Static structure of polydisperse colloidal monolayers

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A generalization of integral equation theory of simple liquids is used to study the structure and thermodynamics of a monolayer of spherical colloidal particles having a continuous distribution \( f(\sigma) \) of diameters \( \sigma \). The quasi-two-dimensional fluid is modeled by a Yukawa potential between charged particles and a Lennard-Jones potential to represent soft spheres, with an effective attractive well. The numerical solution of the integral equations makes essential use of polynomials that are orthogonal with weight function \( f(\sigma) \), which is taken here to be a Schulz distribution. © 1998 American Institute of Physics.

I. INTRODUCTION

Colloidal particles, at the boundary of the microscopic and macroscopic worlds, provided the first direct evidence for the atomic hypothesis through Einstein’s 1905 explanation of Brownian motion and thereby gave credibility to the new techniques of statistical mechanics then being applied to the hypothetical atoms. It seems fitting that nearly a century later colloidal suspensions should also offer a visible model of the hypothetical atoms. Digital video microscopy \(^1\) makes possible the direct measurement of the averaged structure of a colloidal fluid, \(^2\)–\(^4\) a sort of real-world “molecular dynamics simulation.” For suspensions narrowly confined between parallel glass plates, the particles form a quasi-two-dimensional fluid. The direct measurement of the structure of a monolayer of charged polystyrene spheres in micrometer scale in a confined aqueous solution can then be made to yield an effective pair potential. Kepler and Fraden \(^5\) and Carabajal et al. \(^6\) found in this way a potential that is short ranged and a sort of real-world “molecular dynamics simulation.” For suspensions narrowly confined between parallel glass plates, the particles form a quasi-two-dimensional fluid. The direct measurement of the structure of a monolayer of charged polystyrene spheres having a continuous distribution \( f(\sigma) \) of diameters \( \sigma \). The quasi-two-dimensional fluid is modeled by a repulsive Yukawa potential to represent charged hard spheres (with attendant charge polydispersity) and a Lennard-Jones potential to represent soft spheres with an effective attractive well. The numerical solution of the integral equations makes essential use of polynomials that are orthogonal with weight function \( f(\sigma) \), which is taken here to be a Schulz distribution.

II. INTEGRAL EQUATION FORMALISM FOR A MONOLAYER OF POLYDISPERSE SPHERES

We consider a uniform monolayer of \( N \) polydisperse colloidal spheres occupying a plane area \( A \) at temperature \( T \). The density of particles at point \( r \) with diameter \( \sigma \) is given by the one-body density function

\[
\rho(r, \sigma) = \sum_{i=1}^{N} \delta(r-r_i) \delta(\sigma-\sigma_i) = \rho f(\sigma),
\]

where \( \rho = N/A \) and \( f(\sigma) \) is the fixed distribution of particle diameters \( \sigma \). The two-body density function

\[
\rho^{(2)}(r, \sigma, r', \sigma') = \rho^2 f(\sigma) f(\sigma') g(|r-r'|, \sigma, \sigma')
\]

then defines the generalized pair distribution function \( g(r, \sigma, \sigma') \), which is the key quantity needed for a complete description of the structure and thermodynamics of the colloidal monolayer. In these expressions, \( r_i \) is the location of particle \( i \) in the plane and \( \sigma_i \) its diameter; the angular brackets denote a canonical ensemble average.

In classical liquid state theory, the pair distribution function is obtained from the Ornstein-Zernike (OZ) equation combined with a closure relation.\(^1\) The first of these, generalized for polydispersity, reads

\[
\gamma(r_{12}, \sigma_1, \sigma_2) = \rho \int d\sigma_3 \int d\sigma_4 f(\sigma_3) f(\sigma_4) c(r_{13}, \sigma_1, \sigma_3, \sigma_4) + \gamma(r_{13}, \sigma_1, \sigma_3) c(r_{23}, \sigma_3, \sigma_2)
\]

for the indirect correlation function \( \gamma = g - 1 - c \), where \( c \) is the direct correlation function. The second, or closure, relation expresses \( c \) back in terms of \( \gamma \) and the pair interaction \( \phi \),

\[
c(r, \sigma_1, \sigma_2) = \exp[-\beta \phi(r, \sigma_1, \sigma_2)] + g(r, \sigma_1, \sigma_2) + b(r, \sigma_1, \sigma_2) - 1 - \gamma(r, \sigma_1, \sigma_2),
\]

where \( g(r, \sigma_1, \sigma_2) \) is the two-body distribution function.

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\(^1\) Digital video microscopy.\(^2\) A generalization of integral equation theory of simple liquids is used to study the structure and thermodynamics of a monolayer of spherical colloidal particles having a continuous distribution \( f(\sigma) \) of diameters \( \sigma \). The quasi-two-dimensional fluid is modeled by a repulsive Yukawa potential to represent charged hard spheres (with attendant charge polydispersity) and a Lennard-Jones potential to represent soft spheres with an effective attractive well. The numerical solution of the integral equations makes essential use of polynomials that are orthogonal with weight function \( f(\sigma) \), which is taken here to be a Schulz distribution.
where $\beta = 1/k_B T$, with $k_B$ Boltzmann’s constant. This equation must be supplemented with an approximation for $b(r, \sigma_1, \sigma_2)$, the so-called bridge function, whose formal definition as an infinite series in density offers only modest practical guidance. Most approximate closures for $c$ define $b$ implicitly.

The numerical evaluation of the OZ equation is simpler in Fourier transform representation, which deconvolutes the $\mathbf{r}$ integral. Thus, in transform space, Eq. (3) becomes

$$\tilde{\gamma}(k, \sigma_1, \sigma_2) = \rho \int_0^\infty d \sigma f(\sigma) \tilde{c}(k, \sigma_1, \sigma_2),$$

with one remaining integration. We note that the Fourier transform of a circularly symmetric function in two dimensions becomes a Hankel transform,

$$\tilde{w}(k) = 2\pi \int_0^\infty d \sigma \, r w(r) J_0(k r),$$

where $J_0(x)$ is the zeroth-order Bessel function; the inverse of (6) is

$$w(r) = \frac{1}{2\pi} \int_0^\infty d k \, k \tilde{w}(k) J_0(k r).$$

The final integration in Eq. (5) can also be eliminated and the evaluation of the OZ equation reduced to algebra by now expanding all $\sigma$-dependent functions in orthogonal polynomials $p_j(\sigma)$, $j=0,1,2,...$, defined such that

$$\int_0^\infty d \sigma \, f(\sigma) p_j(\sigma) p_k(\sigma) = \delta_{j,k},$$

where $\delta_{j,k}$ is the Kronecker delta. Then with

$$\tilde{\gamma}(k, \sigma_1, \sigma_2) = \sum_{i,j=0}^{\infty} \tilde{\gamma}_{ij}(k) p_i(\sigma_1) p_j(\sigma_2)$$

and a similar expansion of $\tilde{c}(k, \sigma_1, \sigma_2)$, Eq. (5) becomes

$$\tilde{\gamma}_{ij}(k) = \rho \sum_l \left[ \tilde{c}_{il}(k) + \tilde{c}_{jl}(k) \right] \tilde{c}_{ij}(k),$$

or, in matrix notation,

$$\Gamma(k) = \rho \left[ \tilde{C}(k) + \tilde{C}(k) \right] \tilde{C}(k) = \rho \tilde{C}(k) \tilde{C}(k) [I - \rho \tilde{C}(k)]^{-1}.$$  

In these equations $\Gamma(k)$, $\tilde{C}(k)$ are symmetric matrices with elements $\tilde{\gamma}_{ij}(k)$, $\tilde{c}_{ij}(k)$ and $I$ is the unit matrix. Orthonormality allows the easy inversion of Eq. (9) as

$$\tilde{c}_{ij}(k) = \int d \sigma_1 d \sigma_2 f(\sigma_1) f(\sigma_2) \tilde{\gamma}(k, \sigma_1, \sigma_2) p_j(\sigma_1) p_j(\sigma_2).$$

(12)

Similar expansions and inversions hold for functions in $r$ space.

With the substitution of the $J_0$ transforms (6) and (7) for the corresponding sine transforms, these ingredients for a polydisperse fluid in two dimensions are identical to those of a polydisperse fluid in three dimensions and can be solved with the same numerical procedures. The new feature, the Hankel transform, is evaluated using an orthogonality-preserving algorithm.

The generalized pair distribution function

$$g(r, \sigma_1, \sigma_2) = \exp[-\beta \phi(r, \sigma_1, \sigma_2) + \gamma(r, \sigma_1, \sigma_2) + b(r, \sigma_1, \sigma_2)]$$

(13)

is finally constructed from the self-consistent solution of the (OZ+closure) equations for the coefficients $\gamma_i(r)$. The thermodynamic quantities then directly computable from $g$ are the internal energy $U$,

$$\frac{\beta U}{N} = \frac{1}{2} \rho \int d \mathbf{r} \, d \sigma \, d \sigma' \, f(\sigma) f(\sigma') \times g(r, \sigma, \sigma') \beta \phi(r, \sigma, \sigma')$$

(14)

and the pressure $p$,

$$\frac{\beta p}{\rho} = 1 - \frac{1}{4} \rho \int d \mathbf{r} \, d \sigma \, d \sigma' \, f(\sigma) f(\sigma') \times g(r, \sigma, \sigma') \frac{d \beta \phi(r, \sigma, \sigma')}{d r}.$$  

(15)

In addition, the isothermal compressibility $K_T$,

$$\frac{1}{\rho k_B T} = \left( \frac{\partial p}{\partial \rho} \right)_T = 1 - \rho \int d \mathbf{r} \, d \sigma \, d \sigma' \, f(\sigma) f(\sigma') c(r, \sigma, \sigma')$$

$$= 1 - \rho \tilde{c}_0(0),$$

(16)

is obtained from the direct correlation function.

Pair functions of interest can be expressed directly in terms of the computed coefficients. In particular, the number-number pair distribution function and the number-number structure factor are, respectively,

$$g_{NN}(r) = \int d \sigma_1 d \sigma_2 f(\sigma_1) f(\sigma_2) g(r, \sigma_1, \sigma_2) = g_{00}(r),$$

(17)

$$S_{NN}(k) = \int d \sigma_1 d \sigma_2 [f(\sigma_1) \delta(\sigma_1 - \sigma_2)$$

$$+ \rho f(\sigma_1) f(\sigma_2) \tilde{h}(k, \sigma_1, \sigma_2)] = 1 + \rho \tilde{h}_0(k).$$

(18)

Further, low order coefficients of $g(r, \sigma_1, \sigma_2)$ can be given a physical interpretation. Thus, local fluctuations in density and size may be expressed in normalized form as

$$\delta \rho_0(r) = \frac{1}{\rho} \left( \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) - \rho \right),$$

$$\delta \rho_1(r) = \frac{1}{\rho \rho_{\sigma}} \left( \sum_{j=1}^{N} \sigma_j \delta(\mathbf{r} - \mathbf{r}_j) - \sigma_0 \right).$$

(19)

(20)

Their spatial correlations are then given by
\[ \langle \delta \rho_0 (r) \delta \rho_0 (0) \rangle = \frac{\delta (r)}{\rho} + [g_{00} (r) - 1]. \]  
(21)
\[ \langle \delta \rho_1 (r) \delta \rho_0 (0) \rangle = -g_{10} (r), \]  
(22)
\[ \langle \delta \rho_1 (r) \delta \rho_1 (0) \rangle = \frac{\delta (r)}{\rho} + g_{11} (r). \]  
(23)

### III. POTENTIAL MODELS WITHOUT AND WITH AN ATTRACTIVE WELL

Two familiar potentials are used here to model a polydisperse colloidal monolayer: (a) the repulsive part of the DLVO interaction\(^\text{12-14}\) and (b) the Lennard-Jones 12-6 interaction.\(^\text{15}\)

For charged hard spheres of polydisperse diameters \(\sigma\), the repulsive DLVO potential, of Yukawa form, is

\[ \beta \phi (r, \sigma_1, \sigma_2) = \left\{ \begin{array}{ll} \infty, & r < \sigma_{12} \\ A (\sigma_1) A (\sigma_2) \exp (-\kappa r) / r, & r > \sigma_{12} \end{array} \right. \]  
(24)

\[ A (\sigma) = \frac{Z (\sigma) L_B^{1/2} \exp (\kappa \sigma / 2)}{1 + \kappa \sigma / 2}, \]

where \(\sigma_{12} = (\sigma_1 + \sigma_2) / 2\). In these expressions, \(\kappa\) is the inverse Debye-Hückel screening length determined by the counterion concentration and \(L_B = e^{\Delta / 4 \pi e_0 e k_B T}\) the Bjerrum length. The charged mesospheres are assumed to have a constant surface charge density,\(^\text{19}\) so that their resulting charge polydispersity is mapped onto the size polydispersity according to

\[ Z (\sigma) = \frac{\sigma^2}{\bar{\sigma}}, \]  
(25)

where \(\bar{\sigma}\) is the number of elementary charges on a particle of mean diameter \(\bar{\sigma}\). We use the parameter values of Crocker and Grier: \(\bar{\sigma} = 650\) nm, \(L_B = 0.715\) nm, \(\kappa \bar{\sigma} = 4.0\), and \(Z_{\bar{\sigma}} = 1990\). Under these conditions, electrostatic repulsion keeps the hard spheres from touching, so that only charge polydispersity is relevant in practice.

A closure relation proposed by Rogers and Young,\(^\text{20}\)

\[ g^{\text{RY}} (r, \sigma_1, \sigma_2) = e^{-\beta \phi (r, \sigma_1, \sigma_2)} \left\{ 1 + \frac{e^{m(r) / r} - 1}{m (r)} \right\}, \]  
(26)

has proven to be very successful for purely repulsive potentials such as (24). This equation mixes, via the function

\[ m (r) = 1 - e^{-\lambda r}, \]  
(27)

the Percus-Yevick and hypernetted-chain closures,\(^\text{15}\) which separately bracket the exact results. The parameter \(\lambda\) in Eq. (27) is chosen to enforce consistency between the inverse compressibility calculated from Eq. (16) and that obtained by numerical differentiation of Eq. (15). We will use the RY closure below for the DLVO potential.

To model the effective attraction observed between colloidal spheres forming a monolayer between charged glass plates,\(^\text{5,6}\) we use the simple Lennard-Jones potential,

\[ \beta \phi (r, \sigma_1, \sigma_2) = 4 \beta e \left( \frac{\sigma_{12}^6}{r^6} - \frac{\sigma_{12}^2}{r^2} \right). \]  
(28)

where \(\sigma_{12}\) is defined as above. The Percus-Yevick and hypernetted-chain closures do not, in general, bracket the exact results for potentials with an attractive tail and so the RY closure is not as successful for such cases. Here we will use instead a different closure ‘‘mix’’ proposed by Zerah and Hansen,\(^\text{21}\)

\[ g^{\text{ZH}} (r, \sigma_1, \sigma_2) = e^{-\beta \phi (r, \sigma_1, \sigma_2)} \times \left\{ 1 + \frac{e^{m(r) / r} - 1}{m (r)} \right\}, \]  
(29)

where \(m (r)\) and its parameter \(\lambda\) are defined as in the RY closure. The ZH equation requires a separation of the potential \(\phi = \phi_s + \phi_l\) into a repulsive short-range (sr) part and an attractive long-range (lr) part. We use for this the WCA scheme,\(^\text{22}\)

\[ \beta \phi_s (r, \sigma_1, \sigma_2) = \left\{ \begin{array}{ll} \beta \phi (r, \sigma_1, \sigma_2) + \beta \varepsilon, & r < r_{\text{min}} \\ 0, & r > r_{\text{min}} \end{array} \right. \]  
(30)

\[ \beta \phi_l (r, \sigma_1, \sigma_2) = \left\{ \begin{array}{ll} -\beta \varepsilon, & r < r_{\text{min}} \\ \beta \phi (r, \sigma_1, \sigma_2), & r > r_{\text{min}} \end{array} \right. \]

where \(r_{\text{min}} = 2^{1/6} \sigma_{12}\). The well depth is set at \(\beta \varepsilon = 0.25\), between \(\beta \varepsilon = 0.2\) found by Kepler and Fraden\(^\text{5}\) and \(\beta \varepsilon = 0.3\) found by Carbajal et al.\(^\text{6}\)

### IV. RESULTS FOR THE SCHULZ DISTRIBUTION

The results presented in this section for two models of a monolayer of polydisperse colloidal spheres are based on the Schulz distribution\(^\text{23}\) of sphere diameters \(\sigma\). For particles with a mean diameter \(\bar{\sigma}\), this is

\[ f (\sigma) = \left( \frac{\alpha + 1}{\bar{\sigma}} \right)^{\alpha + 1} \sigma^{\alpha - (\alpha + 1) / \bar{\sigma}} e^{-(\alpha + 1) / \bar{\sigma}} \frac{1}{\Gamma (\alpha + 1)}, \]  
(31)

where \(\Gamma (z)\) is the gamma function. The relative standard deviation of this distribution is

\[ s_{\sigma} = \left[ \frac{\langle \sigma^2 \rangle - \langle \sigma \rangle^2}{\langle \sigma \rangle^2} \right]^{1/2} = \frac{1}{(\alpha + 1)^{1/2}}. \]  
(32)

### TABLE I. Computed thermodynamics of a polydisperse colloidal monolayer with repulsive DLVO potential and Schulz distribution of relative standard deviation \(s_{\sigma}\).

<table>
<thead>
<tr>
<th>(\rho \bar{\sigma}^2)</th>
<th>(s_{\sigma})</th>
<th>(\beta U / N)</th>
<th>(\beta \rho / \rho)</th>
<th>(\rho k_B T_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0</td>
<td>0.1336</td>
<td>1.729</td>
<td>0.3587</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1334</td>
<td>1.728</td>
<td>0.3587</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1329</td>
<td>1.727</td>
<td>0.3590</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.1319</td>
<td>1.725</td>
<td>0.3593</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0</td>
<td>0.4544</td>
<td>3.434</td>
<td>0.1168</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4530</td>
<td>3.435</td>
<td></td>
<td>0.1166</td>
</tr>
<tr>
<td>0.2</td>
<td>0.4527</td>
<td>3.437</td>
<td>0.1163</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.4504</td>
<td>3.442</td>
<td>0.1157</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>0</td>
<td>1.3030</td>
<td>7.742</td>
<td>0.0368</td>
</tr>
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<td>7.761</td>
<td>0.0366</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1.3065</td>
<td>7.811</td>
<td>0.0362</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1.3090</td>
<td>7.891</td>
<td>0.0354</td>
<td></td>
</tr>
</tbody>
</table>
which will be used to characterize the suspensions and define the parameter \( \alpha \). The orthonormal polynomials satisfying Eq. (8) for the Schulz distribution \( f_s(s) \) are

\[
p_j(\sigma) = \left[ \frac{j!\Gamma(\alpha+1)}{\Gamma(j+\alpha+1)} \right]^{1/2} \frac{L^{(\alpha)}_j(\alpha \sigma)}{\sigma},
\]

where the \( L^{(\alpha)}_j(t) \) are the associated Laguerre polynomials.

We present first the results for the repulsive DLVO potential. Computed thermodynamic values are shown in Table I for \( \rho \sigma^2 = 0.05, 0.10, 0.15 \) and three Schulz distributions of increasing width, \( s_s = 0.1, 0.2, 0.3 \), as well as the monodisperse case, \( s_s = 0 \), for reference. These quantities are seen to be relatively insensitive to the charge dispersion for the highly charged particles of the present sample. The effect of increasing polydispersity on the number-number distribution function \( g_{NN}(r) \) is seen in Fig. 1 for \( \rho \sigma^2 = 0.15 \). The general pattern of decreasing structure with increasing dispersion reproduces the behavior of polydisperse colloids in three dimensions.19 This is further mirrored in the number-number structure factor \( S_{NN}(k) \), shown in Fig. 2. The \( g_{NN}(r) \) and \( S_{NN}(k) \) curves for \( s_s = 0.1 \) are quite close to their monodisperse limits and are omitted in Figs. 1 and 2 for clarity. The functions \( g_{00}(r) - 1 \), \( g_{10}(r) \), and \( g_{11}(r) \) for correlations of density-density, size-density, and size-size fluctuations, respectively, Eqs. (21)–(23), are shown in Fig. 3 for density \( \rho \sigma^2 = 0.15 \) and dispersion \( s_s = 0.3 \). We see, for example, that at the first peak of \( g_{00}(r) \), which occurs at \( r = 2.54 \sigma \), the size-size fluct-

FIG. 1. The number-number pair distribution function \( g_{NN}(r) = g_{00}(r) \) for a polydisperse colloidal monolayer with repulsive DLVO potential at density \( \rho \sigma^2 = 0.15 \). The size dispersion of the colloidal spheres in descending order of the first peak is \( s_s = 0, 0.2, \) and 0.3.

FIG. 2. The number-number structure factor \( S_{NN}(k) = 1 + \rho \tilde{h}_{nl}(k) \) for a polydisperse colloidal monolayer with repulsive DLVO potential at density \( \rho \sigma^2 = 0.15 \). The size dispersion of the colloidal spheres in descending order of the first peak is \( s_s = 0, 0.2, \) and 0.3. The value at \( k = 0 \) is largest for \( s_s = 0.3 \).

FIG. 3. Pair correlation function coefficients \( g_{00}(r) - 1 \) (solid line), \( g_{10}(r) \\) (dash-dot line), and \( g_{11}(r) \\) (dotted line) for a polydisperse colloidal monolayer with repulsive DLVO potential at density \( \rho \sigma^2 = 0.15 \) and size dispersion \( s_s = 0.3 \).

TABLE II. Computed thermodynamics of a polydisperse colloidal monolayer with Lennard-Jones potential of well depth \( \beta \varepsilon = 0.25 \) and Schulz distribution of relative standard deviation \( s_s \).

<table>
<thead>
<tr>
<th>( \rho \sigma^2 )</th>
<th>( s_s )</th>
<th>( \beta U/N )</th>
<th>( \beta p/\rho )</th>
<th>( \rho k_B T \Gamma )</th>
</tr>
</thead>
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<tr>
<td>0.2</td>
<td>0</td>
<td>-0.0882</td>
<td>1.232</td>
<td>0.6468</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.0887</td>
<td>1.239</td>
<td>0.6449</td>
<td></td>
</tr>
<tr>
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<td>-0.0901</td>
<td>1.239</td>
<td>0.6389</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>-0.0926</td>
<td>1.247</td>
<td>0.6291</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0</td>
<td>-0.1736</td>
<td>1.658</td>
<td>0.3459</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.1745</td>
<td>1.665</td>
<td>0.3426</td>
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<td>0.2</td>
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<td>1.688</td>
<td>0.3328</td>
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<td>0.3</td>
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<td>1.727</td>
<td>0.3168</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0</td>
<td>-0.2383</td>
<td>2.541</td>
<td>0.1540</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.2389</td>
<td>2.568</td>
<td>0.1510</td>
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<td>0.2</td>
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<td>2.651</td>
<td>0.1423</td>
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<tr>
<td>0.3</td>
<td>-0.2431</td>
<td>2.801</td>
<td>0.1287</td>
<td></td>
</tr>
</tbody>
</table>
Turbinations are negatively correlated, while the cross correlation of size and density fluctuations passes through zero. This means that large spheres (large charges) are generally surrounded by small spheres (small charges) and vice versa.

Thermodynamic results for the polydisperse Lennard-Jones potential \( \beta \varepsilon = 0.25 \) are gathered in Table II for three densities, \( \rho \sigma^2 = 0.2, 0.4, 0.6 \), and the same four values of \( s_s \) as above. Here the trends with increasing dispersion are consistent for the three densities—the internal energy becomes more negative, the pressure increases, and the compressibility decreases—in contrast to the mixed behavior seen for the purely repulsive potential in Table I; the percentage changes of these numbers with increasing \( s_s \) are also several times larger than Table I data. The comparatively greater effect of the polydispersity is seen also in the \( g_{NN} \) and \( S_{NN} \) curves for the Lennard-Jones model, Figs. 4 and 5, compared to Figs. 1 and 2 for the repulsive DLVO potential, and further in the larger peaks of \( g_{10}(r) \) and \( g_{11}(r) \) relative to \( g_{00}(r) - 1 \) in Fig. 6, compared to Fig. 3. The phenomenon of small spheres having large nearest neighbors and vice versa, seen again in Fig. 6 for \( s_s = 0.3 \), is shared with the other model.

The model parameters for the curves displayed in Figs. 4–6, namely, a well depth \( \beta \varepsilon = 0.38 \) and a density \( \rho \sigma^2 = 0.48 \), are chosen to approximate the highest density quasi-two-dimensional colloidal suspension reported by Carbajal et al.\(^6\) These authors note that, for their larger plate separations, displacements of the colloidal spheres perpendicular to the midplane between the glass plates lead to changes in the observed structures ("dimensionality effects") that in fact are similar to the effects of polydispersity seen in Figs. 1 and 4. (It is, of course, evident that the Schultz distribution is not an appropriate quantitative model of the effective polydispersity due to such perpendicular displacements.) In absolute terms, the curve for \( s_s = 0 \) in Fig. 4 shows a "compressed" structure compared to the measured \( \rho \sigma^2 = 0.48 \) shape in Fig. 1(b) of Ref. 6, suggesting perhaps that the attractive well of the effective potential for the confined colloid has a shorter range than that of the Lennard-Jones potential.

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