

Phase Diagram of Colloidal Systems

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It is a common procedure to model the interaction between colloidal particles by effectively spherical interactions.¹ These usually include hard-sphere (HS) plus short-ranged, attractive or repulsive, interactions. Nowadays it is already possible to proceed the other way round; that is, colloidal interactions can be chemically tailored to mimic a wide range of spherical potentials. This technique can help to clarify a variety of basic phenomena.¹ For instance, Marcus and Rice² have recently observed the two-dimensional hexatic phase predicted by the well-known Kosterlitz–Thouless–Halperin–Nelson–Young theory³ but not clearly confirmed by computer simulations. The technological implications of colloids have long been recognized as being of paramount importance. Lately, a special effort is being made to obtain colloidal crystallization that would allow the development of practical techniques to fabricate materials with appropriate optical properties, such as optical filters, photonic band gaps, switches, etc. These materials are expected to play a crucial role in the communication world as components of the next generation of devices.⁴ These are but two recent examples of the extraordinary possibilities of these systems. However, despite their enormous practical interest, a general statistical–mechanical description of the phase behavior of spherical-like colloids is still lacking. In this paper we present a well-founded, simple, and controlled theoretical scheme that may prove useful to describe the phase diagram of some colloidal systems, particularly those that can be modeled in terms of steric interactions plus short-range tails.

A recent simulation⁵ seems to confirm that the HS fluid crystallizes in a face-centered cubic (fcc) structure, with the hexagonal close-packed structure having a slightly higher free energy; this conclusion has been (partially) supported by more recent calculations.⁶ The first order transition separates the fluid region (without condensation) from the fcc region, which ends at close packing. The body-centered cubic (bcc) structure has a significantly higher free energy and it is mechanically unstable with respect to shear.⁷ This instability does not make the bcc phase amenable to testing by computer simulation, and

consequently scarce data have been reported.⁸ However, if a repulsive interaction is added to the HS, a bcc phase can be stabilized between the fluid and the fcc phases, as has been observed experimentally⁹ and shown by preliminary simulation results for a model of charge-stabilized colloids.¹⁰ Simulations by Bolhuis and Frenkel¹¹ have shown that a short-ranged interaction, when added to a HS core, generates, in addition to the possible condensation in the fluid region, an isostructural fcc–fcc transition. In this paper we show that the phase diagram of colloids can in fact be even richer; that is, the stabilization of the bcc phase generates an interesting variety of novel transitions and coexistence points. Some of these predictions should be observed experimentally.

The standard theories for simple liquids can be applied to study the colloidal fluid phases.¹² However, two difficult problems arise in the study of the ordered phases of colloidal systems. Despite the success of density–functional theories in the description of the thermodynamics of the fcc phase of HS¹³ and their important extensions to other systems,¹⁴ these theories have partially failed in their attempts at describing the bcc phase.^{8,15} For example, although the close packing density of this structure is $\rho \approx 1.299$ (here and henceforth length is measured in HS diameter units), the functional theories predict the stability of the bcc phase to extend even beyond the fcc close packing density $\rho = \sqrt{2} \approx 1.414$. The reason for this failure is the following. In systems of HS, it is crucial to model particle–exclusion correlations correctly. Standard density–functional theories do this only in an average way because they are based on mappings onto liquid-state structure. Therefore, open crystalline structures such as the bcc structure and, in general, highly anisotropic structures cannot be correctly reproduced. Only theories based on fundamental measures of HS can be expected to contain the correct behavior at close packing and this is so by construction. However, these theories have not yet been implemented for crystalline phases other than the HS fcc phase or in a consistent perturbative scheme. The adequate treatment of correlations is likewise a crucial problem insofar as these correlations are input information for the correct implementation of perturbation theory for more realistic potentials. Therefore, an appropriate description of correlations is absolutely necessary.

The different theoretical approaches proposed up to now, most of them ad hoc for a specific interaction, introduce adjustable parameters and scaled variables to reconstruct the expected colloidal phase diagram.^{16–18} In a previous

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work,¹⁹ using a density-functional approach, we studied the phase behavior of systems of particles interacting via repulsive potentials and some speculations concerning the stability of the bcc phase were advanced. These speculations are to be taken with some circumspection given the aforementioned failure of standard density-functional approximations in their description of the bcc phase.

In the first part of this paper we present a general and simple theoretical approach to describe the phase diagrams of systems of colloidal particles whose interactions can be modeled by isotropic interaction potentials containing a hard core. We shall use a recently proposed perturbation theory for the Helmholtz free energy of ordered and disordered classical systems.²⁰ The exact expression is, to the first order,

$$F(\rho) = F_{\text{HS}}(\rho) + 2\pi\rho^2 \int_1^\infty dr r^2 \tilde{g}_{\text{HS}}(r) \varphi_p(r) \quad (1)$$

where F_{HS} is the free energy of the reference system, in the present case a HS system, ρ is the mean density, $\varphi_p(r)$ is the perturbative interaction and the angle-averaged radial distribution function of the HS, $\tilde{g}(r)$, is defined as

$$\tilde{g}(r) = \frac{1}{4\pi V \rho^2} \int d\Omega \int d\mathbf{r}_1 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}) \quad (2)$$

where V is the volume, $d\Omega$ is the solid-angle differential related to the direction of \mathbf{r} ; and $\rho^{(2)}$ is the two-body distribution function. Equation 1 becomes exact in the close-packing limit when used with accurate approximations for $\tilde{g}(r)$, as pointed out in ref 21. It has been shown²² that, provided the thermodynamics and the local density $\rho(\mathbf{r})$ of the HS reference system are known, it is possible to obtain $\tilde{g}(r)$ with the help of the exact virial, compressibility, and normalization sum rules. The results obtained for this correlation function agree spectacularly with simulation results up to close packing for the fcc crystalline phase. We propose a free-volume approach for the Helmholtz free energy of the HS solid that gives, as we shall see, an excellent description not only for the fcc phase, as it has been suggested recently,^{23,24} but also for the bcc phase over the whole density range. The explicit expression of the Helmholtz free energy per particle is $F/NkT = -\log(\nu(\rho)/\Lambda^3)$, where N is the number of particles, k is Boltzmann constant, T is the temperature, ν is the accessible volume of a HS, which is the volume constrained by its neighbors, assuming they are fixed at their lattice equilibrium sites, and Λ is the thermal wavelength. Now it is important to observe that the symmetry of ν is that of the corresponding Wigner-Seitz (WS) cell. Moreover, the shape of ν is the same as that of the WS cell except by quite small cusps. Neglecting these contributions, we can approximate ν by the volume of the WS cell with the appropriate size scaling. While the extension of the WS cell is limited by the nearest-neighbor distance a , the accessible volume ν is further reduced by the size of the HS. Thus the appropriate length scale parameter is $(a - 1)/a$, and we obtain $\nu_{\text{fcc}} = 8(a(\rho) - 1)^3/\sqrt{2}$ and $\nu_{\text{bcc}} = 32(a(\rho) - 1)^3/3\sqrt{3}$. This is exact in the close-packing limit and a

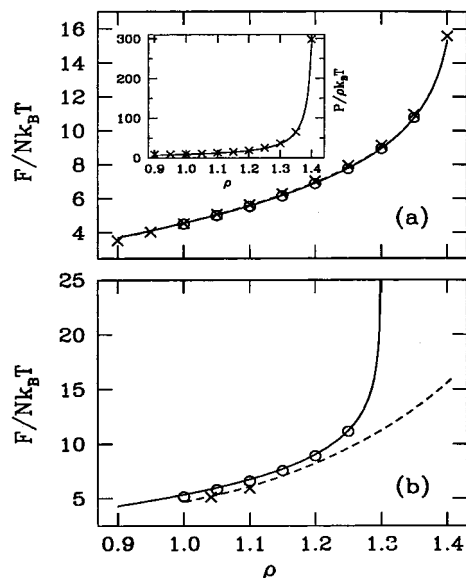


Figure 1. Helmholtz free energy per particle versus mean density: continuous line, present theory; dashed line, from functional theory by Tarazona;²⁷ circles, present theory with accessible volume exactly evaluated by Monte Carlo integration. (a) The fcc phase: crosses, data inferred from simulation by Choi et al.²⁵ and Rascón et al.²⁶ Inset: compressibility factor ($p/\rho kT$) versus mean density. (b) The bcc phase: crosses, simulation data by Curtin and Runge.⁸

very good approximation at low densities. Figure 1a shows the excellent agreement of the Helmholtz free energy of the fcc phase in the present approach with simulation results.^{25,26} The results of a functional theory²⁷ are also included for comparison; the agreement with simulations is similar to that of our simple analytical approach, which obviously is free from the heavy calculations needed in functional theories. We also include results of an exact calculation of the accessible volume $\nu(\rho)$, needed in the free-volume expression for the free energy, as obtained via Monte Carlo integration. These results indicate that our analytical free-volume approach is excellent over the whole density range, differing from the exact Monte Carlo evaluation by $<0.002\%$ even at the lowest densities. In the inset of Figure 1a we also display the pressure of the fcc phase as predicted by the free-volume approach together with the simulation results. The agreement found is especially relevant in the present context because an accurate pressure is crucial to obtain the $\tilde{g}(r)$ correlation function.²² However, the advantage of this approach lies in the quantitative character of the results predicted by the free-volume approach for the bcc phase. Figure 1b shows these results in comparison with the two simulation estimates available so far⁸ and the results from a functional theory.²⁷ Notably, the predictions of our analysis compare very favorably with simulation data and tend to the correct limit at the close-packing density. Despite agreeing with simulations, the functional theory breaks down at high densities. In fact, this behavior is common to all functional theories, except the recent one by Rosenfeld et al.,²⁸ which by construction (as the present case) should give the correct limit at close packing.

We now turn to the correlations in the solid phase. As already mentioned, in addition to the thermodynamics

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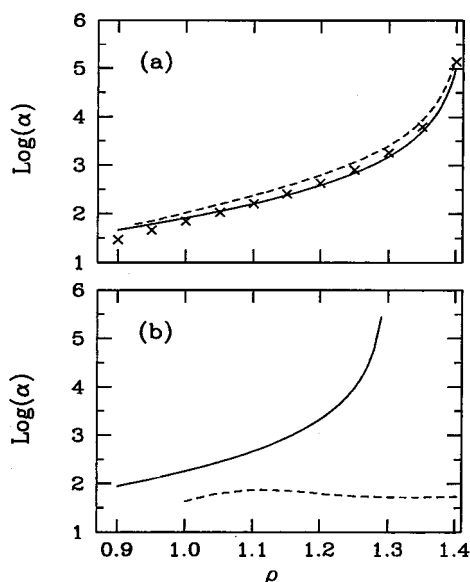


Figure 2. Logarithm of the Gaussian width parameter α versus mean density: continuous line, present theory; dashed line, from functional theory by Tarazona.²⁷ (a) The fcc phase: crosses, data inferred from simulation data by Choi et al.²⁵ and Rascón et al.²⁶ (b) The bcc phase.

we need $\rho(\mathbf{r})$. We take the usual parametrization

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\mathbf{R}} e^{-\alpha(\mathbf{r} - \mathbf{R})^2}$$

where \mathbf{R} is the vector position of the crystal lattice sites and α is the Gaussian parameter. In functional theories, α is determined by minimizing the free energy functional. The Gaussian parameter is directly defined in terms of the mean-square displacement by $r_{\text{rms}}^2 \equiv \langle r^2 \rangle = 3/2\alpha$. Thus, as the density increases, one should expect an increasing behavior for α that must eventually tend to infinity at close packing. The parameter r_{rms} is a measure of the volume accessible to each HS; thus, according with the present free-volume approach, we approximate the accessible volume v in an average way by $4\pi r_{\text{rms}}^3/3$. This estimation provides an analytical expression for the Gaussian parameter: $\alpha_{\text{fcc}} = 3/2(a-1)^2(3\sqrt{2}/\pi)^{2/3}$ and $\alpha_{\text{bcc}} = 3/2(a-1)^2(8/\sqrt{3}/\pi)^{2/3}$. In Figure 2a we show the results for α_{fcc} from this approximation compared with simulation data^{25,26} and results from a functional theory²⁷ (similar results are found using other functionals). Our predictions are even better than those from functional theories. In Figure 2b, our results for the bcc phase are compared with those from the same functional theory. Unfortunately, there are no simulation data for α_{bcc} , but it is apparent that the functional predictions are qualitatively incorrect even at low densities where by contrast the free energy agrees with simulations.

In the following we apply the approach just presented to obtain the phase diagrams of colloidal systems interacting via a HS core plus a short-ranged repulsive square shoulder potential:

$$\phi_p(r) = \begin{cases} \epsilon, & 1 < r < 1 + \delta \\ 0, & r \geq 1 + \delta \end{cases} \quad (3)$$

where ϵ and δ are the height and width of the shoulder, respectively. Kincaid et al. have shown that, disregarding the solid phase, one can expect from this potential high-density phase separation and criticality for sufficiently

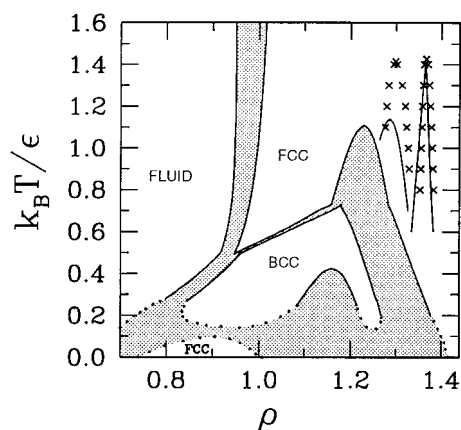


Figure 3. Phase diagram of a colloidal model system interacting via a hard-sphere plus a square shoulder potential. Continuous lines are results of the present theory with a shoulder width $\delta = 0.12$; also indicated are partial results for $\delta = 0.08$ (left set) and $\delta = 0.03$ (right set). Simulations by Bolhuis and Frenkel³² for these latter cases are shown by crosses. Shaded regions correspond to phase coexistence. Dotted lines correspond to extrapolations to the exact behavior at $T = 0$ (see text).

small values of the parameter δ .²⁹ For the fluid phase we use eq 1, in the uniform limit, together with the Carnahan–Starling³⁰ equation of state and the Verlet–Weis HS radial distribution function.³¹ The coexistence densities are determined by the usual common double-tangent method, which ensures the equality of pressures and chemical potentials of the different phases at each temperature. Figure 3 shows the phase diagram for $\delta = 0.12$. This diagram exhibits all the features found for other shoulder widths δ , although its topology can change significantly with δ .

Note that the bcc phase appears in the middle of the diagram, giving rise to a new variety of transitions, triple and critical points. Notice also the prediction of a bcc–bcc isostructural transition similar to that found by Bolhuis and Frenkel¹¹ for the fcc phase. In addition, two triple points, fcc–bcc–fcc and fluid–fcc–bcc, appear in the diagram. For larger values of δ , the bcc phase moves to higher temperatures and the two triple points collapse into a single fluid–bcc–fcc triple point. At the same time, the critical points of both isostructural transitions move slightly toward higher densities, keeping their respective critical temperatures almost constant. As δ decreases, the temperatures of the two triple points decrease, whereas the isostructural transitions move slightly, as mentioned before. The consequence of these changes is the splitting of the stability region of the bcc phase into two islands. In Figure 3 we have also included partial results obtained for the fcc–fcc transition, with $\delta = 0.08$ and 0.03 , which are compared with recent simulation data by Bolhuis and Frenkel.³² The agreement is reasonable. Unfortunately these authors explicitly ignore phases other than the fcc, though they recognize that these phases can be stable below the bcc close-packing density $\rho \approx 1.299$, which is the result we find. The dotted lines in the figure are extrapolations to the exact results at $T = 0$. In the limit

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$T \rightarrow 0$ the densities of the coexisting phases are those corresponding to the fluid–fcc transition of a system of HS of diameter $1 + \delta$: $\rho_{\text{fluid}} \approx 0.946/(1 + \delta)^3 = 0.673$ and $\rho_{\text{solid}} \approx 1.040/(1 + \delta)^3 = 0.740$; at higher densities, the close packing of this fcc structure is reached ($\rho_{\text{cp}} = \sqrt{2}/(1 + \delta)^3 = 1.007$), which finally coexists with the close-packed fcc phase of the HS of diameter 1 ($\rho = \sqrt{2}$). The exact topology of the diagram in the extrapolated region can be different because, as is well known, perturbation theory breaks down at low temperatures. However, we think that the basic features contained in our phase diagram are real. In fact, Young and Alder³³ have computed the first- and second-order terms of the perturbative expansion of the system studied here by conducting molecular dynamics simulations of the reference system (i.e., HS). Their results indicate that the ratio of these two terms is ~ 10 at $T = 0.3 \epsilon/k$ (i.e., below the bcc–bcc critical point), which gives some support to our predicted phase diagram, at least from a qualitative viewpoint.

An important point to bear in mind is that our theory can also be applied to other model interactions, for instance, a HS plus a repulsive Yukawa potential. In this system, a bcc phase and a corresponding fluid–bcc–fcc triple point are expected^{10,19,34} though no isostructural transitions are possible. The phase diagram of systems with short-ranged attractive interactions excludes the bcc

phase and therefore can already be described with the current functionals. The results from the present theory in these cases are practically the same as those obtained by the functionals if correlations are properly taken into account.²⁰

In conclusion, we have presented a theoretical approach that can describe the phase behavior of some model colloidal systems. Despite its simplicity, the approach is well founded and overcomes two common difficulties found in all previous theories; that is, the correct description of the bcc phase and the proper account of correlations. These two ingredients allow us to describe with confidence some features of the phase diagrams of colloidal model systems. Some of the theoretical predictions agree reasonably with the available simulations. In addition, the application of the theory reveals the existence of interesting novel transitions and coexistence points. The theory could also be applied to other classical systems with short-ranged interactions such as the C₆₀ fullerene or classical systems with long-ranged interactions.

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