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Density functional for the Widom-Rowlinson model

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We present a density functional theory for the *m*-component Widom-Rowlinson model, for a mixture of spherical particles where the unlike species interact with a hard-core potential and the interactions between like species vanish. The functional is exact for small densities and in the zero-dimensional limit. It predicts the fluid structure in good agreement with simulations and yields a continuous demixing phase transition for $m=2$. In the limit of large *m* the Widom-Rowlinson model reduces to effective hard spheres in the mixed phase and the Asakura-Oosawa (colloid-ideal polymer) model in the demixed phase. Within the present theory, both cases are captured correctly. For intermediate *m* we find a first order demixing phase transition, with a rapidly broadening density discontinuity upon increasing *m*.

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Whether two or more fluids are miscible is often an important question, e.g., in engineering, physical chemistry, or food science. From a physical point of view, many multicomponent fluids will be in a single phase because of a gain in mixing entropy. Changing the thermodynamical variables then may lead to demixing. There are (at least) two basic mechanisms that explain the phase separation. One is the depletion interaction, where the presence of one of the components generates an effective attraction between particles of the other component(s). The effective attraction accounts for the phase separation via the common entropy-versus-energy mechanism as is present in the gas-liquid transition of simple liquids, say the Lennard-Jones system. The second mechanism for demixing lies in the relative strengths of repulsion between like and unlike particles. If the unlike particles experience a stronger repulsion than the like ones, demixed phases are favored, at least at high density. The prototype for this behavior is the Widom-Rowlinson (WR) model [1–4]. There the interaction between *m* species is such that particles of the same species do not interact; that is, are assumed to be ideal, whereas the unlike species interact with a hard core potential. It is clear that for high densities a mixed phase will suffer from strong packing effects, which are greatly reduced in a demixed phase with a single majority component. At low density the system reaches ideal gas behavior, which, of course, will cause a mixed phase. The intervening phase transition has been studied with a range of approaches, including mean-field theory (MFT) [4], Percus-Yevick (PY) integral equation theory [3,5], scaled-particle theory (SPT) [6], as well as computer simulations [5,7,8].

Essentially all theories give a demixing phase diagram for $m=2$ with a lower critical point (as a function of total density) and a rapidly broadening coexistence region upon increasing density. The precise location of the critical point was a matter of discussion since the introduction of the model, and it is remarkable that only recently two independent simulations located it about 50% higher than previously thought [5,7].

Obviously, the WR model does not possess a solid phase for $m=2$, as any possible solid is preempted by demixing. It has been found, however, that for large number of components $m>31$, a crystal becomes stable for parallel hypercubes [9]. This is a *mixed* phase, as only repulsion is present, which is the essential ingredient for freezing. Apart from this and the study of the free interface between demixed fluid phases [4,10], little is known about inhomogeneous situations. To study those, density-functional theory (DFT) [11] can be an important tool. It accounts for spatially varying density profiles, and, in its sophisticated versions, for the structure at the two- and higher-body level. To our knowledge the WR model has so far resisted any DFT treatment that goes beyond the MFT of Ref. [4].

In this work, we propose an approximation for the density functional of the *m*-component WR model. It is a fundamental-measure theory (FMT), an approximation scheme pioneered by Rosenfeld for hard spheres [12–14], and also applied to hard parallel cubes [15,16], penetrable spheres [17,18], as well as to the Asakura-Oosawa (AO) model [19].

The pair correlations *derived* from the functional are found to be in good agreement with simulation results. The $m=2$ phase diagram is comparable in quality to other theories. For $m\geqslant 3$, we find a first-order fluid demixing phase transition, with an increasingly large coexistence interval (in density) upon increasing *m*. We expect for $m\rightarrow\infty$ hard sphere behavior in the mixed phase and AO [20] behavior in the demixed phase (with the majority component identified as ideal polymer). Indeed we find that the functional reduces to the corresponding DFTs (Refs. [12,14], and [19], respectively) for these systems.

Let us define the WR model as an *m*-component mixture of spherical particles with radii R_i, and particle numbers N_i in a volume *V*. The interaction pair potentials $\phi_{ij}(r)$ between particles of species $i=1,\ldots,N_i$ and $j=1,\ldots,N_j$ are $\phi_{ii}(r)=0$; and $\phi_{ij}(r)=\infty$, if $r<R_i+R_j$, $i\neq j$, and zero else [21]. As reduced densities we use the packing fractions of each species *i*, given as $\eta_i=4\pi N_i R_i^3/(3V)$, and define the total packing fraction as $\eta=\sum_{i=1}^{m}\eta_i$.

Let us give an overview of our DFT. It is a weighted density approximation. This means that in order to smooth the possibly highly inhomogeneous density fields, convolutions with weight functions are performed. Here, the weight functions describe the shape and geometrical properties of

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the particles and are explicitly given. In particular, there is a set of weight functions (and correspondingly weighted densities) for each of the species. The transcription of the weighted densities to the excess (over ideal gas) free energy is done, as usual, via a free energy *density*. Here this is an ordinary function (not a functional) of the weighted densities and is, again, explicitly known (up to a simple numerical root finding problem). Finally the total excess free energy of the inhomogeneous system is obtained as a spatial integral over the free energy density.

In detail, we express the excess Helmholtz free energy as

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

where T is the absolute temperature, and k_B is Boltzmann's constant. The reduced free energy density Φ is a yet to be determined function of a set of weighted densities $\{n_\alpha^{(i)}(\mathbf{x})\}$, where i labels the species and α the type of weighted density. The weighted densities are obtained by convolutions

$$n_\alpha^{(i)}(\mathbf{x})=\int d^3r\,\rho_i(\mathbf{r})\,w_\alpha^{(i)}(\mathbf{x}-\mathbf{r}). \tag{2}$$

As all nonvanishing interactions are hard-core, it is sufficient to take the usual FMT weight functions [12,14]

$$w_3^{(i)}(\mathbf{r})=\theta(R_i-r),\quad w_2^{(i)}(\mathbf{r})=\delta(R_i-r), \tag{3}$$

$$\mathbf{w}_{\mathrm{v}2}^{(i)}(\mathbf{r})=w_2^{(i)}(\mathbf{r})\,\mathbf{r}/r,\quad \hat{\mathbf{w}}_{\mathrm{m}2}^{(i)}(\mathbf{r})=w_2^{(i)}(\mathbf{r})\left[\frac{\mathbf{rr}}{r^2}-\hat{\mathbf{1}}/3\right], \tag{4}$$

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

We determine the functional dependence of Φ on the weighted densities by imposing the exact crossover to zero dimensions (0D). This situation is modeled by $\rho_i(\mathbf{r})=\eta_i\delta(\mathbf{r})$, where the packing fractions η_i describe the average occupation numbers of particles i in a cavity of radius R_i [13]. The exact grand partition sum for the WR model in this situation is

$$\Xi=1-m+\sum_{i=1}^m \exp(z_i), \tag{5}$$

where z_i is the fugacity of species i. Inverting the thermodynamical relation $\eta_i=z_i\partial\ln\Xi/\partial z_i$, we obtain the excess chemical potentials $\mu_{0\mathrm{d},i}=k_BT\ln(z_i/\eta_i)$ as a function of the set of η_i. Integrating with respect to density yields the 0D excess free energy $F_{0D}(\{\eta_i\})$. We follow recent treatments of FMT [14] by considering multicavity limits to obtain $\Phi=\Phi_1+\Phi_2+\Phi_3$, with the contributions

$$\Phi_1=\sum_{i=1}^m n_0^{(i)}\,\varphi_i(\{n_3^{(l)}\}), \tag{6}$$

$$\Phi_2=\sum_{i,j=1}^m (n_1^{(i)}n_2^{(j)}-\mathbf{n}_{\mathrm{v}1}^{(i)}\cdot\mathbf{n}_{\mathrm{v}2}^{(j)})\,\varphi_{ij}(\{n_3^{(l)}\}), \tag{7}$$

$$\Phi_3=\frac{1}{8\pi}\sum_{i,j,k=1}^m (n_2^{(i)}n_2^{(j)}n_2^{(k)}/3-n_2^{(i)}\,\mathbf{n}_{\mathrm{v}2}^{(j)}\cdot\mathbf{n}_{\mathrm{v}2}^{(k)} + 3[\mathbf{n}_{\mathrm{v}2}^{(i)}\hat{\mathbf{m}}_{m2}^{(j)}\mathbf{n}_{\mathrm{v}2}^{(k)}-\mathrm{tr}(\hat{\mathbf{n}}_{m2}^{(i)}\hat{\mathbf{n}}_{m2}^{(j)}\hat{\mathbf{n}}_{m2}^{(k)})]/2)\,\varphi_{ijk}(\{n_3^{(l)}\}), \tag{8}$$

where tr denotes the trace. Derivatives of the 0D free energy are $\varphi_{i,\ldots,k}(\{\eta_l\})\equiv\partial^m\beta F_{0\mathrm{d}}(\{\eta_l\})/\partial\eta_i\ldots\partial\eta_k$, where $\beta=1/k_BT$. This completes the prescription for the functional. Note that the weight functions $w_\alpha^{(i)}$ are constructed to recover the Mayer bond for low densities as well as to gain control over the 0D limit. The thermodynamical input into the DFT solely stems from the 0D statistics, Eq. (5).

Let us investigate some of the properties of the functional. First, the thermodynamics and structural correlations of homogeneous phases, $\rho_i=\mathrm{const}$, are an output of the theory. In this case the weighted densities, Eq. (2), are obtained as $n_3^{(i)}=\eta_i$, $n_2^{(i)}=3\eta_i/R_i$, $n_1^{(i)}=3\eta_i/(4\pi R_i^2)$, $n_0^{(i)}=3\eta_i/(4\pi R_i^3)$. The nonscalar contributions vanish, $\mathbf{n}_{\mathrm{v}1}^{(i)}=\mathbf{n}_{\mathrm{v}2}^{(i)}=\hat{\mathbf{n}}_{\mathrm{m}2}^{(i)}=0$. Inserting this into Eqs. (6)–(8) gives the bulk free energy. Furthermore, the (bulk) direct correlation functions can obtained as $c_{ij}(r)=\Sigma_{\alpha\gamma}\partial^2\Phi/(\partial n_\alpha^{(i)}\partial n_\gamma^{(j)})\ w_\alpha^{(i)}*w_\gamma^{(j)}$, where * denotes the convolution.

Second, the excess free energy density Φ can be calculated analytically in the case of equal (inhomogeneous) density profiles, $\rho_i(\mathbf{r})=\rho_j(\mathbf{r})$. This is valid for equal sizes, $R_i=R_j$, equal chemical potentials, $\mu_i=\mu_j$, and equal external potentials acting on species i and j. Furthermore the system is assumed to be in a mixed phase. Then an effective one-component functional of the total density $\rho(\mathbf{r})=m\rho_i(\mathbf{r})$ is obtained. The weighted densities are $n_\alpha^{(\mathrm{total})}=mn_\alpha^{(i)}$, and the expressions for the free energy density are $\partial\beta F_{0D}/\partial\eta=\ln[m-(m\,w/\eta)]$, $\partial^2\beta F_{0D}/\partial\eta^2=w/(\eta-w\ \eta)$, $\partial^3\beta F_{0\mathrm{d}}/\partial\eta^3=w\,[(w-2)\,w+\eta]/[(w-1)^3\ \eta^2]$, with $w=W[\eta e^{-\eta}(1-m^{-1})]$, where $W(z)$ is product log function, i.e., the solution of $z=W\exp(W)$. In general, however, the above assumptions do not hold, and $\rho_i(\mathbf{r})\neq\rho_j(\mathbf{r})$. Then the $\mu_{0D,i}$ (and F_{0D}) need to be found numerically.

Third, for large number of components, $m\rightarrow\infty$, and fixed total density η, we consider two cases where the WR model reduces to (simpler) effective one- or two-component systems, if the partial densities (or chemical potentials) are chosen appropriately. For equal partial densities $\eta_i=\eta_j$, we expect hard sphere behavior, because each component is at vanishing concentration, so that the ideality between like species is negligible, and only the hard cores between unlike species remain. The 0D statistics [Eq. (5)] takes care of this fact and we recover $\beta F_{0d}=(1-\eta)\ln(1-\eta)+\eta$, which is characteristic of a cavity that can hold at most a single particle [13] (of any species i). Hence, the hard sphere FMT

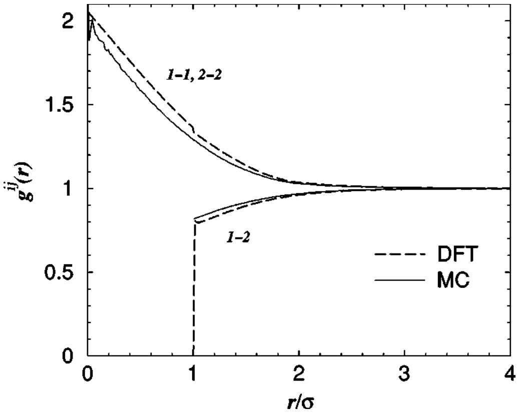

FIG. 1. Pair distribution functions $g_{ij}(r)$ for the $m=2$ component WR model as obtained by density-functional theory (DFT) compared to Monte Carlo simulation (MC) for $\eta_1=\eta_2=0.1$. The symmetric, $i=j$, and asymmetric cases, $i\neq j$, are shown.

[12,14] is obtained. Next we consider the case that one of the components has a large density $\eta_1 \gg \eta_j, j>1$, and the others are at vanishing density $\eta_j \to 0$, so that $\eta^*=\Sigma_{i=2}^{m}\eta_i=\text{const}$. Then we expect ideal particles ($i=1$) with density η_1 mixed with effective one component hard spheres (all $i>1$) at density η^*. This is precisely the behavior of the AO colloid ideal-polymer mixture [20]. Indeed, the WR 0D free energy reduces to $\beta F_{0D}=(1-\eta^*-\eta_1)\ln(1-\eta^*)+\eta^*$, which describes AO behavior, and the recently found DFT [19] for this model is recovered. The correct reduction of the WR functional in both limits demonstrates the internal consistency of constructing DFTs from the 0D limit of the underlying model [22].

Let us turn to the results. As a first test for the ability of the DFT to describe the WR model, we investigate the structural correlations in the bulk fluid with $m=2$ components. To that end, we calculate the pair correlation functions $g_{ij}(r)$ from the direct correlation functions $c_{ij}(r)$ using the Ornstein-Zernike relation. In order to compare these results, we have carried out a canonical Monte Carlo simulation with 512 particles and 10^5 moves per particle. In Fig. 1 we compare both results. One observes that the clustering of like species, as well as the depletion zone of unlike species near contact are reproduced nicely by the DFT. The DFT, however, generally overestimates the correlations and a tiny artificial jump in $g_{ii}(r=\sigma)$ appears, as well as negative values of about -0.2 in the core region, $r<\sigma$. The overall agreement is fair, given that following the OZ route is a severe test for the functional. In accordance with integral equations [5] the pair correlation functions do not exhibit oscillations, not at short nor at long range. The latter behavior may be examined by an analysis of the poles of the structure factor in the complex plane [23]. Here this is technically simple, as the dependence on wave vector is analytically given. It turns out that the leading contribution always comes from the pole with vanishing real part, hence purely monotonic asymptotic decay results.

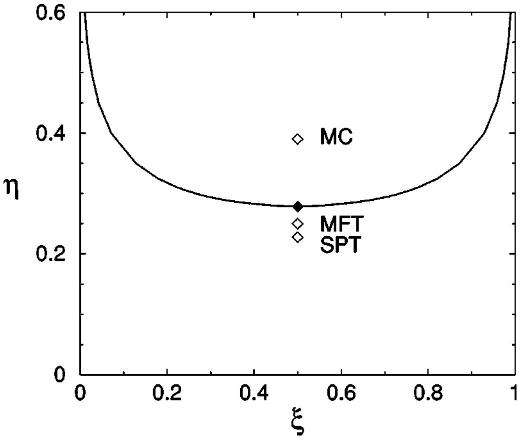

FIG. 2. Phase diagram of the $m=2$ component WR model as a function of relative concentration ξ and total density η as obtained by DFT. The critical points from various approaches are indicated by symbols: Monte Carlo (MC), mean-field theory (MFT), and scaled-particle theory (SPT).

The phase diagram for $m=2$ is depicted in Fig. 2 as a function of the total density η and the relative concentration $\xi=\eta_1/\eta$. For small η a mixed fluid is stable. Above the critical point at $\eta_{\text{crit}}=0.278$ (and $\xi=1/2$ due to symmetry [3]) demixing happens. Upon increasing the density the coexistence interval rapidly broadens. The critical density is slightly higher than the results from mean-field ($\eta_{\text{crit}}=0.25$) and scaled-particle ($\eta_{\text{crit}}=0.228$) theories. However, the simulation values of Ref. [5] is $\eta_{\text{crit}}=0.3990$, and of Ref. [7] $\eta_{\text{crit}}=0.3919$ (obtained from a linear fit to the data from finite systems) are still significantly higher, and to the best of our knowledge, no theory can account for this value. As concerns integral equations [5], Percus-Yevick (PY) theory gives $\eta_{\text{crit}}=0.30$ (see Fig. 4 in Ref. [5]) from the virial route. This is slightly better than the current approach. The compressibility route, however, gives a value of about 0.55. It was found that self-consistent closures, like Rogers-Young, do not improve much over this result [5]. We note that as the present approach performs the approximation on the level of the free energy functional, thermodynamics and structure are consistent, i.e., the structure factors $S_{ij}(k)$ diverge for $k\to 0$ at the critical point obtained from the free energy.

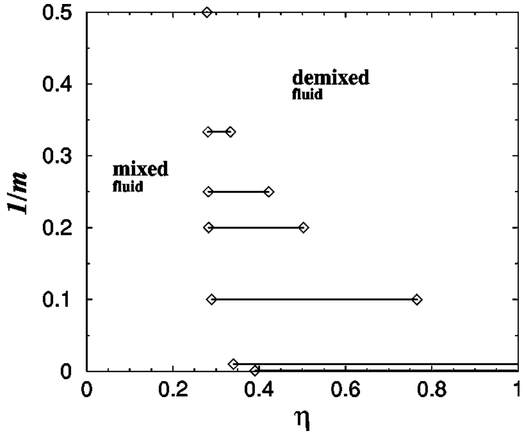

FIG. 3. Phase diagram of the WR model at equal concentrations $\eta_i=\eta_j$ as a function of total density η and inverse number of components $1/m$.

For larger number of components [9], $m>2$, a rich variety of phase transitions is expected, e.g., for $m=3$ tricritical points were found from a mean-field treatment [2]. Here we restrict ourself to the equimolar case, and calculate the phase transition between the mixed phase and m demixed phases; see Fig. 3. In accordance with previous findings the transitions are first order. The coexistence interval in density rapidly broadens upon increasing η. Numerically, the mean-field result [2] for $m=3$ is $\eta=0.3146-0.4789$, whereas the current theory gives lower values of $\eta=0.2815-0.3333$, and the simulation value of a density within the coexistence region [7] is 0.4162.

In view of the successful treatment of the bulk properties, especially the internal consistency, we are confident for future applications to inhomogeneous situations. A preliminary investigation has shown that the DFT accounts for a crystalline phase for large m, with multiply occupied lattice sites. Future investigations may treat the interface between demixed phases, and compare to the MFT results for $m=2$ [4] and $m=3$ [10], as well as adsorption at walls or in pores. Furthermore, whether the current approach can be extended to treat the morphological model [24] constitutes an interesting aspect.

On more general grounds, we conclude that fundamental measures can be used successfully to construct DFTs. The first such theory was Rosenfeld's hard sphere functional [12,14], which is by now well established and has been used for over one decade. Only recently, other models could be treated in a similar manner, namely, penetrable spheres [17] and the Asakura-Oosawa model [19]. The present study adds another member to the family. How large this family can actually become, still is an open question.

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