# Density Functional for a Model Colloid-Polymer Mixture

Matthias Schmidt and Hartmut Löwen
*Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

Joseph M. Brader and Robert Evans
*H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*

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We present a density functional theory for mixtures of (hard sphere) colloidal particles and ideal polymers. For this extreme nonadditive system we employ a fundamental measures approach to construct a functional which incorporates the correct dimensional crossover and the exact low density limit. In bulk fluid mixtures the functional yields the same free energy and, therefore, the same gas-liquid (demixing) transition as given by free-volume theory. It generates consistent pair correlation functions; the partial structure factors $S^{ij}(k)$ diverge, as $k \to 0$, at the critical point obtained from the free energy. Our results for the structure agree well with those from simulation and Percus-Yevick theory.

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Much of soft condensed matter science is concerned with simplifying a complex, multicomponent system to its bare bones so that a tractable theoretical model can be devised which will incorporate the essential physical mechanisms determining the properties of the system. Colloidal suspensions provide an excellent example of this strategy. A monodisperse suspension of colloidal particles can often be treated as a one-component fluid since the details of the solvent and colloid-solvent interactions are not of great importance in determining the equilibrium colloid-colloid structure or the phase behavior. In favorable circumstances, these properties are close to those of the hard sphere fluid.

Moving up one degree in complexity, one knows that the addition of nonadsorbing polymer significantly enriches the phase behavior of the colloidal system. For sufficiently large values of the size ratio $R^{\mathrm{g}}/R^{\mathrm{c}}$, where $R^{\mathrm{g}}$ is the radius of gyration of the polymer and $R^{\mathrm{c}}$ is the radius of the colloid, theory predicts stable colloidal gas, liquid, and solid phases with the fugacity of the polymer reservoir playing a role similar to that of inverse temperature for a simple substance. The theoretical [1–3] and simulation studies [3] are based on an idealized model introduced by Asakura and Oosawa (AO) [4] and independently by Vrij [5], which treats the colloids as hard spheres with radius $R^{\mathrm{c}}$ and the polymer coils as interpenetrating, noninteracting particles as regards their mutual interactions. The polymer particles are excluded from the colloids to a center of mass distance $R^{\mathrm{c}} + R^{\mathrm{p}}$, where the polymer radius $R^{\mathrm{p}} = R^{\mathrm{g}}$. This AO model thus describes an extreme nonadditive binary hard sphere mixture. The assumption of ideal polymer is, of course, a gross oversimplification which can be valid only near the theta point. Nevertheless, the main features of the bulk phase behavior arising from this simple model are found in experimental studies [6,7] which confirm the predicted trends of the phase behavior with increasing size ratio $q = R^{\mathrm{p}}/R^{\mathrm{c}}$.

Given the richness of the bulk phase behavior exhibited by the binary AO model it is somewhat surprising that very little attention has been paid to the equilibrium properties of *inhomogeneous* colloid-polymer mixtures described by this model. One might expect the same entropic depletion mechanism [4,5] that leads to an effective attraction between two colloidal particles and that is responsible for bulk gas-liquid separation [1–3] to yield a wide variety of interfacial and adsorption phenomena. However, we are aware of only one systematic treatment of the inhomogeneous AO mixture, that of Ref. [8], where it was shown that for $q < 2/\sqrt{3} - 1 = 0.1547$ one could derive an explicit effective Hamiltonian for the colloids by integrating out the degrees of freedom of the polymer.

The aim of the present Letter is to introduce a density functional theory (DFT) designed specifically for the binary AO model that will treat arbitrary inhomogeneities and size ratios. We are motivated by DFT studies of simple fluids and their mixtures which have provided much insight into a wide range of interfacial phenomena such as surface phase transitions, wetting, and confined fluids [9]. Our approach has its origins in the fundamental measures theory (FMT) of Rosenfeld [10] which has proved, together with its recent extensions and modifications [11–13], very successful for describing the inhomogeneous hard sphere fluid and additive hard sphere mixtures. FMT has also been applied successfully to hard cubes [14], penetrable spheres [15], and has been generalized to soft interactions [16]. The functional we propose here is exact for zero-dimensional situations of extreme confinement and reduces to the functional for pure hard spheres (no polymer) introduced recently by Tarazona [13] in his treatment of freezing. The bulk fluid equation of state which emerges from the theory is the same as that which results from the free-volume approach of Ref. [2]. Thus, our functional yields the same gas-liquid coexistence curve. Moreover, it provides a means of determining the correlation functions of bulk mixtures as well as the density profiles and thermodynamic properties of inhomogeneous systems. Here we outline the theory and focus on its application to the structure of the bulk colloid-polymer mixture. Applications to interfaces and adsorption problems will be given elsewhere. We present results for the partial pair correlation functions $g^{ij}(r)$ from the Ornstein-Zernike (OZ) route and show that these agree well with the results of simulation and the Percus-Yevick (PY) integral equation theory. Our theory provides a consistent treatment of the fluid-fluid transition in that it predicts that all three partial structure factors diverge, as $k \to 0$, at the critical point and on the spinodal given by the bulk mixture equation of state. To the best of our knowledge this is the first nonperturbative DFT (other than that for the somewhat artificial parallel hard cube system [14]) based on purely repulsive interparticle forces which describes directly fluid-fluid separation.

We first define the AO colloid-polymer model. There are $N^{\mathrm{c}}$ colloids with radii $R^{\mathrm{c}}$ and $N^{\mathrm{p}}$ polymers with radii $R^{\mathrm{p}}$ within a volume $V$. The interaction potential between colloids is hard, i.e., $V^{\mathrm{cc}}(r) = \infty$, if $r \leq 2R^{\mathrm{c}}$, and is zero otherwise. The interaction between colloids and polymers is also hard: $V^{\mathrm{cp}}(r) = \infty$, if $r \leq R^{\mathrm{c}} + R^{\mathrm{p}}$, and is zero otherwise, while the interaction between polymers vanishes: $V^{\mathrm{pp}}(r) = 0$. The state of the system is governed by the packing fractions of colloids, $\eta^{\mathrm{c}} = 4\pi N^{\mathrm{c}}(R^{\mathrm{c}})^3/(3V)$, and of polymers $\eta^{\mathrm{p}} = 4\pi N^{\mathrm{p}}(R^{\mathrm{p}})^3/(3V)$, and the size ratio $q = R^{\mathrm{p}}/R^{\mathrm{c}}$. The diameters are denoted by $\sigma^{\mathrm{c}} = 2R^{\mathrm{c}}$ and $\sigma^{\mathrm{p}} = 2R^{\mathrm{p}}$.

In order to derive a density functional for this system, we follow [10] and express the excess (over ideal) Helmholtz free energy as a spatial integral

$$\beta F_{\mathrm{exc}}[\rho^{\mathrm{c}}(\mathbf{r}), \rho^{\mathrm{p}}(\mathbf{r}')] = \int d^3x\, \Phi(\{n_\nu^{\mathrm{c}}(\mathbf{x})\}, \{n_\lambda^{\mathrm{p}}(\mathbf{x})\}), \quad (1)$$

where $\beta = 1/k_{\mathrm{B}}T$. We assume that the (reduced) free energy density $\Phi$ is some *function* of a set of weighted densities $n_\nu^i$, where index $i = \mathrm{c,p}$ labels the species, and $\nu$ is an index corresponding to the type of weighted density. The weighted densities are obtained by convolutions of the actual colloid and polymer densities, $\rho^{\mathrm{c}}(\mathbf{r})$ and $\rho^{\mathrm{p}}(\mathbf{r})$: $n_\nu^i(\mathbf{x}) = \int d^3r\, \rho^i(\mathbf{r}) w_\nu^i(\mathbf{x} - \mathbf{r})$. The weight functions $w_\nu^i(\mathbf{r})$ are independent of the density profiles and are given by

$$w_3^i(\mathbf{r}) = \theta(R^i - r), \qquad w_2^i(\mathbf{r}) = \delta(R^i - r), \quad (2)$$

$$\mathbf{w}_{\mathrm{v2}}^i(\mathbf{r}) = w_2^i(\mathbf{r})\mathbf{r}/r, \qquad \hat{\mathbf{w}}_{\mathrm{m2}}^i(\mathbf{r}) = w_2^i(\mathbf{r})[\mathbf{rr}/r^2 - \hat{\mathbf{1}}/3], \quad (3)$$

where $r = |\mathbf{r}|$, $\theta(r)$ is the step function, $\delta(r)$ is the Dirac distribution, and $\hat{\mathbf{1}}$ is the identity matrix. Further, linearly dependent weights are $w_1^i(\mathbf{r}) = w_2^i(\mathbf{r})/(4\pi R^i)$, $\mathbf{w}_{\mathrm{v1}}^i(\mathbf{r}) = \mathbf{w}_{\mathrm{v2}}^i(\mathbf{r})/(4\pi R^i)$, $w_0^i(\mathbf{r}) = w_1^i(\mathbf{r})/R^i$. The weight functions are quantities with dimension of length$^{3-\nu}$. They differ in their tensorial rank: $w_0^i, w_1^i, w_2^i, w_3^i$ are scalars; $\mathbf{w}_{\mathrm{v1}}^i, \mathbf{w}_{\mathrm{v2}}^i$ are vectors; $\hat{\mathbf{w}}_{\mathrm{m2}}^i$ is a traceless matrix.

It remains to determine the free-energy density $\Phi$. To this end, we consider the zero-dimensional limit, which we define as $\rho^i(\mathbf{r}) = \eta^i \delta(\mathbf{r})$, where $\eta^i$ are the average occupation numbers. These are also the zero-dimensional packing fractions [11,12]. For the present model this limit corresponds to a cavity that can hold at most one colloid but can hold an arbitrary number of polymers if no colloid is present. The grand partition sum reduces to $\Xi = z^{\mathrm{c}} + \exp(z^{\mathrm{p}})$, where $z^i$ is the fugacity of species $i$. Following Ref. [11] we obtain the excess free energy $\beta F_{0\mathrm{D}}(\eta^{\mathrm{c}}, \eta^{\mathrm{p}}) = (1 - \eta^{\mathrm{c}} - \eta^{\mathrm{p}})\ln(1 - \eta^{\mathrm{c}}) + \eta^{\mathrm{c}}$. We now follow recent treatments [12,13] of FMT which consider multicavity limits and express the excess free-energy density as $\Phi = \Phi_1 + \Phi_2 + \Phi_3$, with contributions

$$\Phi_1 = \sum_{i=\mathrm{c,p}} n_0^i \varphi^i(n_3^{\mathrm{c}}, n_3^{\mathrm{p}}), \quad (4)$$

$$\Phi_2 = \sum_{i,j=\mathrm{c,p}} (n_1^i n_2^j - \mathbf{n}_{\mathrm{v1}}^i \cdot \mathbf{n}_{\mathrm{v2}}^j)\varphi^{ij}(n_3^{\mathrm{c}}, n_3^{\mathrm{p}}), \quad (5)$$

$$\Phi_3 = \frac{1}{8\pi} \sum_{i,j,k=\mathrm{c,p}} (n_2^i n_2^j n_2^k/3 - n_2^i \mathbf{n}_{\mathrm{v2}}^j \cdot \mathbf{n}_{\mathrm{v2}}^k + 3[\mathbf{n}_{\mathrm{v2}}^i \hat{\mathbf{n}}_{\mathrm{m2}}^j \mathbf{n}_{\mathrm{v2}}^k - \mathrm{tr}(\hat{\mathbf{n}}_{\mathrm{m2}}^i \hat{\mathbf{n}}_{\mathrm{m2}}^j \hat{\mathbf{n}}_{\mathrm{m2}}^k)]/2) \times \varphi^{ijk}(n_3^{\mathrm{c}}, n_3^{\mathrm{p}}), \quad (6)$$

where tr denotes the trace. Derivatives of the 0D free energy are $\varphi^{i\cdots k}(\eta^{\mathrm{c}}, \eta^{\mathrm{p}}) \equiv \partial^m \beta F_{0\mathrm{D}}(\eta^{\mathrm{c}}, \eta^{\mathrm{p}})/\partial\eta^i \cdots \partial\eta^k$. This completes the prescription for the functional. Further details will be given elsewhere.

We summarize some of the properties of the functional. Note first that $F_{\mathrm{exc}}[\rho^{\mathrm{c}}, \rho^{\mathrm{p}}]$ reduces to the exact low-density limit [10]. This feature results from the properties of the weight functions, Eqs. (2) and (3), which are constructed to restore the correct Mayer functions for the mixture. The next observation is that the functional is *linear* in the polymer density profile. This originates from the linearity of $F_{0\mathrm{D}}$ and is preserved by the construction of $\Phi$, Eqs. (4)–(6), as an equal number of multiplications and differentiations are applied. Three important consequences arise. First, an alternative way of obtaining the functional can be found. We begin by noting that the free-energy functional for a binary hard sphere mixture is constructed by the same procedure as that above (the weight functions $w_\nu^i$ are unchanged) but with $F_{0\mathrm{D}}$ replaced by $F_{0\mathrm{D}}^{\mathrm{bhs}}$, the 0D excess free energy appropriate to a cavity which can contain one particle of species 1 or species 2, but not more particles [17]. If $F_{0\mathrm{D}}^{\mathrm{bhs}}$ is expanded in powers of the occupation of one of the species (which becomes $\eta^{\mathrm{p}}$) and the expansion is truncated at first order in $\eta^{\mathrm{p}}$, $F_{0\mathrm{D}}^{\mathrm{bhs}}$ reduces to $F_{0\mathrm{D}}$. It follows that the present functional can be recovered by an appropriate linearization of the hard sphere mixture functional. This suggests that a colloid-ideal polymer functional can be derived from any (FMT) hard sphere mixture functional, including the original Rosenfeld functional [10], i.e., $\hat{\mathbf{w}}_{\mathrm{m2}}^i = 0$. Further justification for the linearization comes from considering the pair direct correlation functions of the bulk mixture, given by $c_2^{ij}(|\mathbf{r}_1 - \mathbf{r}_2|) = -\beta\delta^2 F_{\mathrm{exc}}[\rho^{\mathrm{c}}, \rho^{\mathrm{p}}]/\delta\rho^i(\mathbf{r}_1)\delta\rho^j(\mathbf{r}_2)$. The $c_2^{ij}$ generated by the functional are consistent with the first two terms in the known low density (diagrammatic) expansion of these functions. Second, by observing that the one-body direct correlation function of the polymers $c_1^{\mathrm{p}}(\mathbf{r}) = -\beta\delta F_{\mathrm{exc}}[\rho^{\mathrm{c}}, \rho^{\mathrm{p}}]/\delta\rho^{\mathrm{p}}(\mathbf{r})$ depends only on the weighted densities of the *colloid* density profile $\rho^{\mathrm{c}}(\mathbf{r})$, it follows from the Euler-Lagrange equation that the inhomogeneous polymer density profile $\rho^{\mathrm{p}}(\mathbf{r})$ is an explicit functional of $\rho^{\mathrm{c}}(\mathbf{r})$ (and of the external potential coupling to the polymers). This feature of the theory constitutes an important simplification for calculations of the equilibrium properties as only $\rho^{\mathrm{c}}(\mathbf{r})$ needs to be determined by numerical minimization. The third consequence of the linearity in $\rho^{\mathrm{p}}(\mathbf{r})$ is that the pair direct correlation function for the polymers vanishes, i.e., $c_2^{\mathrm{pp}} = 0$, as in the PY approximation. As a further remark, we note that our functional generates the correct AO depletion potential between two colloids in a sea of ideal polymer at arbitrary density [18].

We now apply the functional to the determination of some properties of the homogeneous (bulk) mixture. The excess Helmholtz free-energy density is given by $\beta F_{\mathrm{exc}}(\rho^{\mathrm{c}}, \rho^{\mathrm{p}})/V = \beta f_{\mathrm{hs}}(\rho^{\mathrm{c}}) - \rho^{\mathrm{p}} \ln\alpha(\rho^{\mathrm{c}})$, where $f_{\mathrm{hs}}(\rho^{\mathrm{c}})$ is the excess free-energy density of pure hard spheres in the scaled-particle (PY compressibility) approximation and $\alpha = (1 - \eta^{\mathrm{c}})\exp(-A\gamma - B\gamma^2 - C\gamma^3)$, with $\gamma = \eta^{\mathrm{c}}/(1 - \eta^{\mathrm{c}})$, $A = q^3 + 3q^2 + 3q$, $B = 3q^3 + 9q^2/2$, and $C = 3q^3$. This result is *identical* to that of free-volume theory for the AO model [2], which is known to yield stable gas-liquid coexistence for size ratios $q \gtrsim 0.32$. For smaller $q$ this fluid-fluid transition becomes metastable with respect to a broad, in $\eta^{\mathrm{c}}$, fluid-solid transition [2,3]. Within DFT there are two routes to the pair correlation functions $g^{ij}$ of the homogeneous fluid. One is the test-particle route whereby a particle of a given species is fixed at the origin and the one-body density profiles of the resulting inhomogeneous fluid determine the $g^{ij}(r)$.

The other route, which we pursue here, is based on the OZ relations. The pair direct correlation functions obtained by differentiating the functional are given analytically by $c_2^{ij} = \sum_{\nu,\lambda} \psi_{\nu\lambda}^{ij} w_\nu^i * w_\lambda^j$, where $*$ denotes the convolution and $\psi_{\nu\lambda}^{ij} = \partial^2\Phi/\partial n_\nu^i \partial n_\lambda^j$ [19]. The OZ relation then yields the partial structure factors $S^{ij}(k)$ and a numerical Fourier transform gives the $g^{ij}(r)$.

In Fig. 1 we compare our results with those from the PY approximation for a given state point. The structure factors almost coincide, except for $S^{\mathrm{pp}}(k)$ at small $k$. Note that the PY results were obtained numerically [20], as there are no analytical solutions for the AO model. The $g^{ij}(r)$ are also very close to PY. In the case of $g^{\mathrm{cc}}(r)$ the DFT result violates the core condition, i.e., $g^{\mathrm{cc}}(r) \neq 0$ at small $r$, but this is numerically small.

Performing simulations for highly asymmetric mixtures is beset by problems of slow equilibration, as huge numbers of polymers are required per colloidal particle. However, one can map the binary AO model onto an effective one-component system, in which the colloids interact via the AO pairwise depletion potential and for $q < 0.1547$ the mapping is exact [3,20]. This enables $g^{\mathrm{cc}}(r)$ to be obtained by simulation of the one-component system and in Fig. 2 we compare such results [3] with those of our DFT. Although the structure factor $S^{\mathrm{cc}}(k)$ is a little out of phase with the simulation result and the DFT underestimates the very high contact value $g^{\mathrm{cc}}(\sigma^{\mathrm{c}})$, the overall performance is reasonable, given that the effective AO depletion potential is very deep and short ranged for this size ratio. Indeed we expect the binary mixture PY, and other integral equation closures, to exhibit similar failings for such state points

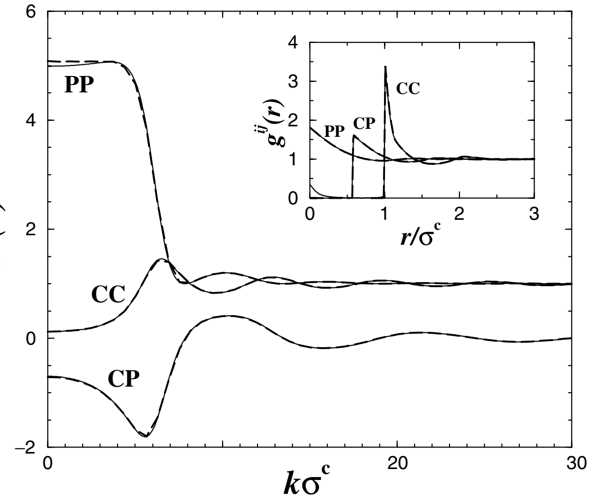

FIG. 1. Partial structure factors $S^{ij}(k)$ at $q = 0.15$, $\eta^{\mathrm{c}} = 0.3$, $\eta^{\mathrm{p}} = 0.05$, for colloid-colloid (CC), colloid-polymer (CP), and polymer-polymer (PP) pairs. Solid lines are DFT; dashed lines are PY results [20]. The inset shows the corresponding partial pair correlation functions $g^{ij}(r)$.

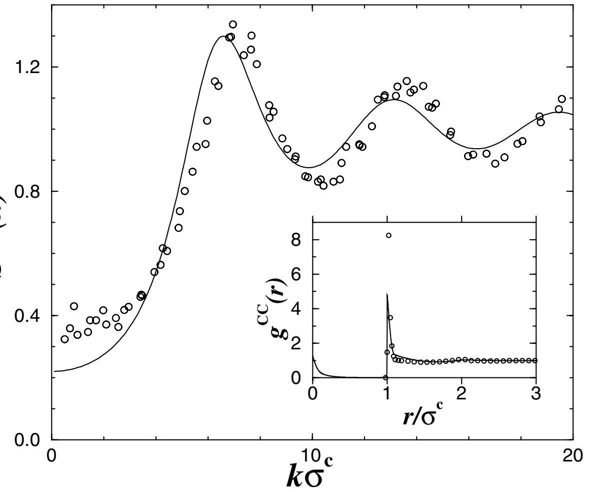

FIG. 2. Colloidal structure factor $S^{\mathrm{cc}}(k)$ for $q = 0.1$, $\eta^{\mathrm{c}} = 0.25$, and $\eta^{\mathrm{p}} = 0.107$. The solid line is the DFT result; symbols are simulation data [3]. The inset shows the corresponding pair correlation function $g^{\mathrm{cc}}(r)$.

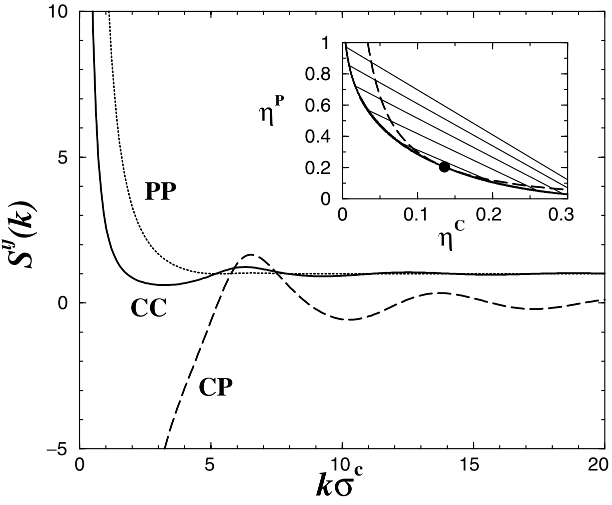

FIG. 3. Partial structure factors $S^{ij}(k)$ at the critical point for $q = 0.8$. The inset is the gas-liquid portion of the phase diagram obtained from DFT plotted in terms of packing fractions $\eta^c$, $\eta^p$. The binodal (thick line), spinodal (dashed line), tielines between coexisting gas and liquid phases (thin lines) and the critical point (dot) are shown.

[21]. It is likely that the test-particle route will improve the accuracy of the $g^{ij}(r)$, albeit at the expense of more numerical work.

The main advantage of the present route to structure is that the free energy of the homogeneous mixture is equivalent to that one would obtain from the compressibility route, i.e., by integrating the $S^{ij}(k = 0)$, calculated as above, with respect to density. For example, this ensures that the thermodynamic and structural routes to the spinodal and critical point are consistent. We illustrate this in Fig. 3 for $q = 0.8$, where gas-liquid coexistence is stable. The inset shows the gas-liquid portion of the phase diagram in the $\eta^c$-$\eta^p$ plane, while the main plot shows the three partial structure factors calculated at the critical point; all three diverge as $k \to 0$ (in particular, $S^{cp} \to -\infty$). For states slightly removed from criticality we expect OZ behavior: $S^{ij}(k) = S^{ij}(0)[1 - \xi^2 k^2 + O(k^4)]$, where $\xi$ is the *common* correlation length. As our $S^{ij}(k)$ are given analytically we can confirm explicitly the OZ behavior. The common correlation length diverges with the mean-field exponent $\nu = 1/2$ and on a path at fixed $\eta^c = \eta^c_{\rm crit}$ we define the amplitude $\xi_0$ via $\xi = \xi_0/(\eta^p_{\rm crit} - \eta^p)^{1/2}$. $\xi_0/\sigma^c$ depends only on the size ratio $q$. It is roughly proportional to the mean diameter and is conveniently expressed as $\xi_0 = \frac{1}{2}(\sigma^c + \sigma^p)/K(q)$, where typical values are $K(q) = 3.00, 2.36, \sqrt{5}$, for $q = 0.4, 0.8, \infty$, respectively.

That our DFT generates very satisfactory pair correlation functions in the bulk mixture provides an excellent indication [9] that it will yield accurate one-body correlation functions for an inhomogeneous AO mixture, e.g., for density profiles at walls or in model pores. Its roots in fundamental measure theory ensure that short-ranged correlations, arising from packing of colloids, are properly incorporated. Since the DFT describes the bulk gas-liquid transition we can employ it for investigations of the "free" interface between the coexisting fluid phases and of depletion induced wetting phenomena at substrates. Moreover, the DFT is well suited for studies of bulk freezing and of "local" freezing of colloid layers at walls [22].

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[18] See the procedure in B. Götzelmann *et al.,* Europhys. Lett. **47**, 398 (1999).
[19] Note that the colloid-polymer functional we obtain from the original Rosenfeld functional (i.e., $\hat{\mathbf{w}}^i_{\rm m2} = 0$) generates identical bulk $c_2^{ij}(r)$ and free-energy density.
[20] M. Dijkstra, R. van Roij, and R. Evans (to be published).
[21] For small densities of colloids we expect that $g^{cc}(r) \propto \exp[-\beta\phi_{\rm eff}(r)]$, where $\phi_{\rm eff}(r)$ is the effective AO pair potential (see Ref. [3]). This is *not* found in our DFT, nor in the PY treatment of the binary AO model. Rather one finds that $g^{cc}(r) \propto -\beta\phi_{\rm eff}(r)$.
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