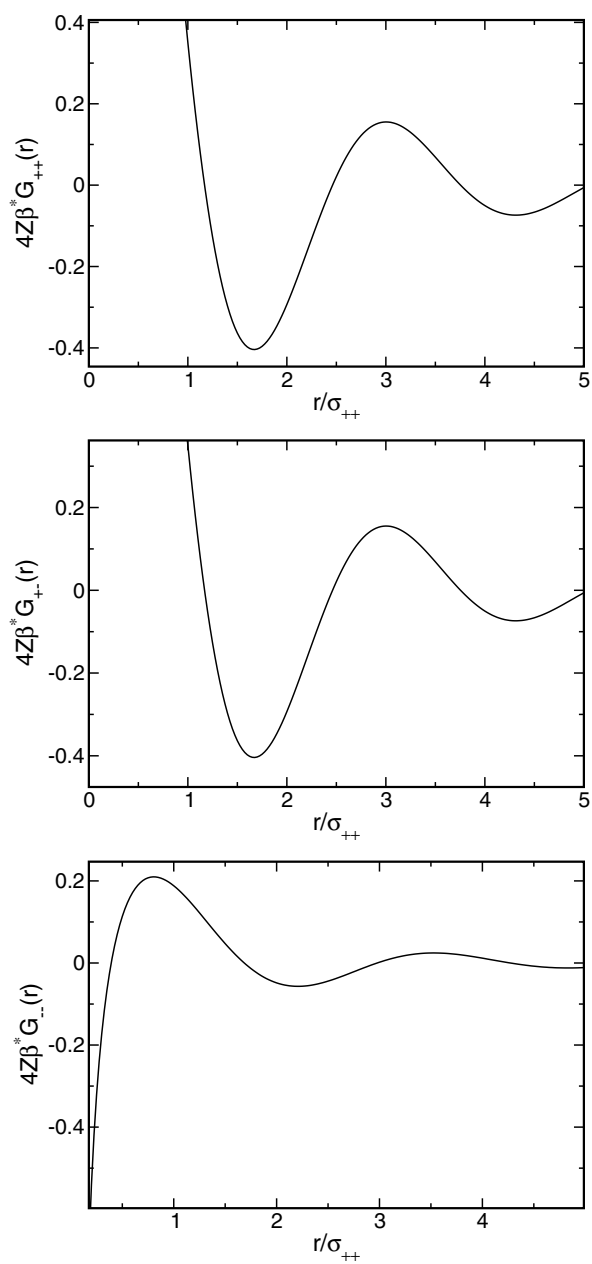
Figure 4. Correlation functions $4Z\beta^* G_{\alpha\beta}(r)$ (dimensionless) for $S = 1.712$, i.e. in the uniform phase at the transition to the bcc crystal. The characteristic lengths in equation (55) are $\alpha_0 = 0.3$ and $\alpha_1 = 2.43$. Distance is in units of the particle diameter. As discussed in section 2.3, results of the mesoscopic theory for $r \leqslant \sigma$ are not expected to be correct.

counterions are attached to the colloid surface, consistent with the formation of a thin and dense layer of counterions around each colloid particle. The subsequent, positive maximum of $4Z\beta^* G_{++}(r)$ occurs at $r \approx 3\sigma_+$. This maximum is much higher than away from the

phase transition (figure 3), and suggests rather strong tendency for location of colloids at such distances. Note that the clouds of counterions around the colloid particles separated by the distance $r \approx 3\sigma_+$ do not overlap. The second maximum of $4Z\beta^*G_{+-}(r)$ at $r \approx 3\sigma_+$, i.e. at a similar distance, shows again that each colloid particle is surrounded by a dense and thin cloud of counterions.

The correlation functions $g_{\alpha\beta}$ were obtained in simulations [12] for $Z = 10, \lambda = 19$. These asymmetry parameters are too small for our asymptotic regime $\lambda, Z \to \infty$, and the correction terms in equations (50)–(52) may well be of the same order as the terms which in the asymptotic regime dominate. This may be an important source of discrepancy between our theory and simulations. Also, we only obtained the Gaussian correlation functions in the local density approximation. The main discrepancy between our results and the results of simulations concerns the positions of the maxima of the correlation functions. Note, however that in experiments the colloidal crystals are formed in the case of very strong size and charge asymmetry [32], two–three orders of magnitude larger than those studied in simulations [12].

4. Summary and discussion

We have developed a mesoscopic theory for the PM with arbitrary size and charge asymmetry. Our theory allows for systematic studies of phase transitions and structure for any charge and size ratio. The results obtained in MF and Gaussian approximations can be improved by adding fluctuation corrections obtained in perturbation theory.

Explicit results for phase transitions and structure in the uniform phase were obtained in the colloid limit ($\lambda \to \infty$ first, and next the asymptotic regime of $Z \to \infty$ with $n_p = O(1/Z)$ is considered) in the MF approximation. We found a coexistence of a very dilute phase with the bcc crystal formed by the colloid particles. The lattice constant was found to be $a \approx 3.6\sigma_+$. Very strong dilution of colloids in the 'gas' phase, structure of the crystalline phase and the lattice constant agree with experimental results. The correlation functions $G_{\alpha\beta}(r)$ for density deviations of the species $\alpha, \beta = \pm$ at the distance r show the known monotonic decay for large values of S defined in equation (53) (high temperatures T^* and/or low densities s). For decreasing S the short-range order in the uniform phase increases.

In this work the analysis of the colloid limit is restricted to the MF approximation. Inclusion of fluctuations will certainly change the quantitative results, in particular the location of the phase transition. We expect that the fluctuations do not play a dominant role in the colloid limit, but the role of fluctuations certainly deserves attention in future works. In the full theory two spinodal lines occur, and coupling between the fields $\tilde{\rho}_+^*$ and $\tilde{\rho}_-^*$ in $\Delta\Omega^{MF}$ may lead to an increased role of fluctuations. By analogy with the RPM [23, 68] we expect that for not too large values of λ, Z and/or for volume fractions larger than $\sim 1/Z$, fluctuations may induce significant shifts of the spinodal lines, including the change of metastable transitions into stable ones and vice versa. Hence, beyond MF the crystallization may be pre-empted at low concentrations and temperatures by the gas–liquid-type separation for certain values of Z and λ. The role of fluctuations for different asymmetry parameters will be studied in future works.

We should emphasize that the foundations of the mesoscopic description and the asymptotic analysis for large asymmetry are based on first-principles considerations rather than having been fitted to the results of experiments. Mesoscopic field theories turned out to be appropriate for a description of a weak ordering, including a weak crystallization. Because the unit cell of the experimentally observed bcc crystal [28] is rather large, one may expect that the corresponding transition is not associated with close packing. The nearest-neighbour distance in the ordered structure corresponds to the second maximum in the corresponding

correlation function in the uniform phase close to the phase coexistence. As the results of mesoscopic theories are quite accurate down to such distances [59–61], it is plausible that in this particular case our theory yields correct results on a semiquantitative level. Obviously, our mesoscopic field theory has its limitations, and the structure for distances $\approx\sigma$ cannot be correctly reproduced, as is also the case in the commonly accepted Landau–Ginzburg–Wilson and Brazovskii theories. Our theory should be considered as a contribution to the discussion concerning the thermodynamics and structure in the charged colloidal systems. Both the experiments and our theory show the formation of the bcc structure with a large unit cell. To confirm that this is a real phenomenon it is desirable that microscopic theories and/or simulations yield similar results.

Acknowledgments

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