Density functional for additive mixtures

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We present a density functional theory for mixtures of particles interacting with a radially symmetric pair potential. The approach is suitable for systems with soft or hard interactions between like species. The cross interactions between unlike species are restricted to obey an additivity constraint. The functional is a generalization of the soft fundamental measure theory (SFMT) for one-component systems and reduces to Rosenfeld's functional in the case of hard sphere mixtures. It respects both, the zero-dimensional limit and the virial expansion. The structure of the homogeneous fluid phase is an output. As an application, we calculate the pair distributions of colloidal hard spheres mixed with star polymers and find good agreement with computer simulation results.

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I. INTRODUCTION

One way of proceeding from simple to complex fluids is by increasing the number of different components in a system. Many new physical phenomena arise, like mixing and demixing, depletion effects or freezing into complicated crystalline structures. Hence it is fair to say that mixtures are intriguing systems.

One theoretical tool for studying mixtures is density-functional theory (DFT) [1]. In particular for hard body mixtures powerful approaches are known [2–5]. Recently, a density functional theory for soft interactions was proposed [6]. This soft fundamental measure theory (SFMT) is based on the dimensional crossover from zero to three dimensions, and does not require input from the bulk liquid. Instead, the correlation functions in the homogeneous fluid are an output of the theory. SFMT was applied successfully to structure and freezing of star polymer solutions [7].

Here we demonstrate that the theory can be generalized to mixtures in a straightforward way. The generalization keeps the simplicity of the approach, as well as its desirable features, namely an exact zero-dimensional limit, exact virial expansion up to second order in density and *prediction* of the correlations and thermodynamics of the bulk liquid.

There is, however, an additivity constraint. This means that only the pair interactions between like species can be prescribed. The cross interactions between unlike species are not at our disposal. Nevertheless, these interactions turn out to have a physically reasonable form. For example, for mixtures of hard and soft spheres, a hard core is preserved. As an application we calculate pair distribution functions for a mixture of star polymers and colloids. When compared to simulation results, we find nice agreement.

In Sec. II the SFMT density functional is described; we give its definition Sec. (II A), explain the additivity constraint Sec. (II B), summarize the properties of the functional Sec. (II C), and treat mixtures of hard spheres and soft spheres Sec. (II D) as one special case. As an application we consider star polymers mixed with colloidal particles in Sec. III. We define the theoretical model (Sec. III A), set up the density functional (Sec. III B), and show results for the fluid

structure (Sec. III C). We finish with concluding remarks in Sec. IV.

II. DENSITY FUNCTIONAL THEORY

A. Definition

Consider a system with m components that interact with pair potentials $V^{(ij)}(r)$, and possess density fields $\rho^{(i)}(\mathbf{r})$, $i,j=1,\ldots,m$. The discrete picture of mixtures is adopted; all consideration equally apply to polydisperse systems. The excess free energy functional is expressed as

$$F_{\mathrm{exc}}[\{\rho^{(i)}(\mathbf{r})\}]=k_BT\int d^3x\,\Phi(\{n_\alpha(\mathbf{x})\}). \qquad (1)$$

The density profiles are convolved with weight functions; summation over all species yields weighted densities as

$$n_\alpha(\mathbf{x})=\sum_{i=1}^m\int d^3r\,\rho^{(i)}(\mathbf{r})w_\alpha^{(i)}(\mathbf{x}-\mathbf{r}). \qquad (2)$$

Within the set of weight functions, the following relations hold:

$$w_2^{(i)}(r)=-\frac{\partial}{\partial r}w_3^{(i)}(r), \qquad (3)$$

$$\mathbf{w}_{v2}^{(i)}(\mathbf{r})=w_2^{(i)}(r)\mathbf{r}/r, \qquad (4)$$

$$w_1^{(i)}(r)=w_2^{(i)}(r)/(4\pi r), \qquad (5)$$

$$\mathbf{w}_{v1}^{(i)}(\mathbf{r})=w_1^{(i)}(r)\mathbf{r}/r, \qquad (6)$$

$$w_0^{(i)}(r)=w_1^{(i)}(r)/r, \qquad (7)$$

where $w_\alpha^{(i)}(r),\alpha=0,1,2,3$ are scalar quantities and $\mathbf{w}_{v1}^{(i)}(r),\mathbf{w}_{v2}^{(i)}(r)$ are vectors. The weight functions are quantities with dimension of length scale to the power of $\alpha-3$.

The weight functions for species i are determined so that the Mayer bond $f^{(ii)}(r)=\exp(-V^{ii}(r))-1$ between particles of the same species is obtained. This intraspecies deconvolution is

$$-\tfrac{1}{2}f^{(ii)}(r)=w_0^{(i)}*w_3^{(i)}+w_1^{(i)}*w_2^{(i)}-\mathbf{w}_{v1}^{(i)}*\mathbf{w}_{v2}^{(i)}, \quad (8)$$

where the convolution product, denoted by *, also implies scalar products between vectors.

The free energy density is $\Phi=\Phi_1+\Phi_2+\Phi_3$, with the contributions

$$\Phi_1=-n_0\ln(1-n_3), \quad (9)$$

$$\Phi_2=\frac{n_1n_2-\mathbf{n}_{v1}\cdot\mathbf{n}_{v2}}{1-n_3}, \quad (10)$$

$$\Phi_3=\frac{(n_2)^3(1-(\mathbf{n}_{v2}/n_2)^2)^3}{24\pi(1-n_3)^2}. \quad (11)$$

We note that recently, more sophisticated versions of Φ_3 using tensorial weights have been successfully used [7,8].

B. Cross interactions

Once the weight functions $w_\alpha^{(i)}$ are calculated by solving the deconvolution equation (8), the interactions between unlike species are restricted to obey

$$-f^{(ij)}(r)=w_0^{(i)}*w_3^{(j)}+w_1^{(i)}*w_2^{(j)}-\mathbf{w}_{v1}^{(i)}*\mathbf{w}_{v2}^{(j)}+w_0^{(j)}*w_3^{(i)}$$
$$+w_1^{(j)}*w_2^{(i)}-\mathbf{w}_{v1}^{(j)}*\mathbf{w}_{v2}^{(i)}. \quad (12)$$

Loosely speaking, the cross interactions are a combination of the intraspecies interactions. This behavior is also present in the hard sphere FMT [2], that is primarily a theory for additive mixtures of hard spheres.

C. Properties

We show that the functional is exact in the zero-dimensional limit and gives the virial expansion up to second order correctly.

The zero-dimensional limit for a mixture is defined by density distributions $\rho^{(i)}(\mathbf{r})=\eta^{(i)}\delta(\mathbf{r})$, where $\eta^{(i)}$ is the average occupation number of species i. We assume that all pair interactions diverge at the origin. Then the delta-spike can be occupied by at most one single particle. The excess free energy is $F_{0d}=(1-\eta)\ln(1-\eta)+\eta$, where $\eta=\sum_{i=1}^m\eta^{(i)}$ is the total number of particles. In the following we show that the functional gives F_{0d} exactly. We observe that Φ_2 and Φ_3 vanish, because $|\mathbf{n}_{v2}|=n_2$, and $|\mathbf{n}_{v1}|=n_1$, and the antisymmetry upon exchanging scalar and vectorial densities.

We still have to evaluate the remaining Φ_1 contribution

$$F[\{\eta^{(i)}\delta(\mathbf{r})\}]=-\int_0^\infty dr\,4\pi r^2\,n_0(r)\ln[1-n_3(r)], \quad (13)$$

$$n_\alpha(r)=\sum_{i=1}^m\eta^{(i)}w_\alpha^{(i)}(r). \quad (14)$$

From the hierarchy of weight functions, Eqs. (3)–(7), we obtain the relation

$$w_0^{(i)}(r)=-(4\pi r^2)^{-1}\partial w_3^{(i)}(r)/\partial r. \quad (15)$$

Integrating and using the boundary conditions $w_3^{(i)}(0)=1$, $w_3^{(i)}(\infty)=0$ yields the 0d excess free energy F_{0d}.

The correct virial expansion can be checked by Taylor expanding for low densities $\Phi\to n_0n_3+n_1n_2-\mathbf{n}_{v1}\cdot\mathbf{n}_{v2}$, and using the deconvolution equations (8) and (12).

We finally note that in the case of hard spheres, Rosenfeld's functional is recovered.

D. Hard and soft spheres

As an important case we consider the cross interaction between a hard sphere i with radius $R^{(i)}$ and a soft sphere j for which the functional is valid. Deconvolution of the step function yields the well-known hard sphere weights [2] (also given in Sec. III B)

From Eq. (12) we obtain the cross-Mayer function with the particularly simple form

$$-f^{(ij)}=\begin{cases}1 & \text{if } r<R^{(i)} \\ w_3^{(j)}(r-R^{(i)}) & \text{else.}\end{cases} \quad (16)$$

We observe that the hard core with radius R is preserved, and that the interaction outside the core is given by a shifted $w_3^{(j)}(r)$ function.

III. STAR POLYMERS AND COLLOIDS

The star polymer system has attracted considerable recent interest [9–16]. In this work we investigate a mixture of star polymers and colloidal hard spheres.

A. The model

We consider N^c colloids with radii R^c and N^s star polymers with radii R^s within a volume V. The interaction potential between colloids is hard,

$$V^{(cc)}(r)=\begin{cases}\infty & \text{if } r\leq 2R^c \\ 0 & \text{else.}\end{cases} \quad (17)$$

The interaction between the star polymers is logarithmic

$$\beta V^{(ss)}(r)=\begin{cases}-2q\ln(r/R^s)+\ln\binom{2q}{q} & 0\leq r<R^s \\ \phi_q(r)+\ln\binom{2q}{q} & R^s\leq r<2R^s \\ 0 & 2R^s\leq r,\end{cases} \quad (18)$$

where $\binom{2q}{q}$ is the binomial coefficient. The crossover function between small and large distances is given by $\phi_q(r)=-\ln[(1+\xi)^{2q}-\xi^{q+1}B_{q2}F_1(1,1-q;2+q;-\xi)]$, where $\xi=(r/R^s)-1$, $B_q=2\Gamma(1+2q)\Gamma^{-1}(q)\Gamma^{-1}(2+q)$, and $_2F_1$ is the hypergeometric function (see Ref. [7] for a discussion).

The interaction between colloids and polymers is assumed to have a hard core due to the excluded volume induced by a colloid and an additional logarithmic repulsion

$$V^{(cs)}(r) = \begin{cases} \infty & \text{if } r \leqslant R^c \\ -q \ln\left(\dfrac{r-R^c}{R^s}\right) & \text{if } R^c < r \leqslant R^c + R^s \quad (19) \\ 0 & \text{else.} \end{cases}$$

This form is similar to the result from a microscopic analysis of the interactions between star polymers and hard spheres [17].

The system is governed by the packing fractions of colloids, $\eta^c = 4\pi N^c (R^c)^3/(3V)$, and of polymers $\eta^s = 4\pi N^s (R^s)^3/(3V)$, and the size ratio $a = R^s/R^c$.

B. The weights functions

The set of weight functions for the colloids is identical to the pure hard sphere case and is given by

$$w_3^{(c)}(\mathbf{r}) = \theta(R^c - r), \qquad (20)$$

$$w_2^{(c)}(\mathbf{r}) = \delta(R^c - r), \qquad (21)$$

$$w_1^{(c)}(\mathbf{r}) = \delta(R^c - r)/(4\pi r), \qquad (22)$$

$$w_0^{(c)}(\mathbf{r}) = \delta(R^c - r)/(4\pi r^2), \qquad (23)$$

$$\mathbf{w}_{v2}^{(c)}(\mathbf{r}) = \delta(R^c - r)\mathbf{r}/r, \qquad (24)$$

$$\mathbf{w}_{v1}^{(c)}(\mathbf{r}) = \delta(R^c - r)\mathbf{r}/(4\pi r^2), \qquad (25)$$

where $r = |\mathbf{r}|$, and $\Theta(r)$ is the Heaviside step function, $\delta(r)$ denotes the Dirac delta function.

The weight functions for the star polymers are

$$w_3^{(s)}(\mathbf{r}) = [1 - (r/R^s)^q]\theta(R^s - r), \qquad (26)$$

$$w_2^{(s)}(\mathbf{r}) = q r^{q-1}(R^s)^{-q}\theta(R^s - r), \qquad (27)$$

$$w_1^{(s)}(\mathbf{r}) = q r^{q-2}(R^s)^{-q}(4\pi)^{-1}\theta(R^s - r), \qquad (28)$$

$$w_0^{(s)}(\mathbf{r}) = q r^{q-3}(R^s)^{-q}(4\pi)^{-1}\theta(R^s - r), \qquad (29)$$

$$\mathbf{w}_{v2}^{(s)}(\mathbf{r}) = q r^{q-1}(R^s)^{-q}\theta(R^s - r)\mathbf{r}/r, \qquad (30)$$

$$\mathbf{w}_{v1}^{(s)}(\mathbf{r}) = q r^{q-2}(R^s)^{-q}(4\pi)^{-1}\theta(R^s - r)\mathbf{r}/r. \qquad (31)$$

These are the same as for the one-component case considered in Refs. [6,7].

C. Results

In order to calculate the partial pair correlation functions we do not make use of the test-particle limit. Instead, the partial direct correlation functions are calculated from the density functional via $c_{ij}(r) = -(k_B T)^{-1}\delta^2 F^{\text{exc}}/(\delta\rho^{(i)}\delta\rho^{(j)})$. Using the Ornstein–Zernike relation gives the partial structure factors in reciprocal space [18] and a Fourier transform yields the pair correlations. We adopt this method, because no density profile equation is solved. This is a severe test for the quality of the density functional. To compare the results, we have carried out standard canonical Monte Carlo computer simulations.
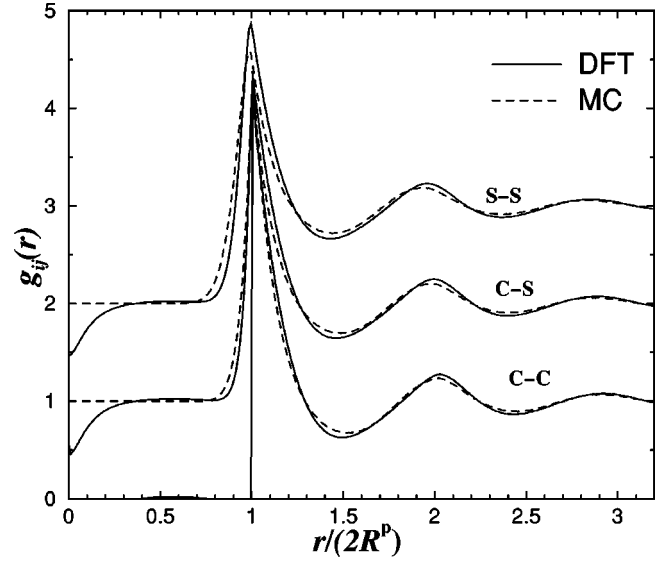

FIG. 1. Pair correlation functions $g^{cc}(r)$, $g^{cs}(r)$, and $g^{ss}(r)$ for a mixture of hard spheres and star polymers as a function of the scaled distance $r/(2R^s)$ at packing fractions $\eta^c = 0.25, \eta^s = 0.25$, and size ratio $a = 1$. Full lines are DFT, dashed lines are simulation results. The curves are shifted upwards one unit for reasons of clarity.

We investigate the partial pair distribution functions between pairs of colloids $g^{cc}(r)$, pairs of stars $g^{ss}(r)$ and between a colloid and a star polymer, $g^{cs}(r)$ for the intermediate softness $q = 12$, and for equal number densities of colloids and stars, hence $\eta^c a^3/\eta^s = 1$. In Figs. 1, 2, and 3 results for the size ratios $a = 1, 0.5, 2$ are given, respectively. The general agreement is good. Phase and amplitude are correct. However, the DFT peaks are slightly to steep. The worst case is $g^{ss}(r)$, $a = 2$, Fig. 3, Also small spurious values inside the core appear, especially for the cross correlations $g^{cs}(r)$. Using the test-particle limit, one could get rid of these values.
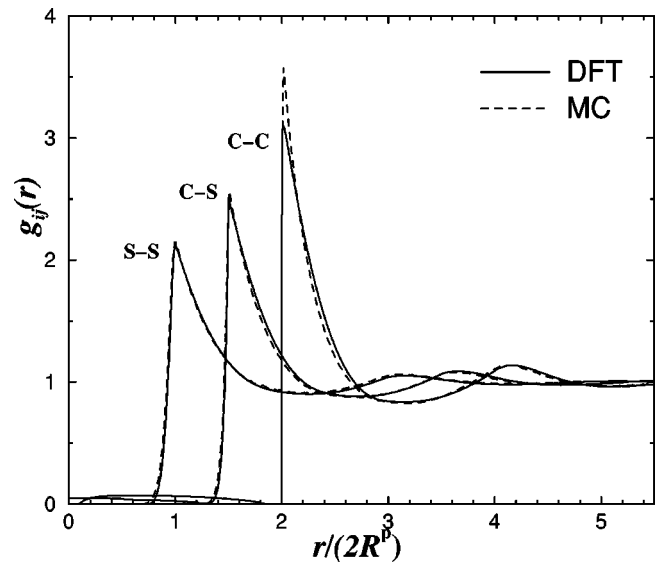

FIG. 2. Same as Fig.1, but at densities $\eta^c = 0.35$, $\eta^s = 0.04375$, and size ratio $a = 0.5$, corresponding to small stars.
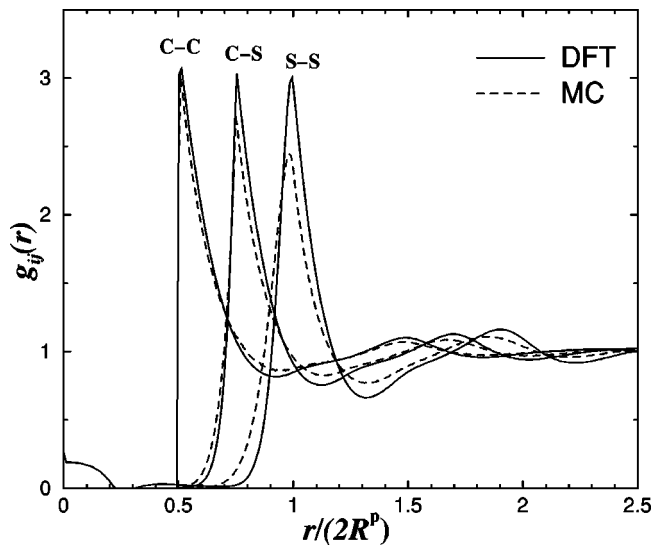
FIG. 3. Same as Fig. 1, but at densities $\eta^c = 0.0625$, $\eta^s = 0.5$, and size ratio $a = 2$, corresponding to large stars.

IV. CONCLUSIONS

We have shown that the soft fundamental measure theory can be formulated for multi-component mixtures. The properties of the theory are preserved in comparison to the one-component case. In particular, the virial expansion and the zero-dimensional limit for the mixture are exact.

The current theory can only be applied to a limited class of systems, that we call additive. This constraint enforces the cross interactions to be a combination of the interactions between the like species. However, for mixtures of soft and hard spheres the cross interaction was shown to be meaningful, because a hard core is preserved.

As an application, we have investigated the fluid structure of a mixture of colloidal hard spheres and star polymers. When compared to simulation results, we find a remarkable agreement.

It is intriguing that the fluid structure of a multicomponent system can be understood on the basis of two simple ingredients: First, particles cannot sit on top of each other. Second, the Mayer f-bond governs the behavior at low densities.

As possible future applications we mention the investigation of depletion potentials that has attracted considerable recent interest [19–22] in the context of hard sphere mixtures. The current functional offers the possibility to study the effects of soft interactions essentially with the same theoretical tools as developed in Ref. [19].

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