

A boot-strap Poisson–Boltzmann theory for the structure and thermodynamics of charged colloidal solutions

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The structural properties and thermodynamics of one- and two-component solutions of charged colloidal particles with explicit counterions have been investigated by Monte Carlo simulation. A boot-strap Poisson–Boltzmann (BSPB) theory has been developed to interpret these results and the accuracy of its predictions is compared with other existing theories. The BSPB was also used to predict the gas–liquid binodal and spinodal curves for a one-component system with colloid charge to counterion-charge ratio $Z_r=10$. © 2003 American Institute of Physics.

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I. INTRODUCTION

Over the past decade, the interest in charged colloidal solutions has grown enormously. Charged colloidal solutions can be investigated using the primitive model, in which all charged species are treated on an equal footing. The structural and thermodynamic properties of the solution can be calculated by Monte Carlo (MC) simulations, and within statistical uncertainty, they provide exact answers for the given model. However, this approach is highly resource consuming and the time needed to complete the simulations can be quite substantial, particularly for highly charged systems. Therefore it is desirable to develop a simple but reliable theoretical approximation to determine the structural and thermodynamic properties of these systems.

Charged colloidal solutions can be investigated experimentally using small-angle neutron scattering (SANS) experiments. Partial structure factors may be measured in solutions containing various proportions of heavy water and directly compared with simulation results and predictions from simple liquid theories. Lutterbach *et al.*^{1,2} have presented SANS measurements for a two-component dispersion of highly charged polystyrene and perfluorinated particles at a volume fraction of approximately 9%. They compared their partial structure factor measurements between the colloidal particles with theoretical predictions from the hypernetted chain integral equation and found good agreement. Ottewill *et al.*³ have used SANS to measure partial structure factors for more dilute two-component suspensions containing salt, for volume fractions around 3%. In general, relatively low volume fraction solutions are desirable for SANS experiments to reduce the effects of multiple neutron scattering. However, due to long-ranged interparticle interactions such systems can exhibit significant liquid-like structure.

Here we present a new theoretical approach to calculate the structural and thermodynamic properties of charged colloidal solutions using a boot-strap Poisson–Boltzmann (BSPB) theory. Comparisons of the structure, internal energy, and pressure are made with Monte Carlo simulations of one- and two-component charged colloidal solutions to assess the accuracy of the BSPB theory.

II. MODEL

Charged colloidal solutions can be investigated using the primitive model (PM), in which the large colloidal particles and small ions are represented as charged hard-spheres with differing hard-sphere radii R_α , number density n_α , and valence Z_α , obeying the electroneutrality condition

$$\sum_{\alpha} n_{\alpha} Z_{\alpha} = 0. \quad (1)$$

The interaction potential between two ionic species α and β at a distance r between their centers, is taken to be made up of a hard-sphere (hs) part and a Coulomb (Coul) part,

$$u_{\alpha\beta}(r) = u_{\alpha\beta}^{\text{hs}}(r) + u_{\alpha\beta}^{\text{Coul}}(r), \quad (2)$$

where the hard-sphere and the Coulomb interactions are given by

$$u_{\alpha\beta}^{\text{hs}}(r) = \begin{cases} \infty, & r < (R_{\alpha} + R_{\beta}) \\ 0, & r \geq (R_{\alpha} + R_{\beta}) \end{cases}, \quad (3)$$

$$u_{\alpha\beta}^{\text{Coul}}(r) = \frac{Z_{\alpha} Z_{\beta} e^2}{\epsilon r}, \quad r > 0, \quad (4)$$

where e is the protonic charge. The solvent is treated as a dielectric continuum with a relative dielectric permittivity ϵ .

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III. SIMULATION ASPECTS

Simulation studies of one-component charged colloidal solutions with explicit counterions have been done by Linse and they are described in an earlier publication.⁴ It contains a comprehensive set of MC results over a wide range of salt-free colloidal solutions for structure, internal energy, and pressure. Although there are both colloidal particles and counterions in the system, it is referred to as a one-component colloidal solution because the number density of counterions is directly proportional to the number density of colloidal particles due to electroneutrality.

Simulation studies of two-component colloidal solutions have recently been undertaken. The system consists of a common counterion species and two like-charged but different sized colloidal particles, denoted as the large (*L*) and small (*S*) colloids. The number ratio of small to large colloids was varied to investigate the effect on (i) the structure and (ii) the electrostatic internal energy of the two-component colloidal solutions.

All of the MC simulations were done using the canonical ensemble. The particles were enclosed in a cubic box and periodic boundary conditions were applied. The long-ranged Coulomb interaction was handled by the Ewald summation technique using conducting boundary conditions, and the mobility of the colloids was enhanced by the use of the cluster move technique.⁵ The simulations involved 20 000 MC passes (attempted moves per particle) for equilibration and then 60 000 passes for production runs. All the simulations were performed using the integrated Monte Carlo/molecular dynamics/Brownian dynamics simulation package MOLSIM.⁶

IV. THEORY

A. General theory

The structure of a colloidal solution can be quantified by means of radial distribution functions (rdf's) $g_{\alpha\beta}(r)$, which measures the relative density of a particle of type β at a distance r from a particle of type α . The total correlation functions $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ can be calculated directly from computer simulations or from liquid state theory by solving the Ornstein–Zernike (OZ) equation, which relates total correlation functions $h_{\alpha\beta}(r)$ to direct correlation functions $c_{\alpha\beta}(r)$,

$$h_{\alpha\beta}(\mathbf{r}) = c_{\alpha\beta}(\mathbf{r}) + \sum_{\gamma} n_{\gamma} \int c_{\alpha\gamma}(\mathbf{r}') n_{\gamma} h_{\gamma\beta}(\mathbf{r} - \mathbf{r}') d\mathbf{r}', \quad (5)$$

where n_{γ} is the bulk number density of species γ . The rdf's also obey the local electroneutrality conditions about an ionic species of valence Z_{α} ,

$$Z_{\alpha} = - \sum_{\beta} n_{\beta} Z_{\beta} \int g_{\alpha\beta}(r) dr. \quad (6)$$

This condition expresses the requirement that the total net charge surrounding a particular charge of valence Z_{α} must exactly cancel the charge on that particle. This condition provides a check on any approximate expressions for $g_{\alpha\beta}(r)$.

Determination of the rdf's enables the calculation of the electrostatic internal energy per unit volume of the system,

$$\begin{aligned} \frac{E^{\text{Coul}}}{V} &= \frac{1}{2} \sum_{\alpha,\beta} n_{\alpha} n_{\beta} \int u_{\alpha\beta}^{\text{Coul}}(r) g_{\alpha\beta}(r) dr \quad (7) \\ &= \frac{2\pi e^2}{\epsilon} \sum_{\alpha,\beta} n_{\alpha} Z_{\alpha} n_{\beta} Z_{\beta} \int_{R_{\alpha}+R_{\beta}}^{\infty} r h_{\alpha\beta}(r) dr \\ &\quad - \frac{\pi e^2}{\epsilon} \sum_{\alpha,\beta} n_{\alpha} Z_{\alpha} n_{\beta} Z_{\beta} (R_{\alpha} + R_{\beta})^2. \quad (8) \end{aligned}$$

Taken individually, each integral in Eq. (7) diverges because of the long-ranged nature of the electrostatic potential; however, the divergences, when taken together, will cancel because of the bulk electroneutrality condition, Eq. (6). In Eq. (8), the integrals that determine the electrostatic internal energy per unit volume have been broken down into components. The first term comes from integrating beyond the hard-core radii of the charged species α and β to infinity. The second term comes from integrating inside the hard-core radii of the particles and will be referred to as the electrostatic excluded volume contribution.

The Helmholtz free energy F is the important thermodynamic quantity required to investigate phase behavior. The Helmholtz free energy of this system can be separated into an ideal gas contribution F^{id} , a hard-sphere contribution F^{hs} , and an electrostatic contribution F^{Coul} ,

$$F = F^{\text{id}} + F^{\text{hs}} + F^{\text{Coul}}. \quad (9)$$

By employing a coupling constant or charging integration, the electrostatic contribution to the Helmholtz free energy can be evaluated using the formally exact relation

$$F^{\text{Coul}} = \int_0^1 E^{\text{Coul}}(\lambda) \frac{d\lambda}{\lambda}, \quad (10)$$

where $E^{\text{Coul}}(\lambda) \equiv E^{\text{Coul}}(e^2 \rightarrow \lambda e^2)$. This method is often referred to as the charging process. The Coulomb free energy contribution is always cohesive and tends to destabilize the system. In other words, the net Coulomb repulsion between like charged species is outweighed by the net Coulomb attraction between species of opposite charge. The ideal and hard-sphere contributions are stabilizing terms and the combination of all three terms allows for the possibility of a liquid–gas like phase separation under certain circumstances.

The total system pressure P can be calculated from differentiation of the Helmholtz free energy with respect to volume,

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (11)$$

Alternatively, the total pressure P can be calculated using the virial path⁷

$$\begin{aligned} \frac{PV}{NkT} &= 1 + \frac{E^{\text{Coul}}}{3NkT} + \frac{2\pi V}{3N} \sum_{\alpha} \sum_{\beta} n_{\alpha} n_{\beta} g_{\alpha\beta}(R_{\alpha} + R_{\beta}) \\ &\quad \times (R_{\alpha} + R_{\beta})^3, \quad (12) \end{aligned}$$

where N is the total number of particles in the system. The first term in Eq. (12) is the ideal contribution, while the second and third terms account for the Coulomb and hard-sphere contributions, respectively. For a one-component system, the critical point and spinodal curve of the gas–liquid phase transition can be obtained through

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = \left(\frac{\partial^2 P}{\partial V^2}\right)_T \quad (\text{critical point}),$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad (\text{spinodal}). \quad (13)$$

However, for two or more components the technique for locating the critical point and the spinodal curve is more complicated. Up until now, all the results are completely general and a theoretical method is required to calculate the distribution functions and then the subsequent thermodynamic quantities.

B. Boot-strap Poisson–Boltzmann (BSPB) theory

We will now outline the BSPB theory, which can be used to calculate the approximate rdfs for a general solution of colloidal particles and point ions. Let n_J be the number density of colloids of valence Z_J and hard-sphere radius R_J and n_i be the number density of point counterions of valence Z_i . Electroneutrality requires that

$$\sum_i n_i Z_i + \sum_J n_J Z_J = 0. \quad (14)$$

There are three distinct types of rdfs that characterize this type of solution. These are the colloid–colloid, $g_{JK}(r)$, colloid–ion, $g_{Ji}(r)$, and ion–ion rdfs, $g_{il}(r)$.

Consider the mean electrostatic potential $\Psi_J(r)$ about a given colloidal particle J , which obeys the Poisson equation

$$\nabla^2 \Psi_J(r) = -\frac{4\pi}{\epsilon} \rho(r)$$

$$= -\frac{4\pi e}{\epsilon} \left[\sum_i n_i Z_i g_{Ji}(r) + \sum_K n_K Z_K g_{JK}(r) \right], \quad r > R_J. \quad (15)$$

We adopt this approach in order to make mean-field approximations for the colloid–ion and ion–ion interactions. Let us assume at this stage we have expressions for all the colloid–colloid rdfs $g_{JK}(r)$ and that the colloid–ion rdfs are given by the Boltzmann approximation

$$g_{Ji}(r) \approx \exp[-\beta Z_i e \Psi_J(r)], \quad (16)$$

then Poisson's equation for the potential $\Psi_J(r)$ becomes

$$\nabla^2 \Psi_J(r) = -\frac{4\pi e}{\epsilon} \left(\sum_i n_i Z_i \exp[-\beta Z_i e \Psi_J(r)] + \sum_K n_K Z_K g_{JK}(r) \right), \quad r > R_J \quad (17)$$

with the following boundary conditions:

$$\left. \frac{\partial \Psi_J(r)}{\partial r} \right|_{r=R_J} = -\frac{Z_J e}{\epsilon R_J^2},$$

$$\Psi_J(r) \rightarrow 0, \quad r \rightarrow \infty. \quad (18)$$

Equation (17) is a nonlinear differential equation for $\Psi_J(r)$ if all the $g_{JK}(r)$ are known. Now consider the mean electrostatic potential $\Psi_i(r)$ about a given point ion i , which obeys the Poisson equation

$$\nabla^2 \psi_i(r) = -\frac{4\pi}{\epsilon} \rho(r)$$

$$= -\frac{4\pi e}{\epsilon} \left[\sum_l n_l Z_l g_{il}(r) + \sum_K n_K Z_K g_{iK}(r) \right], \quad r > 0. \quad (19)$$

This time, we shall assume to have expressions for all the colloid–ion rdfs $g_{iK}(r)$ and use the linearized Boltzmann approximation for the ion–ion rdf

$$g_{il}(r) \approx \exp[-\beta Z_l e \psi_i(r)] \approx 1 - \beta Z_l e \psi_i(r), \quad (20)$$

Poisson's equation for the potential $\psi_i(r)$ becomes

$$\nabla^2 \psi_i(r) = -\frac{4\pi e}{\epsilon} \left(\sum_l n_l Z_l (1 - \beta Z_l e \psi_i(r)) + \sum_K n_K Z_K g_{iK}(r) \right), \quad r > 0 \quad (21)$$

with the appropriate boundary conditions

$$\psi_i(r) \rightarrow \frac{Z_i e}{\epsilon r}, \quad r \rightarrow 0,$$

$$\psi_i(r) \rightarrow 0, \quad r \rightarrow \infty. \quad (22)$$

Equation (21) is a linear differential equation for $\psi_i(r)$ if all the $g_{iK}(r)$ are known.

V. ONE-COMPONENT SOLUTIONS

To begin with, we shall focus on the one-component solutions consisting of one type of colloidal particle and one type of point counterion species. Let n_M be the number density of colloids of valence Z_M and hard sphere radius R_M and n_I be the number density of counterions of valence Z_I . Electroneutrality requires that

$$n_I Z_I + n_M Z_M = 0. \quad (23)$$

The BSPB initially relies on the knowledge of the colloid–colloid rdfs to calculate the colloid–ion rdfs by solving Eq. (17) and then calculate the ion–ion rdfs by solving Eq. (21). For a one-component system, the colloid–colloid rdf can be calculated approximately using an effective Yukawa pair potential in which the presence of the counterions is taken into account via a screening constant. For the effective pair potential between colloidal particles, we use the form⁸

$$u^{\text{eff}}(r) = \frac{(Z_M^{\text{eff}})^2 e^2 \exp(2\kappa R_M)}{\epsilon (1 + \kappa R_M)^2}$$

$$\times (1 + \phi_M)^2 \frac{\exp(-\kappa r)}{r}, \quad r > (2R_M), \quad (24)$$

where ϕ_M is the total volume fraction and Z_M^{eff} is the effective colloidal charge, which may be much smaller than the actual charge Z_M . An effective charge is used to adequately account for the non-linear accumulation of counterions near the colloids while still using a linear theory. We followed the charge renormalization procedure proposed by Alexander *et al.*⁹ In this procedure, the linearized Poisson–Boltzmann (PB) equation in a spherical Wigner–Seitz cell is solved with the effective charge Z_M^{eff} adjusted to match the counterion density at the cell boundary (i.e., the pressure) obtained from the nonlinear PB equation. We used the same screening parameter for the pair potential as specified by Alexander *et al.*⁹ as K^* in their Eq. (I.4), which depends on the effective density of counterions, where

$$n_I^{\text{eff}} Z_I + n_M Z_M^{\text{eff}} = 0 \quad (25)$$

and

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} n_I^{\text{eff}} Z_I^2 = \frac{4\pi e^2}{\epsilon kT} n_M |Z_M^{\text{eff}} Z_I|. \quad (26)$$

This definition of κ was found to give good agreement with the MC simulations in a previous study by Lobaskin and Linse.⁷

For a one-component system of colloids interacting via a Yukawa pair potential, Hayter and Penfold¹⁰ obtained an analytic solution of the OZ equation using the closure of the mean spherical approximation (MSA). With dilute dispersions, however, this solution yields unphysical, negative values of the rdf at small separations. Hansen and Hayter¹¹ overcame this problem by assuming the existence of an impenetrable boundary layer around each particle and rescaling the MSA solution, which became known as the renormalized mean spherical approximation (RMSA).

We used the RMSA to calculate a rescaled particle diameter and then the colloid–colloid rdf $g_{MM}(r)$, and found this to be an effective technique to initiate the BSPB. With an expression for $g_{MM}(r)$, Eq. (17) for the potential $\Psi_M(r)$ around a colloid was solved numerically to determine the colloid–counterion rdf $g_{MI}(r)$. Finally, using the approximate form for $g_{MI}(r)$, Eq. (21) for the potential $\psi_I(r)$ around a counterion is solved numerically to determine the counterion–counterion rdf $g_{II}(r)$.

Linse⁴ has previously reported a comprehensive set of MC results for the structure, reduced internal energy, and reduced pressure for a wide range of solutions. We present predictions of the BSPB model for structure, internal energy, and pressure and compare them with the corresponding MC results. The system can be completely described in terms of three nondimensional variables (i) the colloid to counterion charge ratio Z_r , (ii) the colloid volume fraction ϕ_M , and (iii) the electrostatic coupling parameter or inverse temperature Γ_{II} , defined according to the following:

$$Z_r = -\frac{Z_M}{Z_I},$$

$$\phi_M = \frac{4\pi R_M^3}{3} n_M, \quad (27)$$

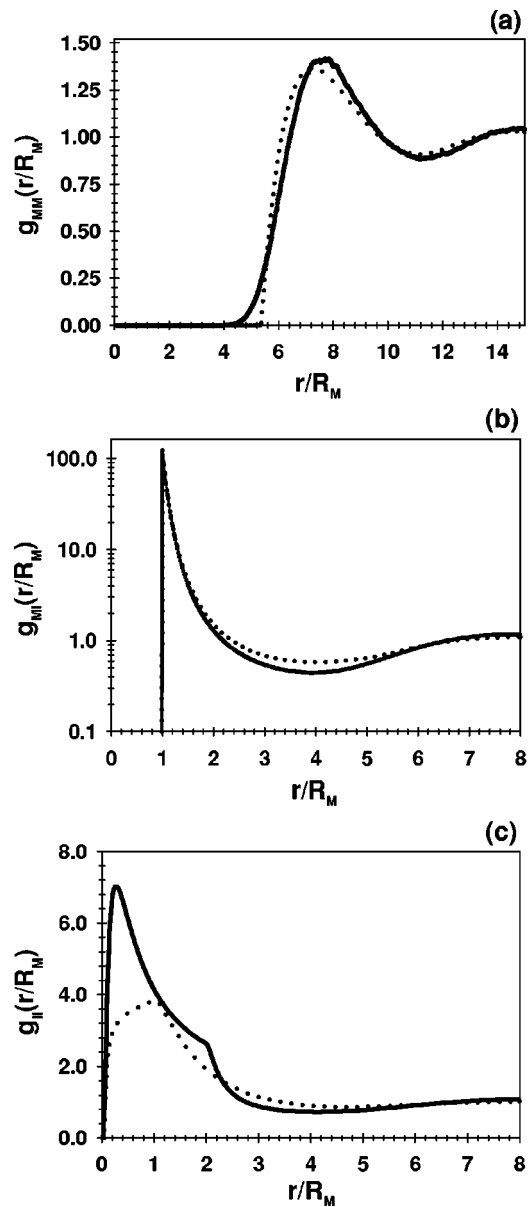


FIG. 1. (a) Colloid–colloid, (b) colloid–counterion, and (c) counterion–counterion rdfs from MC simulation 4 (solid curves) and BSPB theory (dotted curves) for a one-component system at $(Z_r, \phi_M, \Gamma_{II}) = (80, 0.01, 0.178)$.

$$\Gamma_{II} = \frac{e^2}{\epsilon k T R_M} = \frac{L_B}{R_M},$$

where $L_B = e^2/\epsilon kT$ is the Bjerrum length, k is the Boltzmann constant, and T is the temperature. In the following, separations will be scaled by the colloid radius R_M .

A. Structural properties

A typical structure comparison is presented in Fig. 1 for $Z_r=80$ and $\phi_M=0.01$, at an intermediate coupling strength of $\Gamma_{II}=0.178$. At this state point, $\kappa R_M=0.46$ and the renormalized colloidal valence is $Z_r^{\text{eff}} = -Z_M^{\text{eff}}/Z_I=40.2$, approximately half the actual valence. The renormalized colloidal valence is strongly dependent on the coupling strength and only weakly dependent on the colloid volume fraction. The

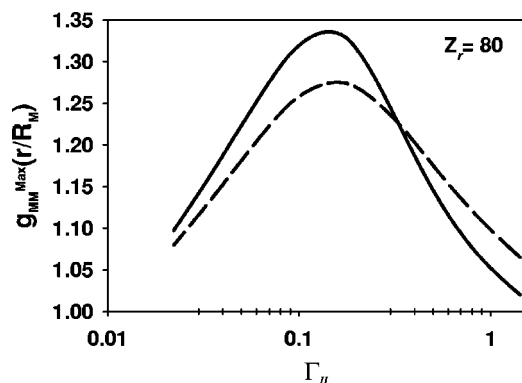


FIG. 2. Colloid-colloid rdf peak values $g_{MM}^{\max}(r/R_M)$ from MC simulation⁴ (solid curves) and BSPB theory (dashed curves) obtained for a one-component system at $(Z_r, \phi_M) = (80, 0.01)$ over a range of Γ_{II} .

BSPB and MC colloid-colloid rdfs are shown in Fig. 1(a). Each curve displays the typical characteristics for a fluid, which has a pronounced first maximum at some interparticle distance, followed by successive minima and maxima of reduced amplitude. The general agreement between the two curves is very good and remains so for lower and higher coupling strengths. The BSPB first maximum occurs at $r/R_M = 7.3$ and the amplitude value is 1.36, while the MC first maximum occurs at $r/R_M = 7.9$ and the amplitude value is 1.41.

The BSPB and MC colloid-counterion rdfs are shown in Fig. 1(b). The curves are sharply peaked at $r/R_M = 1$, which demonstrates a strong accumulation of counterions near the colloid surface in the double layer. The BSPB contact value at $r/R_M = 1$ is 122, which is near the extrapolated MC value of 124. The BSPB first minimum occurs at $r/R_M = 4.03$ and the amplitude value is 0.58, which compares well with the MC minimum at $r/R_M = 3.88$ with an amplitude value of 0.44. The agreement between the two curves remains good at lower and higher coupling strengths, although the predicted contact values are better for low coupling strengths.

The BSPB and MC counterion-counterion rdfs are compared in Fig. 1(c). There is an inconsistency in that the counterion-counterion rdf is linearized with respect to the mean electrostatic potential, whereas these correlations can be quite large at high coupling strengths. For $r/R_M \geq 3$, the agreement is very good, but inside this region the BSPB cannot predict the intricate details of the MC counterion-counterion rdf. The broad MC peak for $r/R_M \leq 2$ reflects the strong spatial correlations between counterions in the double layer of the same colloid. There is a sharp edge in the MC curve at $r/R_M \approx 2$, which indicates a rapid drop in the local density of counterions outside the double layer that the mean-field BSPB cannot reproduce. The MC peak value occurs at $r/R_M \approx 0.3$, and its position changes as the state point is varied. There is a less pronounced peak in the BSPB curve at $r/R_M = 1$, which does not change as the state point is varied. It is due to the discontinuity in the function $g_{MI}(r/R_M)$ at $r/R_M = 1$ when solving Eq. (17) for the potential around a counterion.

In Fig. 2, the heights of the colloid-colloid rdf first maximum from the BSPB model and MC simulations, $g_{MM}^{\max}(r/R_M)$, are plotted against coupling strength for $Z_r = 80$ and $\phi_M = 0.01$. For very low coupling strengths, the height of the first maximum increases with coupling strength, which corresponds to a more ordered colloid-colloid structure. The height of the first maximum reaches a peak value at the coupling strength $\Gamma_{II} = 0.178$ and above this value, the height decreases due to increased screening effects of the counterions. The BSPB model is capable of predicting all of these features in very close agreement with the MC simulations.

B. Thermodynamics

1. Internal energy

Internal energies were calculated via Eq. (8) using the BSPB distribution functions. This method allows the separation of the electrostatic internal energy into the following

TABLE I. Reduced electrostatic internal energy ($-E/NkT$) for different Z_r and Γ_{II} values at $\phi_M = 0.01$.

Z_r		Γ_{II}						
		0.0222	0.0445	0.0889	0.178	0.356	0.712	1.42
10	MC	0.0226	0.0546	0.131	0.312	0.772	2.11	5.99
	BSPB	0.0220	0.0552	0.132	0.314	0.786	2.18	5.99
	SPB	0.0216	0.0520	0.122	0.284	0.653	1.49	3.34
	MSA	0.0225	0.0561	0.137	0.331	0.785	1.84	4.25
20	MC	0.0615	0.142	0.327	0.786	2.10	5.79	14.3
	BSPB	0.0625	0.143	0.327	0.798	2.19	6.02	14.4
	SPB	0.0575	0.130	0.286	0.629	1.36	2.90	6.16
	MSA	0.0659	0.158	0.372	0.862	1.97	4.43	9.86
40	MC	0.151	0.338	0.794	2.09	5.64	13.7	30.3
	BSPB	0.150	0.335	0.805	2.20	6.00	14.4	30.5
	SPB	0.135	0.288	0.602	1.26	2.62	5.41	11.3
	MSA	0.181	0.417	0.945	2.11	4.66	10.2	22.0
80	MC	0.345	0.800	2.08	5.54	13.3	29.1	^a
	BSPB	0.346	0.808	2.19	6.01	14.4	30.4	60.6
	SPB	0.285	0.584	1.19	2.45	4.98	10.2	21.1
	MSA	0.462	1.030	2.26	4.90	10.5	13.7	47.4

^aUnstable system.

TABLE II. Reduced excess internal energy ($-E/NkT$) for different ϕ_M and Γ_{II} values at $Z_r=40$.

ϕ_M		Γ_{II}					
		0.0222	0.0445	0.0889	0.178	0.356	0.712
0.001 25	MC	0.0735	0.168	0.415	1.35	4.91	13.2
	BSPB	0.0748	0.170	0.427	1.49	5.76	16.2
	SPB	0.0678	0.149	0.324	0.709	1.53	3.25
	MSA	0.101	0.25	0.602	1.42	3.3	7.51
0.0025	MC	0.0944	0.215	0.526	1.60	5.17	13.4
	BSPB	0.0956	0.217	0.543	1.75	5.95	15.7
	SPB	0.0861	0.187	0.402	0.862	1.83	3.84
	MSA	0.125	0.303	0.713	1.65	3.76	8.41
0.005	MC	0.120	0.271	0.654	1.85	5.41	13.5
	BSPB	0.121	0.273	0.671	1.99	6.04	15.1
	SPB	0.108	0.233	0.495	1.05	2.11	4.55
	MSA	0.152	0.359	0.828	1.88	4.21	9.30
0.01	MC	0.151	0.338	0.794	2.09	5.64	13.7
	BSPB	0.150	0.335	0.805	2.20	6.00	14.4
	SPB	0.135	0.288	0.602	1.26	2.62	5.41
	MSA	0.181	0.417	0.945	2.11	4.66	10.2
0.02	MC	0.186	0.412	0.943	2.32	5.86	13.8
	BSPB	0.182	0.402	0.930	2.36	5.97	13.7
	SPB	0.165	0.350	0.731	1.51	3.12	6.42
	MSA	0.211	0.477	1.060	2.34	5.09	11.0
0.04	MC	0.226	0.493	1.10	2.55	6.08	14.0
	BSPB	0.214	0.466	1.05	2.49	5.91	13.2
	SPB	0.198	0.420	0.874	1.80	3.69	7.57
	MSA	0.242	0.537	1.18	2.56	5.52	11.8
0.08	MC	0.268	0.578	1.25	2.78	6.32	14.1
	BSPB	0.241	0.520	1.14	2.59	5.90	13.0
	SPB	0.234	0.492	1.02	2.11	4.32	8.81
	MSA	0.274	0.598	1.29	2.78	5.94	12.7

four components (i) colloid–colloid, E_{MM} , (ii) colloid–counterion, E_{MI} , (iii) counterion–counterion E_{II} , and (iv) excluded volume, E_{excl} :

$$E^{\text{Coul}} = E_{MM} + E_{MI} + E_{II} + E_{\text{excl}}. \quad (28)$$

It is useful to separate the total energy into these components and compare the BSPB and MC values to examine the accuracy of each term. In Tables I and II, we compare the BSPB internal energies in two planes, with the MC values of Linse⁴ and the symmetric Poisson–Boltzmann (SPB) and mean spherical approximation (MSA) values of Bhuiyan and Outhwaite.¹² The energies are for state points in the (Z_r, Γ_{II}) plane at volume fraction $\phi_M=0.01$ and on state points in the (ϕ_M, Γ_{II}) plane at $Z_r=40$. The BSPB internal energy predictions are in excellent agreement with the MC values for all the state points considered in Tables I and II, whereas the SPB and MSA are only in good agreement with the MC values for a small number of state points. The BSPB energies are in particularly good agreement with the MC values for low volume fraction ϕ_M and low coupling parameter Γ_{II} , because the BSPB predictions of the colloid–colloid distribution function $g_{MM}(r/R_M)$ and consequently the colloid–colloid energy E_{MM} (which comes from integrating $g_{MM}(r/R_M)$) are very accurate. In this region of phase space, E_{MM} is the dominant contribution to the total internal energy. The colloid–counterion E_{MI} and counterion–counterion E_{II} energy contributions are less significant because the accumu-

lation of counterions near the colloid surface is relatively low, so correlations between these species are weak in this region.

In general, the BSPB internal energy estimates become less accurate as either ϕ_M or Γ_{II} is increased. The main source of error in the BSPB model comes from the relatively poor prediction of ion–ion correlations. As either the volume fraction ϕ_M or coupling parameter Γ_{II} is raised, the accumulation of counterions near the colloid surface increases and colloid–counterion and counterion–counterion correlations become more significant. As a consequence, the colloid–counterion E_{MI} and counterion–counterion E_{II} contributions to the internal energy become relatively more important. For $\Gamma_{II} \geq 0.178$, E_{MI} replaces E_{MM} as the dominant contribution to the internal energy.

2. Pressure

The BSPB pressures were calculated via the virial path (BSPB_v) using Eq. (12). In Table III, they are compared with the MC pressures, and the SPB pressures via the virial (SPB_v), charging (SPB_{ch}), and compressibility routes (SPB_c) in the (ϕ_M, Γ_{II}) plane at $Z_r=40$. Like the internal energy values, the BSPB pressures are in excellent agreement with MC values for low ϕ_M and low Γ_{II} , but become less accurate as either of these system parameters is increased. There is considerable uncertainty in the virial path

TABLE III. Reduced pressure PV/NkT for different ϕ_M and Γ_{II} values at $Z_r=40$. The MC values are from Linse⁴ and the SPB values are from Bhuiyan and Outhwaite¹².

ϕ_M		Γ_{II}					
		0.0222	0.0445	0.0889	0.178	0.356	0.712
0.001 25	MC	0.978	0.949	0.882	0.713	0.446	0.258
	BSPB _v	0.978	0.949	0.878	0.671	0.108	-1.120
	SPB _v	0.980	0.955	0.902	0.793	0.568	0.103
	SPB _c	1.08	0.991	0.921	0.839	0.733	0.598
	SPB _{ch}	0.985	0.961	0.914	0.821	0.648	0.321
0.0025	MC	0.974	0.938	0.857	0.673	0.410	0.247
	BSPB _v	0.973	0.937	0.852	0.628	0.099	-0.941
	SPB _v	0.976	0.946	0.882	0.752	0.486	-0.064
	SPB _c	1.03	0.968	0.907	0.821	0.704	0.555
	SPB _{ch}	0.985	0.956	0.900	0.790	0.584	0.189
0.005	MC	0.967	0.927	0.834	0.641	0.387	0.241
	BSPB _v	0.969	0.926	0.828	0.596	0.125	-0.704
	SPB _v	0.973	0.937	0.862	0.709	0.395	-0.253
	SPB _c	1.00	0.954	0.893	0.801	0.672	0.513
	SPB _{ch}	0.989	0.956	0.889	0.761	0.517	0.045
0.01	MC	0.967	0.917	0.814	0.621	0.379	0.231
	BSPB _v	0.968	0.918	0.811	0.583	0.198	-0.419
	SPB _v	0.974	0.932	0.846	0.668	0.305	-0.449
	SPB _c	0.990	0.948	0.883	0.783	0.642	0.474
	SPB _{ch}	1.00	0.966	0.889	0.740	0.456	-0.100
0.02	MC	0.941	0.915	0.804	0.608	0.379	0.213
	BSPB _v	0.972	0.918	0.807	0.595	0.274	-0.140
	SPB _v	0.983	0.938	0.845	0.650	0.248	-0.512
	SPB _c	0.990	0.951	0.884	0.776	0.624	0.447
	SPB _{ch}	1.04	0.999	0.913	0.745	0.421	-0.220
0.04	MC	0.987	0.929	0.811	0.618	0.383	0.213
	BSPB _v	0.989	0.920	0.822	0.629	0.371	0.090
	SPB _v	1.02	0.976	0.889	0.697	0.278	-0.635
	SPB _c	1.00	0.975	0.917	0.810	0.646	0.451
	SPB _{ch}	1.13	1.08	0.993	0.812	0.454	-0.263
0.08	MC	1.03	0.970	0.851	0.656	0.421	0.225
	BSPB _v	1.03	0.973	0.869	0.692	0.467	0.206
	SPB _v	1.12	1.11	1.07	0.920	0.544	-0.401
	SPB _c	1.05	1.07	1.09	1.09	0.945	0.610
	SPB _{ch}	1.34	1.29	1.20	1.01	0.637	-0.129

to calculate the pressure because it requires a very precise knowledge of the colloid-counterion contact value $g_{MI}(R_M)$. The pressure is determined by the small difference of two large numbers—a negative Coulombic contribution and a positive hard-core repulsion.⁷ The BSPB contact values $g_{MI}(R_M)$ are most accurate for low coupling strengths Γ_{II} , and become less accurate as Γ_{II} is increased. This explains why at the highest coupling strength, $\Gamma_{II}=0.712$, the BSPB_v, SPB_v, and SPB_{ch} can predict unphysical negative pressures.

C. Phase Behavior

Spinodal and binodal curves were determined using the BSPB internal energy path (BSPE_e) and they are compared in Fig. 3 with the MSA curves¹³ and the MC simulation curves of Reščič and Linse,¹⁴ which are only available for $Z_r=10$. The BSPB_e binodal and critical point are in much better agreement with the MC results than the MSA. A comparison of the critical point predictions using the BSPB_e, SPB_{ch}, MSA_e and extended Debye-Huckel (EDH_e)¹⁵ theories for $Z_r=10$, is presented in Table IV.

It was not possible to locate any spinodal curves for $Z_r \geq 20$ using the BSPB_e. This is somewhat surprising considering the good agreement between the BSPB and MC rdffs and internal energies, but if one examines the internal energies in the (ϕ_M, Γ_{II}) plane at $Z_r=40$ in Table II it can be understood. For the highest coupling strength, $\Gamma_{II}=0.712$, the BSPB internal energies are in better agreement with the MC values than the SPB or MSA values for all the volume fractions considered. However, the trend is for the BSPB internal energies to decrease as ϕ_M is raised. Whereas the MC, SPB, and MSA internal energies all increase as ϕ_M is raised, which is the correct type of trend conducive to a liquid-gas type separation. Hence the trend in the BSPB internal energies is in error at high coupling strengths, which leads to its failure to predict spinodal curves for $Z_r \geq 20$. This failure in the BSPB theory can be attributed to its underestimation of the counterion-counterion repulsion at small separation. For $Z_r=10$, it is still possible to find the spinodal using the BSPB model because the error in predicting ion-ion correlations is not significant enough to inhibit the liquid-gas separation.

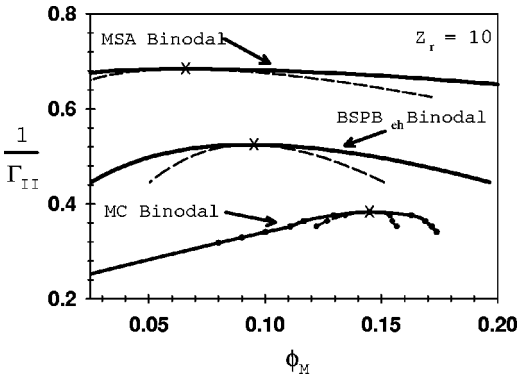


FIG. 3. Gas–liquid binodal (solid) and spinodal (dashed) curves from the MSA_e, BSPB_e, and MC simulation¹⁴ for a one-component system with $Z_r = 10$. The critical points are marked with an \times on each curve.

VI. TWO-COMPONENT SOLUTIONS

Subsequent to the work of Hayter and Penfold, Ginoza^{16–18} developed an analytic solution of the OZ equation for mixtures of Yukawa particles under the MSA closure. We used Ginoza’s solution with a rescaling argument (RMSA), together with a charge renormalization⁹ scheme to calculate the correlation functions between mixtures of colloidal particles. Ginoza¹⁷ provides a method for solving the OZ equation (4) with the Yukawa closure

$$h_{\alpha\beta}(r) = -1, \quad r < (R_\alpha + R_\beta),$$

$$c_{\alpha\beta}(r) = K d_\alpha d_\beta \frac{\exp(-zr)}{r}, \quad r > (R_\alpha + R_\beta), \quad (29)$$

where R_α and R_β are the radii of species α and β , K , z , d_α and d_β are constants. Ginoza’s solution builds on the previous work by Baxter¹⁹ and Blum and Høye.²⁰

To apply Ginoza’s solution to the model system we need to express the direct correlation functions $c_{\alpha\beta}(r)$ in the form of Eq. (29) using the MSA,

$$c_{\alpha\beta}(r) = -\frac{u_{\alpha\beta}^{\text{eff}}(r)}{kT}. \quad (30)$$

For the effective pair potential between colloidal particles of type J and K , we use the general form derived for large colloidal size and charge⁸

$$u_{JK}^{\text{eff}}(r) = \frac{Z_J^{\text{eff}} Z_K^{\text{eff}} e^2}{\epsilon} \frac{\exp(\kappa R_J)}{1 + \kappa R_J} \frac{\exp(\kappa R_K)}{1 + \kappa R_K}$$

$$\times (1 + \phi)^2 \frac{\exp(-\kappa r)}{r}, \quad r > (R_J + R_K), \quad (31)$$

where ϕ is the total volume fraction, Z_J^{eff} and Z_K^{eff} are the effective colloidal charges, and κ is the screening parameter, which depends on the effective density of counterions, where

$$n_i^{\text{eff}} Z_i + \sum_{J, J \neq i} n_J Z_J^{\text{eff}} = 0 \quad (32)$$

and

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} n_i^{\text{eff}} (Z_i)^2. \quad (33)$$

TABLE IV. Comparison of the MC critical values with those from the BSPB, MSA, SPB, and EDH theories for $Z_r = 10$.

	MC	BSPB _e	MSA _e	SPB _{ch}	SPB _v	EDH _e (high)
ϕ_M	0.15	0.10	0.07	0.01	0.02	0.24
Γ_{II}	2.6	1.9	1.5	2.3	1.5	0.32

The constants in Eq. (29) can now be specified

$$K = \frac{e^2}{\epsilon kT} (1 + \phi)^2,$$

$$d_J = \frac{Z_J^{\text{eff}} \exp(\kappa R_J)}{1 + \kappa R_J}, \quad (34)$$

$$z = \kappa.$$

In the RMSA, particles are assigned an effective hard sphere diameter larger than or equal to their true diameter by some scale factor $s \geq 1$. Ginoza^{16–18} outlines an iteration scheme, which we have followed to find this s .

The BSPB was applied to a system containing like charged large (L) and small (S) colloidal particles and a common neutralizing counterion species (I). We used Ginoza’s RMSA solution to determine the rdfs between the colloidal particles and then the BSPB theory in Sec. IV to calculate the remaining rdfs involving the counterion species. In such a system there are now six relevant distribution functions to consider; namely the (i) $L-L$, (ii) $L-S$, (iii) $S-S$, (iv) $L-I$, (v) $S-I$, and (vi) $I-I$. Let n_L be the number density of large colloids of valence Z_L and hard sphere radius R_L , n_S be the number density of large colloids of valence Z_S and hard sphere radius R_S and n_I be the number density of point counterions of valence Z_I . Electroneutrality requires that

$$n_I Z_I + n_L Z_L + n_S Z_S = 0. \quad (35)$$

The state of the two-component colloidal solution is uniquely specified in terms of six nondimensional variables:

$$Z_L = -\frac{Z_L}{Z_I},$$

$$Z_S = -\frac{Z_S}{Z_I},$$

$$N_R = \frac{n_S}{n_L},$$

$$R_R = \frac{R_S}{R_L},$$

$$\Gamma_{II} = \frac{e^2}{\epsilon kT R_L},$$

$$\phi_L = \frac{4\pi R_L^3}{3} n_L. \quad (36)$$

We investigated the effect of adding different number ratios ($N_R = n_S/n_L$) of small colloids on (i) the structure of the large colloids and (ii) the electrostatic internal energy. The

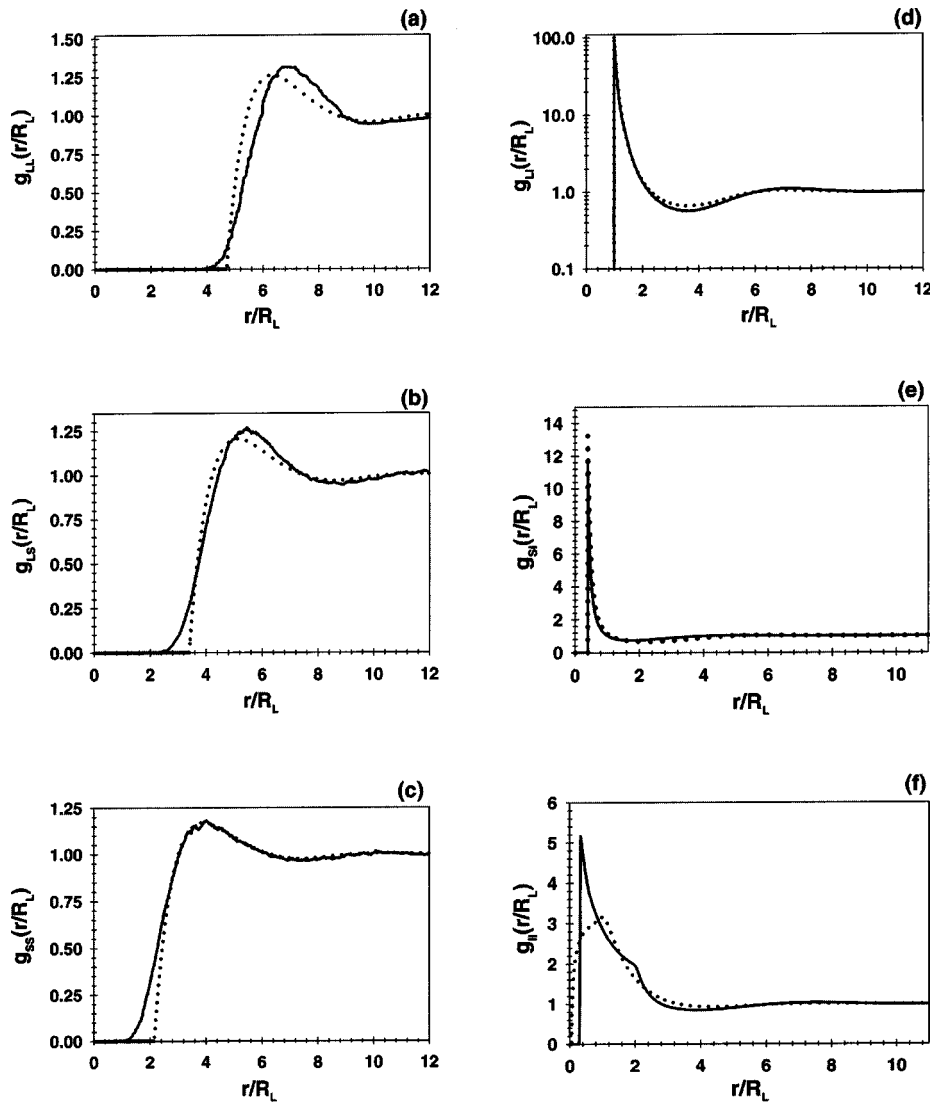


FIG. 4. (a) Large–large, (b) large–small, (c) small–small, (d) large–counterion, (e) small–counterion, and (f) counterion–counterion rdfs from MC simulation (solid curves) and BSPB theory (dotted curves) for a two-component colloidal system at $(Z_L, Z_S, N_R, R_R, \phi_L, \Gamma_{II}) = (80, 10, 2, 0.4, 0.01, 0.178)$.

properties of the system were chosen to be similar to those used in the SANS experiments of Ottewill *et al.*,³

$$\begin{aligned}
 Z_L &= -80, \\
 Z_S &= -10, \\
 N_R &= 1, 2, 4, 8, 16, \\
 R_R &= 0.4, \\
 \Gamma_{II} &= 0.178, \\
 \phi_L &= 0.01.
 \end{aligned}
 \tag{37}$$

The coupling strength and large colloid volume fraction are the same as in the one-component example in Fig. 1, which is the system with no small colloids. All separations have been scaled by the large colloid hard sphere radius R_L .

A. Structural properties

The BSPB and MC rdfs are compared in Fig. 4 at this point in phase space $(Z_L, Z_S, N_R, R_R, \phi_L, \Gamma_{II})$

$= (80, 10, 2, 0.4, 0.01, 0.178)$, where the number ratio of small colloids to large colloids is $N_R = n_S/n_L = 2$. The renormalized charges were determined by considering the two-component system as a mixture of separate one-component systems of L and S colloids. The renormalized valences for the L and S colloids in their respective one-component solutions are $Z_L^{\text{eff}} = 40.2$ and $Z_S^{\text{eff}} = 9.35$ and $\kappa R_L = 0.56$. In Figs. 4(a), 4(b), and 4(c) the BSPB and MC $L-L$, $L-S$, and $S-S$ colloid–colloid rdfs are shown. The colloid–colloid rdfs display the typical characteristics for a fluid, which has a pronounced first maximum at some interparticle distance, followed by successive minima and maxima of reduced amplitude. The amplitudes and positions of the maxima and minima from theory and simulation agree well, in particular the $S-S$ curves, which are almost identical. The BSPB $L-L$ first maximum occurs at $r/R_L = 6.4$ and the amplitude value is 1.26, while the MC $L-L$ first maximum occurs at $r/R_L = 6.8$ and the amplitude value is 1.31.

In Figs. 4(d) and 4(e) the BSPB and MC large-counterion ($L-I$) and small-counterion ($S-I$) rdfs are shown. The $L-I$ curve is sharply peaked at $r/R_L = 1$, and indicates a

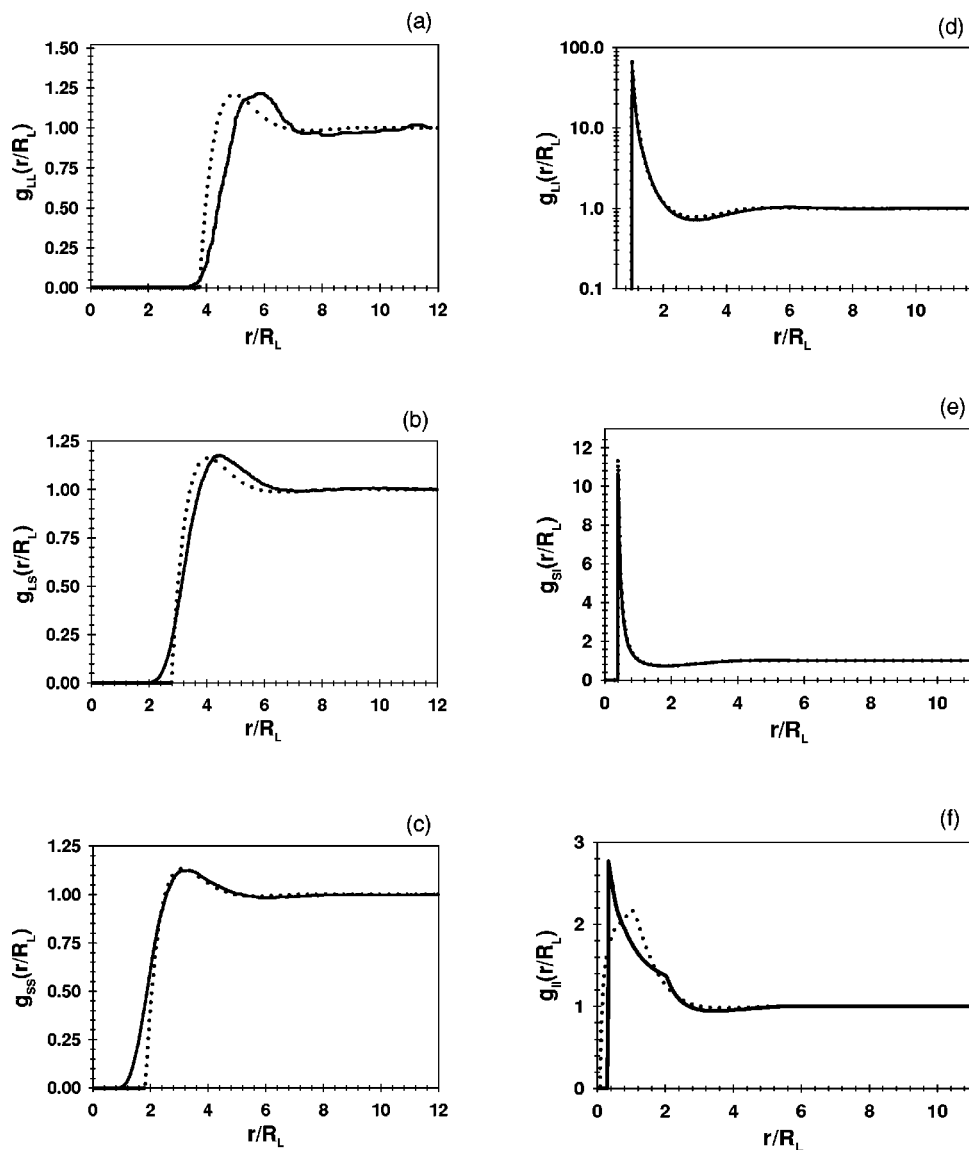


FIG. 5. (a) Large–large, (b) large–small, (c) small–small, (d) large–counterion, (e) small–counterion, and (f) counterion–counterion rdf’s from MC simulation (solid curves) and BSPB theory (dotted curves) for a two-component colloidal system at $(Z_L, Z_S, N_R, R_R, \phi_L, \Gamma_{II}) = (80, 10, 8, 0.4, 0.01, 0.178)$.

strong accumulation of counterions near the surface of the large colloid, analogous to the one-component system. The BSPB $L-I$ contact value is 101, which is a slight overestimate of the extrapolated MC value of 93. The $L-I$ contact value in the two-component solution is approximately 25% lower in comparison with the $M-I$ contact value in the one-component solution. The main explanation for the reduced $L-I$ contact value is that the average concentration of counterions has increased due to the extra counterions accompanying the small colloids. The $S-I$ curve peaks at $r/R_L = 0.4$, and indicates a reasonable accumulation of counterions near the small colloid surface. The BSPB contact value is 13.2, which also is a slight overestimate of the extrapolated MC value of 11.5. The $I-I$ rdf in Fig. 4(f) is very similar to Fig. 1(c) for the one-component solution.

The BSPB and MC two-component rdfs are shown in Figure 5 at a higher ratio of small colloids to large colloids of $N_R = 8$ at the same coupling strength. Using the phase space point $(Z_L, Z_S, N_R, R_R, \phi_L, \Gamma_{II}) = (80, 10, 8, 0.4, 0.01, 0.178)$, the renormalized charges for the L and S colloids in their respective one-component solutions are $Z_L^{\text{eff}} = 40.2$ and Z_S^{eff}

$= 9.1$ and $\kappa R_L = 0.78$. In Figs. 5(a), 5(b), and 5(c) the BSPB and MC $L-L$, $L-S$, and $S-S$ colloid–colloid rdfs are shown. The BSPB $L-L$ first maximum is at $r/R_L = 4.94$ and the peak value is 1.21, while the MC $L-L$ first maximum is at $r/R_L = 5.88$ and the peak value is 1.22. The BSPB prediction of the $L-L$ first maximum position gets progressively worse as the ratio of small to large colloids is increased. In Figs. 5(d) and 5(e) the BSPB and MC $L-I$ and $S-I$ rdfs are shown. The BSPB $L-I$ contact value is 63, which very slightly overestimates the extrapolated MC value of 61.1. The $L-I$ contact value is considerably reduced compared with the value for the ratio of $N_R = 2$. The BSPB and MC $S-I$ contact values are 11.3 and 10.7, respectively, which are also lower than the respective values for the ratio of $N_R = 2$.

B. Thermodynamics

Internal energies were calculated using Eq. (8) from the BSPB distribution functions using the charging process. For

TABLE V. Reduced internal energy E/NkT for a binary colloid solution at different N_r values at $\Gamma_{II}=0.178$.

		<i>LL</i>	<i>LS</i>	<i>SS</i>	<i>LI</i>	<i>SI</i>	<i>II</i>	Excl	E/NkT
$N_r=0$	MC	-2.02	0	0	-4.20	0	0.89	-0.21	-5.54
	BSPB	-2.06	0	0	-4.54	0	0.79	-0.21	-6.02
$N_r=1$	MC	-1.73	-0.23	-0.0031	-3.58	0.094	0.71	-0.20	-4.96
	BSPB	-1.79	-0.21	-0.0050	-4.25	0.070	0.81	-0.20	-5.58
$N_r=2$	MC	-1.44	-0.34	-0.016	-3.34	0.13	0.67	-0.20	-4.54
	BSPB	-1.34	-0.36	-0.018	-3.93	0.11	0.77	-0.20	-4.97
$N_r=4$	MC	-1.12	-0.43	-0.055	-2.84	0.12	0.56	-0.20	-3.97
	BSPB	-0.87	-0.51	-0.055	-3.47	0.14	0.72	-0.20	-4.23
$N_r=8$	MC	-0.69	-0.52	-0.11	-2.32	0.11	0.44	-0.20	-3.28
	BSPB	-0.47	-0.57	-0.14	-2.80	0.12	0.63	-0.20	-3.43
$N_r=16$	MC	-0.31	-0.57	-0.19	-1.65	0.011	0.29	-0.21	-2.63
	BSPB	-0.19	-0.49	-0.27	-2.02	0.020	0.48	-0.21	-2.69

this system, the electrostatic internal energy can be separated into seven terms to examine the strengths and weaknesses of the BSPB theory,

$$E^{\text{Coul}} = E_{LL} + E_{LS} + E_{SS} + E_{LI} + E_{SI} + E_{II} + E_{\text{excl}}. \quad (38)$$

The BSPB reduced internal energies are compared term by term with the MC values in Table V for selected number ratios of small to large colloids between 0 and 16. The BSPB energy terms become less accurate compared with the MC terms as the ratio of small to large colloids is increased. This trend reflects the agreement between the BSPB and MC structures, which is generally better for low number ratios such as the $N_R=2$ case in Fig. 4 than for high number ratios such as the $N_R=8$ case in Fig. 5. The *LL*, *SI* and *II* energy terms are in considerable error for the $N_R=16$ case. However, the BSPB and MC total energies remain in good agreement for all the number ratios considered. This is misleading since it is due to the cancellation of errors between overestimated and underestimated energy terms. Overall, the BSPB theory is more reliable for low ratios of small to large colloids.

VII. CONCLUSIONS

We have developed the BSPB theory to calculate the distribution functions and thermodynamic quantities for one- and two-component charged colloidal solutions. The BSPB distribution functions have been compared with MC simulations with explicit counterions, and the thermodynamic quantities have been compared with both MC simulations and other theoretical predictions. The BSPB appears to give better agreement with the MC simulations for the thermodynamic quantities than any of the other existing theories. The strength of the BSPB theory is that it takes into account, to some extent, the effect of colloid–colloid correlations and high charge asymmetries in the thermodynamics and colloid–ion correlations. At this stage, the BSPB does a relatively poor job of predicting ion–ion correlations, but these are normally small contributions to the thermodynamics, except for very high coupling strengths.

The BSPB was used to predict the gas–liquid binodal and spinodal curves for a one-component solution with a colloid charge to counterion-charge ratio $Z_r=10$, in good agreement with the MC simulation curves. At this stage, we have not searched for any spinodal curves for systems with two colloidal species using the BSPB, because of the inability of the BSPB to predict a spinodal curve for one-component solutions with $Z_r \geq 20$. However, we hope to make improvements to the BSPB theory in the near future, such as to improve the prediction of ion–ion correlations at small separations, which will hopefully allow for a more detailed investigation of the phase behavior of charged colloidal solutions.

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