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Density functional theory of ordering in charge-stabilized colloidal dispersions

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We employ a simple density functional approach to predict the phase diagram of charge-stabilized colloidal dispersions consisting of bcc, fcc, and liquid phases. The systems are modeled to consist of charged hard sphere macroions interacting through a screened Coulomb potential for which the rescaled mean spherical approximation is used for the direct correlation function. The three-body effect is found to play a significant role and is incorporated here through a simple parametrization of the corresponding correlation function in a perturbative approach and also alternatively using a suitable version of the nonperturbative modified weighted density approach. The calculated phase diagrams for two different colloidal systems are shown to be in excellent agreement with the corresponding experimental results.

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I. INTRODUCTION

Density functional theory (DFT) [1] provides a conceptually simple and practically useful tool for the study of an inhomogeneous many-particle system using its single-particle density [2] as the basic variable. It has found wide applications in the study of not only electronic structure [3] theory, but the structure of inhomogeneous neutral [4] and ionic classical fluids [5] as well. In the past decade, DFT has also been proved to be a powerful tool for the investigation of phase transitions, initiated mainly by the pioneering work of Ramakrishnan and Youssouff (RY) [6] on the theory of freezing. Although originally proposed for the freezing of neutral classical fluids, its applicability has now been extended to ionic systems, liquid crystals, one-component plasma, and many other diverse systems [7]. In DFT, the free energy for the many-particle system is expressed as a functional of its single-particle density and this functional attains a minimum value at the equilibrium density. The DFT of freezing involves calculation of the difference in free energy between the liquid phase with uniform density and the solid phase with an inhomogeneous density distribution at different values of the external parameter (e.g., temperature or the average density), and the phase transition is predicted from the relative stability of the two phases.

Charge-stabilized colloidal suspensions have displayed a variety of phase transitions [8] as the density of the colloidal particles and the concentration of the dissolved electrolyte are varied. These are rather easy to follow experimentally and also the interaction between the particles can be tuned continuously from almost hard-sphere-like behavior to a soft long range Coulombic potential by controlling the composition of the suspension medium. The interaction between the colloidal macroions is well represented by the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential, which corresponds to the screened Coulomb interaction resulting from the linearized Poisson Boltzmann theory. Although linearization may not be a good approximation, Alexander *et al.* [9] have shown that the Yukawa form of the potential can still be used if the actual charge is replaced by an effective renormalized charge. The interaction potential is thus given by

$$V(r)=(Z^2e^2/\varepsilon)(1+\kappa d/2)^{-2}\exp[-\kappa(r-d)]/r \tag{1}$$

for the interionic distance r higher than the hard sphere diameter d and infinity otherwise (i.e., for $r<d$). Here the inverse screening length κ is given by

$$\kappa^2=(4\pi\beta/\varepsilon)\left[\rho_0 Ze^2+\sum_\alpha n_\alpha Z_\alpha^2 e^2\right], \tag{2}$$

where ρ_0 is the number density of the colloidal particles of charge Ze with e as the electronic charge, n_α is the number density of ions of type α with charge $Z_\alpha e$, ε is the dielectric constant of the medium, and β $(=1/k_BT)$ represents the inverse temperature.

Two rather recent studies on experimental phase diagrams that have been reported are the study of Monovoukas and Gast [10] for a colloidal suspension of charged polystyrene spheres in an aqueous medium and that of Sirota *et al.* [11] for the same system in 90% methanol solvent using synchrotron x-ray scattering. The accurate values of the effective charges of the particles in a colloidal suspension are not always known. In the absence of any straightforward and unambiguous method for

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their experimental determination, the effective charges are usually estimated using suitable models from measurements of some suitable properties of the dispersions. For the former study (referred to as system I), the effective charge $Z=880$, $d=1334$ A, and $\varepsilon=78$, while for the latter (system II) $d=910$ A and $\varepsilon=38$, but the effective charge is not established properly. We consider this Z to be a parameter and assume that it is equal to 350. Although this choice of Z is not unique, it is found to yield a phase diagram in good agreement with the experimental results. For system I, the concentration range of KCl is up to 3.8 μM, while in system II, electrolyte used is HCl and the concentration range is up to 700 μM. The ranges of the packing fraction η $[=(\pi/6)\rho_0 d^3]$ at which the liquid-bcc-fcc transitions are observed are also different in both cases and are $\eta=0.004-0.009$ in the first case and $\eta=0.05-0.20$ in the second case.

Recently several studies that have employed DTF for understanding the phase diagram of colloidal systems (for a recent review, see Ref. [8]) have been reported. The earlier study of Alexander *et al.* [12] has been shown to be of limited applicability. The more recent studies of Sengupta and Sood [13] (hereinafter referred to as SS) and Salgi and Rajagopalan [14] (hereinafter referred to as SR) have led to the conclusion that the inclusion of three-body correlation in some form or the other is important for predicting the phase diagram of colloidal systems. The study of SS attempts to predict the phase diagram observed experimentally (system I) by Monovoukas and Gast [10] and that of SR is concerned with system II, studied by Sirota *et al.* [11]. While SS employ a purely perturbative approach and include the three-body correlation in an approximate manner using only two parameters for the three-body correlation function $c^{(3)}$, irrespective of the concentration and density, SR employ the modified weighted density approach (MWDA) of Denton and Ashcroft [15], which includes all higher-order correlations in an approximate manner. Another major difference is that SS employ a reciprocal space representation for the density of the ordered phase, while SR employ a summation of the Gaussian representation in direct space. The calculated results of SS show quite good agreement with experimental results, while those of SR demonstrate only a qualitative similarity with the experimental results of Sirota *et al.* [11], differing considerably from the actual density range and details of the experimentally observed phase diagram.

The purpose of the present work is to compare and contrast both the perturbative and MWDA based methods as employed to colloidal systems and attempt to predict the phase diagram of both these experimentally studied systems. The perturbation approach that we employ is quite similar to that of SS, but differs in that we employ a much simpler Gaussian representation for the density of the ordered phase characterized by only a single exponent, which leads to considerable simplicity. Like SS, we have only two parameters for $c^{(3)}$, which are chosen empirically. In the nonperturbative scheme, we modify the conventional MWDA, which is known [16–19] to be rather poor for long range potentials. Although the conventional MWDA is parameter free, we employ two parameters here in order to compensate for the fact that only the hard sphere correlations are treated within the MWDA scheme. As will be shown here, we have been able to reproduce the experimental results for both the systems through this MWDA procedure.

In what follows, we first present in Sec. II the theoretical formalism of both the perturbative and the MWDA based schemes and discuss the results in Sec. III. Finally, we offer a few concluding remarks in Sec. IV.

II. THEORY

In DFT, the free energy of the system has been proved to be a unique functional of the single-particle density $\rho(\mathbf{r})$ and can be expressed as

$$F[\rho]=F_{id}[\rho]+F_{\mathrm{ex}}[\rho] , \tag{3}$$

where

$$F_{id}[\rho]=\beta^{-1}\int d\mathbf{r}\,\rho(\mathbf{r})\{\ln[\rho(\mathbf{r})\Lambda^3]-1\} \tag{4}$$

with Λ representing the thermal wavelength. The true equilibrium density corresponds to a minimum of this free-energy functional. In the DFT of freezing proposed by RY, one compares the free energy of the uniform density liquid phase with that of the solid phase corresponding to a periodic inhomogeneous density distribution. The exact expression for the excess free-energy functional $F_{ex}[\rho]$ is, however, unknown for a general inhomogeneous density distribution, although the same is often known for systems with uniform density and a suitable model two-body interaction. For the system under consideration where the particles interact through the DLVO potential given by Eq. (1), the two-particle direct correlation function $c^{(2)}(\mathbf{r},\mathbf{r}')$ defined as the second-order functional derivative

$$c^{(2)}(\mathbf{r},\mathbf{r}')=-\beta^{-1}[\delta^2 F_{\mathrm{ex}}[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')] , \tag{5}$$

has been obtained [20] within the rescaled mean spherical approximation (RMSA) when the density is uniform. The objective of a successful density functional procedure is to make use of this information to predict the free energy corresponding to the inhomogeneous density distribution, for which we now consider two approaches.

A. Perturbation theory approach

In a perturbative approach, one can express the difference between the free energies of the solid and the liquid phases as

$$\begin{aligned}\beta\Delta F[\rho]=&\int d\mathbf{r}\,\rho(\mathbf{r})\ln[\rho(\mathbf{r})/\rho_0]-\int d\mathbf{r}[\rho(\mathbf{r})-\rho_0]-\tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'c^{(2)}(\mathbf{r},\mathbf{r}')[\rho(\mathbf{r})-\rho_0][\rho(\mathbf{r}')-\rho_0]\\&-\tfrac{1}{6}\int\int\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{r}''c^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')[\rho(\mathbf{r})-\rho_0][\rho(\mathbf{r}')-\rho_0][\rho(\mathbf{r}'')-\rho_0] ,\end{aligned} \tag{6}$$

correct up to third order. For simplicity, we parametrize the density in the crystal phase using a superposition of normalized Gaussian distributions centered at each lattice point, viz.,

$$\rho(\mathbf{r})=\sum_i(\alpha/\pi)^{3/2}\exp[-\alpha(\mathbf{r}-\mathbf{R}_i)^2] , \tag{7}$$

which can also be written as a sum in the reciprocal space, viz.,

$$\begin{aligned}\rho(\mathbf{r})&=\sum_G\rho(\mathbf{G})\exp(i\mathbf{G}\cdot\mathbf{r}),\\ \rho(\mathbf{G})&=\rho_0\exp[-G^2/4\alpha] ,\end{aligned} \tag{8}$$

where $(\mathbf{R}_i)$ represent the Bravais lattice vectors of the crystal structure and **G** stand for the corresponding reciprocal lattice vectors (RLV's). Clearly both the forms [Eqs. (7) and (8)] correspond to the average density ρ_0 $[=\int d\mathbf{r}\,\rho(\mathbf{r})/\int d\mathbf{r}]$. Using this form of density, the difference in the free energy of Eq. (6) can be written in the simple form

$$\beta\Delta F[\rho]/N=[\ln(\alpha/\pi)^{3/2}-\ln(\rho_0)-\tfrac{3}{2}]-\tfrac{1}{2}\sum_G{}'\rho(\mathbf{G})^2c^{(2)}(\mathbf{G})-\tfrac{1}{6}\sum_G{}'\sum_{G'}{}'\sum_{G''}{}'\rho(\mathbf{G})\rho(\mathbf{G}')\rho(\mathbf{G}'')c^{(3)}(\mathbf{G},\mathbf{G}',\mathbf{G}'') , \tag{9}$$

where the ideal free energy (the first term on the right-hand side) has been approximated by using a single Gaussian since the region of interest corresponds to values of the parameter α for which the Gaussians are almost nonoverlapping. In Eq. (9), the primed summation excludes the $G=0$ terms. The Gaussian approximation characterizes the density of the ordered phase in terms of a single order parameter α, the inverse width of the Gaussians, which is determined by the minimization of ΔF given by Eq. (9). Clearly the homogeneous fluid phase corresponds to $\alpha=0$. While $c^{(2)}(\mathbf{G})$ is easily available in the present case within the RMSA solution of Hansen and Hayter [20], $c^{(3)}$ is in general not known for colloidal systems. Numerical results on the same function are, however, available for systems with the r^{-12} interaction potential from computer simulation of Barrat, Hansen, and Pastore [21]. It has been concluded by Barrat, Hansen, and Pastore [21] that $c^{(3)}$ appears to be rather insensitive to the precise forms of the interactions between particles, at least in the thermodynamical states near freezing. We therefore consider $c^{(3)}$ to be an empirical parameter, as has also been done by SS, and assume that it is independent of changes in the interaction potential due to changes in screening as the density and the electrolyte concentration are varied for a particular system.

Although the last term of Eq. (9) consists of many terms, only the few that involve small RLV's have been shown to have an important contribution, while those with higher RLV's are believed to be less significant. Following the argument of SS [13], we consider $c^{(3)}$ corresponding to only the $(1,1,0)+(1,-1,0)=(2,0,0)$ triangle in the bcc lattice and those corresponding to the $(1,1,1)+(1,-1,-1)=(2,0,0)$ and $(1,1,1)+(1,1,-1)=(2,2,0)$ triangles in the fcc lattice. Although the triangle $(1,1,0)+(0,-1,1)=(1,0,1)$ in the bcc lattice involves RLV's from the first shell, the corresponding $c^{(3)}$ seems to be close to zero, as shown by computer simulation [21]. Simulation studies have also shown that $c^{(3)}$ corresponding to the two triangles considered for the fcc lattice are roughly equal. Thus the three-body term in Eq. (9) involves essentially two unknown parameters c_{bcc} and c_{fcc} corresponding to bcc and fcc lattice, respectively.

B. Effective modified weighted density approach

We now consider the MWDA based prescription in the spirit of the work of Denton and Ashcroft [15] for hard sphere (HS) fluids as well as Curtin and Ashcroft [22] for Lennard-Jones fluids. We obtain an effective hard sphere contribution to the free energy of the ordered phase using the MWDA here. The essence of the MWDA is that the excess free energy of the inhomogeneous phase is obtained from the expression for the excess free energy for the corresponding homogeneous phase evaluated at an effective density $\bar{\rho}$, which is different from the bulk density ρ_0, i.e.,

$$F_{\text{ex}}^{\text{MWDA}}[\rho(\mathbf{r})]/N=f_0(\bar{\rho}) , \tag{10}$$

where f_0 denotes the excess free energy per particle for an N-particle system of uniform density. The effective density $\bar{\rho}$ is obtained through a suitable averaging of the inhomogeneous density distribution, viz.,

$$\bar{\rho}=(1/N)\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')\tilde{w}(\mathbf{r}-\mathbf{r}';\bar{\rho}) , \tag{11}$$

where $\tilde{w}$ denotes a weight function normalized to unity. Demanding that the correct second-order correlation function be reproduced from the second derivative of the MWDA expression for the excess free energy, in the uniform density limit, Denton and Ashcroft [15] have arrived at an explicit expression for the weight function. When the inhomogeneous density distribution $\rho(\mathbf{r})$ is assumed to be given by Eq. (7), one has a simple expression for $\bar{\rho}$ given by

$$\bar{\rho}(\rho_0,\alpha)=\rho_0\left[1-[2\beta f_0'(\bar{\rho})]^{-1}\times\sum_G{}'\exp(-G^2/2\alpha)c^{(2)}(G;\bar{\rho})\right] , \tag{12}$$

where $c^{(2)}(G;\bar{\rho})$ is evaluated at the RLV **G** and the effective density $\bar{\rho}$ and f_0' denotes the derivative with respect to its argument.

In the spirit of the work of Curtin and Ashcroft [22], we employ the MWDA only for an effective hard sphere contribution to the excess free energy. Thus the effective HS contribution to the excess free energy difference in the present MWDA prescription is given by

$$(\Delta F_{\rm HS}^{\rm ex})_{\rm MWDA}/N = f_0^{\rm HS}(\bar{\rho}) - f_0^{\rm HS}(\rho_0) \tag{13}$$

and hence the total free energy difference between the ordered and the uniform phases can be written as

$$\beta\Delta F[\rho]/N = [\ln(\alpha/\pi)^{3/2} - \ln(\rho_0) - \tfrac{3}{2}] - \tfrac{1}{2}\sum_{G}{}' \rho(\mathbf{G})^2 c^{(2)}(\mathbf{G}) + \Delta F_{\rm ex}^{(3)}[\rho]/N \ , \tag{14}$$

with the effective higher-order correlation contribution $\Delta F_{\rm ex}^{(3)}$ defined as

$$\Delta F_{\rm ex}^{(3)} = (\Delta F_{\rm HS}^{\rm ex})_{\rm MWDA}[\rho] - (\Delta F_{\rm HS}^{\rm ex})_{\rm pert}[\rho] \ , \tag{15a}$$

with

$$(\Delta F_{\rm HS}^{\rm ex})_{\rm pert}[\rho] = -\tfrac{1}{2}N\sum_{G}{}' \rho(\mathbf{G})^2 c_{\rm HS}^{(2)}(\mathbf{G}) \ . \tag{15b}$$

Here $f_0^{\rm HS}$ and $c_{\rm HS}^{(2)}$ in Eqs. (13) and (15b) correspond to the Percus-Yevick solution for a hard sphere system and $\bar{\rho}$ is obtained from Eq. (12) using the same $f_0^{\rm HS}$ and $c_{\rm HS}^{(2)}$. In Eq. (14), the second term on the right-hand side denotes the total second-order perturbation contribution to the excess free energy and is evaluated using the RMSA solution for $c^{(2)}(G)$.

III. RESULTS AND DISCUSSION

Thus Eq. (9) forms the basis of the proposed perturbation approach (which we call scheme *A*) for the calculation of free-energy difference between the ordered and uniform phases. Analogously Eqs. (13)–(15) define the proposed effective HS MWDA procedure (scheme *B*) for the same. In the perturbative as well as the MWDA based prescriptions, summations over RLV's are involved. The RLV's are directly related to the lattice parameters a in real space. Conventionally, in perturbative approaches the smallest RLV is chosen such that it corresponds to the first peak of the structure factor or $c^{(2)}(q)$. In MWDA based theories, on the other hand, usually the lattice parameter a (defined as $a_{\rm av}$) is chosen such that the average density corresponds to the proper number of particles in the unit cell of the particular lattice type. In the present study, for the perturbative approach (scheme *A*), we employ the conventional assumption that the smallest RLV corresponds to the first peak of $c^{(2)}(q)$ and the corresponding lattice parameter a is denoted as $a_{\rm peak}$. The two parameters $c_{\rm bcc}$ and $c_{\rm fcc}$ needed for the calculation are chosen empirically. For the sake of simplicity, we assume that these numbers are independent of all external parameters, as has also been done by SS, and fix them so that our results reproduce the experimental phase diagram essentially at two points at a particular excess ion concentration (which we choose here as $c = 1.848$ μM for the system studied by Monovoukas and Gast, i.e., system I, and zero for the system of Sirota *et al.*, i.e., system II). We get $c_{\rm bcc} = 0.3385$ and $c_{\rm fcc} = 0.1809$ for system I and $c_{\rm bcc} = 0.4185$ and $c_{\rm fcc} = 0.1809$ for system II, which are within the error bar of the computer simulation [21] results for the r^{-12} system. It may be noted that we have chosen $c_{\rm fcc}$ to be the same for both systems, although slightly different values could have been chosen as well. With these fixed values of the $c^{(3)}$ parameters, we minimize the energy obtained from Eq. (9) with respect to α for different values of η and c and thus calculate the entire phase diagram for both systems. The calculated results are compared with the corresponding experimental results for systems I and II in Figs. 1 and 2, respectively. The present results are found to be in excellent agreement with the experimental predictions of the phase transition. Although the ultimate success of the prescription might depend heavily on the cancellation of errors due to various approximations, we only conclude that within the present set of assumptions and approximations, the choice of the $c^{(3)}$ parameters, as well as the assumptions of their insensitivity to external parameters, is reasonable.

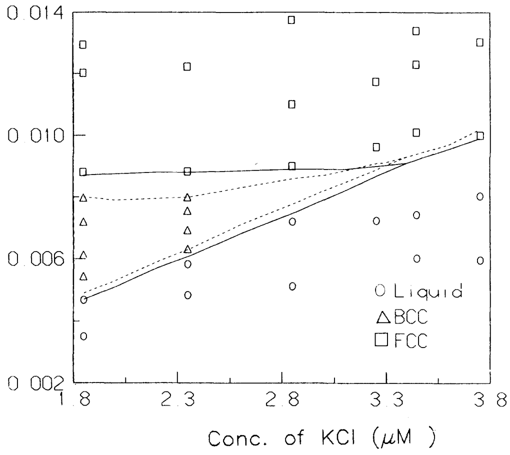

FIG. 1. Phase diagram of charge-stabilized colloidal dispersion of a polystyrene sphere in water (system I): — — —, calculated results using scheme *A*; ——, calculated results using scheme *B*. The circles, triangles, and squares denote the experimental points of Monovoukas and Gast.

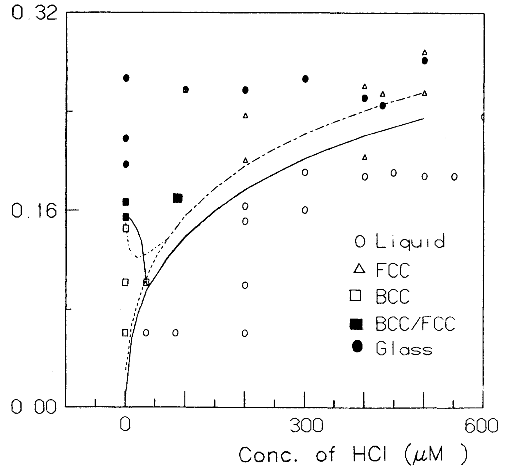

FIG. 2. Phase diagram of charge-stabilized colloidal dispersion of a polystyrene sphere in methanol (system II): —·—·—· calculated results using scheme *A*; —— calculated results using scheme *B*. The squares, circles, and triangles denote the experimental points of Sirota *et al.*

For the effective HS MWDA, the second-order perturbation term in Eq. (14) is evaluated as in the perturbation method discussed above, but with a lattice parameter $a=a_{\mathrm{av}}$. For the MWDA term [the last term in Eq. (14)], however, it is difficult to use a prescription involving total $c^{(2)}$, since an explicit expression for the corresponding free energy f_0 is not available. Therefore we have evaluated the third-order contribution due to hard sphere interaction alone, but incorporated approximately the effect of the electrical interaction by assuming that the particles are hard spheres of modified effective hard sphere diameters. For this effective additional higher-order contribution, the choice of $\Delta F_{\mathrm{ex}}^{(3)}[\rho]$ of Eq. (15), through the MWDA involving only HS contribution, amounts to using alternative values for the RLV's or the lattice parameters. In the MWDA, the ordered phase with an inhomogeneous density is viewed as a fluid phase of a uniform effective density $\bar{\rho}$, which is calculated using a scheme given by Eq. (12) involving a sum over the reciprocal lattice vectors. Although these RLV's might in general correspond to the average lattice parameter a_{av}, in the present case we propose to scale it by a constant multiplicative factor k in order to approximately account for the fact that we are calculating the contribution only from the HS correlation. This is equivalent to scaling a_{av} by a factor f $(=1/k)$, which is considered to be an empirical parameter here. Scaled lattice parameters have also been employed in a previous density functional study [23], where this treatment has been interpreted as allowing for vacancies and interstitials. We determine the factor f here empirically by assuming the points ($\eta=0.0053$ and $c=1.848$ for system I and $\eta=0.05$ and $c=0.0$ for system II) and ($\eta=0.0089$ and $c=1.848$ for system I and $\eta=0.16$ and $c=0.0$ for system II) to be the points of coexistence of liquid-bcc and bcc-fcc phases, respectively. The factors f_{bcc} and f_{fcc} turn out to be equal to 1.004 60 and 1.004 82, respectively, for system I and 1.028 93 and 1.015 33, respectively, for system II. However, since the effective hard sphere diameter should depend on the screening factor κ given by Eq. (2), it is expected that the factor f should depend on η as well as on c. In order to model this dependence, we make use of the other lattice parameter a_{peak}, which depends on both η and c, unlike a_{av}, which depends only on η. Thus we propose $f_{\mathrm{bcc}}(\eta,c)=(f_{\mathrm{bcc}})_0(a_{\mathrm{peak}}/a_{\mathrm{av}})/(a_{\mathrm{peak}}/a_{\mathrm{av}})_0$ for the bcc phase and $f_{\mathrm{fcc}}(\eta,c)=(f_{\mathrm{fcc}})_0(a_{\mathrm{av}}/a_{\mathrm{peak}})/(a_{\mathrm{av}}/a_{\mathrm{peak}})_0$ for the fcc phase, where the subscript zero refers to the respective reference points mentioned above. Since it is observed that $a_{\mathrm{peak}}>a_{\mathrm{av}}$ for the bcc phase and $a_{\mathrm{peak}}<a_{\mathrm{av}}$ for the fcc phase, we have chosen the ratio $(a_{\mathrm{peak}}/a_{\mathrm{av}})$ and its reciprocal as representing the correlation factors for the bcc and fcc phases, respectively. We then calculate the phase diagram using this scheme of obtaining lattice parameters for the MWDA and hence the higher-order correlation function contributions. The calculated phase diagram using this effective MWDA based methods (scheme *B*) for system I is compared to the experimental results of Monovoukas and Gast in Fig. 1, where results from scheme *A* are also included. Similarly, the calculated phase diagrams for system II using the two schemes are compared with the experimental results of Sirota *et al.*, in Fig. 2. The results obtained for the perturbative (scheme *A*) and the MWDA based methods (scheme *B*) are quite close to each other and agree quite well with the experimental results in both cases.

It may be noted that the Gaussian representation for the density of the ordered phase involving only one variational parameter, as has been used here, leads to considerable computational simplicity. The alternative method of using the Fourier expansion coefficients as variational parameters is a much more accurate and involved method in comparison to the Gaussian approximation, since the latter cannot address the possible anharmonicities and anisotropies of the crystal density. Laird, McCoy, and Haymet [24] have shown that both methods (Fourier expansion and Gaussian approximation) predict a phase diagram for hard sphere and Lennard-Jones systems with almost the same level of accuracy, although there are considerable differences in the crystal densities. The Gaussian approximation has also been successfully applied [25] to study the freezing of a one-component plasma into bcc as well as fcc structures. This suggests that a little anharmonicity in the crystal density might not affect the study of freezing significantly since it involves only energetics, with a globally averaged energy quantity. However, molecular dynamics, lattice dynamics, and earlier density functional studies by SS show that the bcc crystal density is slightly anisotropic (at small RLV's). The Gaussian approximation is thus not ideal since it cannot represent the anharmonicities in the density of the ordered phase. However, it is very convenient due to its computational simplicity and within the present set of assumptions and approximations, we have been able to predict results in good agreement with experiments.

IV. CONCLUDING REMARKS

We have shown that using a simple prescription of incorporating the effects of higher-order terms in a functional Taylor expansion of the free-energy difference between the ordered and uniform phases within the framework of the RY theory it is possible to predict the liquid-bcc-fcc phase transitions in colloidal systems in quite good agreement with the results of experimental observations. The two experimental results considered here cover different ranges of packing fraction as well as electrolyte concentrations. In the purely perturbative approach, the parameter c_{fcc} is taken to be the same in the two cases; for the bcc phase, slightly different values for c_{bcc} have been used in the two systems for obtaining prediction of the liquid-bcc transition, in agreement with the experimental results.

In the effective MWDA prescription proposed here, we have a scheme predicting the phase diagrams properly for both systems I and II. In all cases, the Gaussian form for the density of the ordered phase has been used. A modified effective lattice parameter depending on the density and the screening parameter of the potential can easily be interpreted as the variable effective diameter of the reference hard sphere system considered for the MWDA. Recently, modifications of the MWDA have been proposed [16] in alternative directions for the proper treatment of systems involving long range potentials. It would be of interest to apply them to the study of ordering in colloidal systems.

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