

An Integral Equation Theory for the Widom–Rowlinson Mixture

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The Widom–Rowlinson mixture is a two-component fluid in which like species do not interact and unlike species interact via a hard-core repulsion. As the density is increased, this fluid phase separates. Standard integral equation approaches, such as the Percus–Yevick or hypernetted chain, or thermodynamically self-consistent hybrids of these two, make very inaccurate predictions for the location of this critical point in the three-dimensional model. In this article we suggest a family of new approximations for this model that rely on incorporating terms in the density expansion of the direct correlation function into the closure approximation. We show that the simplest of these closures is significantly more accurate than previous theories for the structure and thermodynamics of the fluid.

KEY WORDS: Widom–Rowlinson; model; phase transition; diagrams; integral equations; nonadditive hard sphere.

I. INTRODUCTION

The Widom–Rowlinson (WR) mixture⁽¹⁾ is a simple two component (A and B) mixture where the interaction potentials are $u_{AA} = u_{BB} = 0$, and $u_{AB}(r) = \infty$ for $r < \sigma$ and $u_{AB}(r) = 0$ for $r > \sigma$. In three dimensions, and at high densities, this fluid phase separates into an A rich and a B rich phase. Since this model is athermal, the fluid separation, which is associated with a critical point, is a purely entropic effect.

In the late 1970's one of us (GS) became interested in applying the revised Enskog theory (RET) to the WR model, as part of a transport theory study he was doing with John Karkheck⁽²⁾. The RET requires

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accurate equations of state as input, for which Karkheck and Stell could find no simulation results against which to test the thermodynamic approximations then available for the WR model. Sometime thereafter C. Hoheisel volunteered to obtain some molecular dynamic simulation results to fill the gap, using a model in which the hard-core was replaced by a smooth and steep repulsion, and subsequently he published the results⁽³⁾. (To his surprise and chagrin, GS found that he had been listed as a co-author of this paper⁽³⁾, and other publications⁽⁴⁾, which he had not even been aware had been submitted for publication.)

The relative simplicity of the interactions in the WR model make it an attractive one to use for the study of critical phenomena, and this has generated considerable interest in the model⁽⁵⁻⁹⁾, as well as in a Gaussian f -function version⁽¹⁰⁻¹²⁾ and a lattice gas version⁽¹³⁻¹⁵⁾. Despite its apparent simplicity, however, definitive results on the location and universality class of the WR critical point were lacking until quite recently. Because the interactions are short ranged with a simple binary symmetry, one would expect the WR model to be Ising-like. However, the initial series analysis of the Gaussian f -function version were disturbingly inconclusive^(10, 11). The Monte Carlo study of the lattice version of the WR model using finite-size scaling analysis by Dickman and Stell⁽¹⁴⁾ yielded the first compelling evidence for Ising-like behaviour in such models. Recent series expansion analyses of the Gaussian f -function version of the model⁽¹²⁾ are also consistent with Ising behaviour, and explain the source of ambiguities in the earlier series analyses.

The first computer simulations that established the critical behaviour of the continuum version of the model were performed by Shew and Yethiraj (SY)⁽⁸⁾ who obtained a critical density of $\rho_c \sigma^3 = 0.76 \pm 0.02$. (More recent simulations⁽⁹⁾ using a different computer simulation algorithm are in excellent agreement with this estimate.) This value for the critical density was in strong disagreement with the estimate found in Borgelt *et al.*⁽³⁾ for which a critical density $\rho_c \sigma^3 = 0.41$ was obtained. SY also investigated a number of integral equation theories including the Percus–Yevick (PY), hypernetted chain (HNC)⁽¹⁶⁾ and Martynov–Sarkisov (MS)⁽¹⁷⁾ closure to the Ornstein–Zernike (OZ) equation, as well as some self-consistent approaches including the Rogers–Young (RY)⁽¹⁸⁾ and Ballone–Pastore–Galli–Gazzillo (BPGG)⁽¹⁹⁾ closures. They found that none of these theories was accurate for the phase boundary or the pair correlation functions.

In this work we present a new integral-equation approach to this problem by including the first few terms in the density expansion of the direct correlation function into the closure approximation. The simplest of these approximations, in which the direct correlation function includes all

terms up to the second power in the density, is significantly more accurate than previous theories.

The rest of the paper is organized as follows: The theory is presented in Section 2, a comparison with simulations is presented in Section 3, and some conclusions are presented in Section 4.

II. THEORY

The OZ equation relates the total correlation functions, $h_{ij}(r) \equiv g_{ij}(r) - 1$ to the direct correlation functions, $c_{ij}(r)$ and, for a binary mixture, may be written (in Fourier space) as

$$\hat{h}_{AA}(k) = \hat{c}_{AA}(k) + \rho_A \hat{c}_{AA}(k) \hat{h}_{AA}(k) + \rho_B \hat{c}_{AB}(k) \hat{h}_{AB}(k) \quad (1)$$

$$\hat{h}_{AB}(k) = \hat{c}_{AB}(k) + \rho_A \hat{c}_{AA}(k) \hat{h}_{AB}(k) + \rho_B \hat{c}_{AB}(k) \hat{h}_{BB}(k) \quad (2)$$

$$\hat{h}_{BB}(k) = \hat{c}_{BB}(k) + \rho_A \hat{c}_{AB}(k) \hat{h}_{AB}(k) + \rho_B \hat{c}_{BB}(k) \hat{h}_{BB}(k) \quad (3)$$

where the carets denote Fourier transforms. For the WR mixture $h_{AB}(r) = -1$ for $r < \sigma$. Other ‘‘closure’’ relations between $h_{ij}(r)$ and $c_{ij}(r)$ must be invoked in order to solve for the structure and thermodynamics. For example, the PY closure⁽¹⁶⁾, in terms of the function $\gamma_{ij}(r) \equiv h_{ij}(r) - c_{ij}(r)$, is given by

$$c_{ij}(r) = [e^{-u_{ij}(r)/kT} - 1][1 + \gamma_{ij}(r)] \quad (4)$$

The density, ρ , and composition, ϕ , are defined by $\rho = \rho_A + \rho_B$, and $\phi = \rho_A/\rho$. σ is used as the unit of length in this paper.

The majority of closure approximations are not thermodynamically consistent, i.e., different values are obtained from the virial and compressibility routes. We therefore calculate two phase envelopes, and refer to them as the binodal and spinodal curves. The binodal curve is obtained via a double tangent construction to the virial free energy. For the WR model this Helmholtz free energy, F , is given by

$$F = F^{IG} + 4\pi N k_B T \rho \sigma^3 \phi (1 - \phi) \int_0^1 \xi^2 g_{AB}(\xi \sigma^+) d\xi \quad (5)$$

where N is the total number of atoms, k_B is Boltzmann’s constant, T is the temperature, $g_{AB}(\xi \sigma^+)$ is the contact value of the pair correlation function in a mixture with hard sphere diameter $\xi \sigma$ and number density ρ , and F^{IG} is the ideal gas contribution to the free energy. The spinodal curve is

defined as the locus of points where all the partial structure factors diverge, i.e., where

$$\hat{A}(0) \equiv 1 - \rho_A \hat{c}_{AA}(0) - \rho_B \hat{c}_{BB}(0) + \rho_A \rho_B (\hat{c}_{AA}(0) \hat{c}_{BB}(0) - \hat{c}_{AB}^2(0)) = 0 \quad (6)$$

Shew and Yethiraj⁽⁸⁾ considered the PY and a number of other closures and found that none of these were accurate for the phase behaviour or structure of the liquid. Most approximations, such as the HNC, MS, BPGG, or RY did not even converge near the critical point and it was not possible to obtain the binodal curve. The least inaccurate of the tested approximations was the venerable PY theory which predicted a critical density of $\rho_c \sigma^3 = 0.57$ and 1.17 from the virial and compressibility routes, respectively, which is not very close to the simulation results.

The main objective of this work is to develop closure approximations that take into account the peculiar non-additive nature of the interactions in the WR mixture. Our approach is to incorporate the first few terms in the density expansion of the direct correlation functions into the closure approximation. Some of the diagrams that appear in the density expansion of $c_{AA}(r)$ and $c_{AB}(r)$ (for $r > \sigma$) are shown in Fig. 1. In the figure, the solid lines are f -bonds and dashed lines are e -bonds, both drawn between circles of different species (because $f_{ii}(r) = 0$ and $e_{ii}(r) = 1$). Unfortunately, none of the diagrams in Fig. 1(a) or (c) can be evaluated exactly for the WR model without numerical computation. On the other hand, all the diagrams in Fig. 1(b) can be evaluated exactly. Our approach here is to include those terms that we can evaluate exactly. This gives,

$$c_{AB}(r) = 0, \quad r > \sigma \quad (7)$$

and

$$c_{AA}(r) = \exp[\rho_B O(r)] - \rho_B O(r) - 1 \quad (8)$$

$$c_{BB}(r) = \exp[\rho_A O(r)] - \rho_A O(r) - 1 \quad (9)$$

for all r , where $O(r)$ is the overlap integral,

$$O(r) = \frac{4\pi}{3} \left[1 - \frac{3r}{4\sigma} + \frac{1}{2} \left(\frac{r}{2\sigma} \right)^3 \right] \quad (10)$$

The exact core condition, $g_{AB}(r) = 0$ for $r < \sigma$ is still used, of course. The present work therefore includes all diagrams to second order in the density and some other diagrams of higher order.

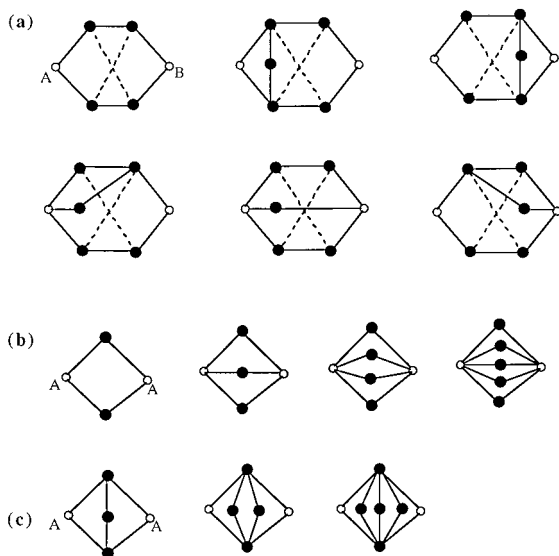


Fig. 1. Diagrams that appear to fifth order in the density in the expansion of the direct correlation functions: (a) Diagrams in $c_{AB}(r)$ (for $r > \sigma$), (b) Diagrams in $c_{AA}(r)$ (or $c_{BB}(r)$, for all r) that can be evaluated analytically, and (c) Diagrams in $c_{AA}(r)$ that cannot be evaluated analytically. Solid lines are f -bonds, dashed lines are e -bonds, and all bonds connect circles of different species.

III. RESULTS

Figure 2 compares theoretical predictions for the phase diagram of the Widom–Rowlinson mixture to computer simulations⁽⁸⁾. The solid and dot-dashed lines are, respectively, the binodal and spinodal curve predicted by the theory of this work. The dashed line is the binodal curve predicted by the PY theory. Both theories considered significantly underestimate the critical density from the virial route (binodal) although the present theory is somewhat more accurate than the PY theory. The critical density obtained from the compressibility route is in excellent agreement with the simulation results in contrast to the PY theory in which the compressibility route significantly overestimates the critical density. This is shown in Fig. 3 which compares predictions of this work to the PY theory of the denominator of the partial structure factors at zero wavevector, $\hat{A}(0)$, as a function of density for $\phi = 0.5$. (The compressibility route critical point occurs at the density where $\hat{A}(0) = 0$.) The PY prediction is $\rho\sigma^3 \approx 1.17$, which is quite a large density. The new theory therefore has two advantages

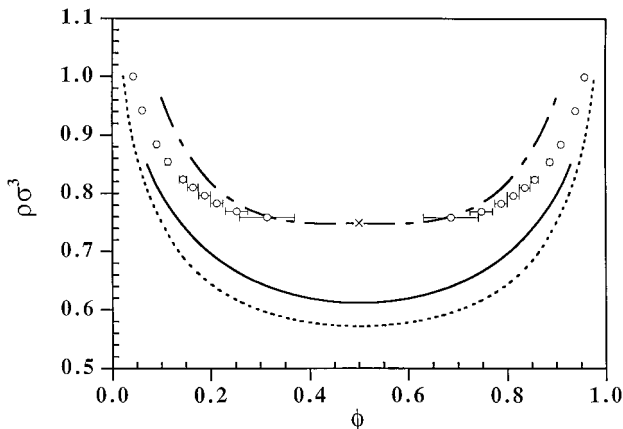


Fig. 2. Phase diagram of the Widom-Rowlinson mixture from simulations⁽⁸⁾ (symbols), theory of the present work (—) and the PY theory (---). The dot-dashed line is spinodal curve from the theory of this work.

over the PY theory: It is more accurate for the location of the critical point, and it is more thermodynamically consistent.

Figures 4(a)–(c) compare the pair correlation functions obtained from theory to computer simulations⁽⁸⁾ for $\rho\sigma^3 = 0.65$, $\phi = 0.11$, $\rho\sigma^3 = 0.65$, $\phi = 0.5$, and $\rho\sigma^3 = 0.85$, $\phi = 0.11$, respectively. The first two cases are at different concentrations in the one-phase region, and the third is a state point right at the coexistence curve. In all three figures, the pair correlation

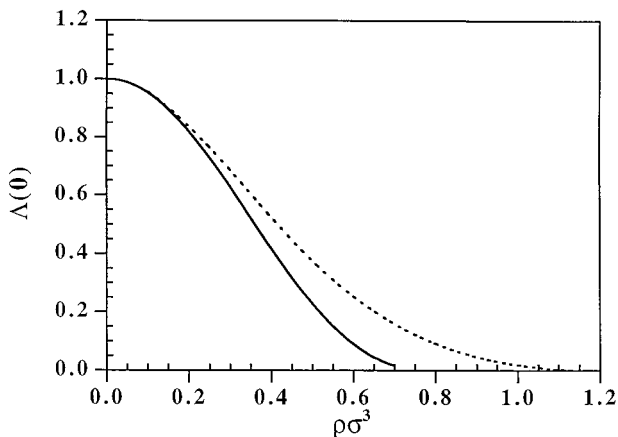


Fig. 3. Comparison of the $\hat{\Lambda}(0)$ from the PY theory (---) to the theory of this work (—). The critical point from the fluctuation rout occurs at $\hat{\Lambda}(0) = 0$.

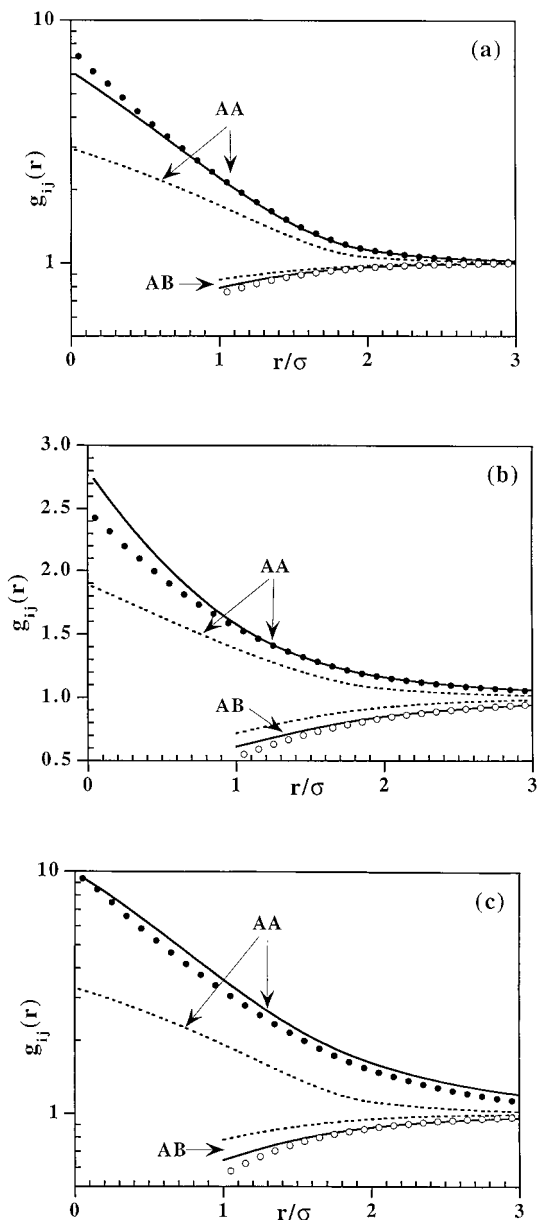


Fig. 4. Comparison of pair correlation functions from simulations (symbols) to predictions of this work (—) and the PY theory (---) for (a) $\rho=0.65$ and $\phi=0.11$, (b) $\rho=0.65$ and $\phi=0.50$, and (c) $\rho=0.85$ and $\phi=0.11$ (i.e. at two-phase coexistence). Note that a logarithmic scale is used for the ordinate in parts a and c.

functions are monotonic, i.e. there is no layering evident, and at short distances there is a clustering of like species and a depletion of unlike species. This is to be expected because the atoms of the like species would like to avoid the hard cores of the other species. The theory of this work is in excellent agreement with the computer simulations in all cases. There is a considerable improvement over the PY theory which significantly underestimates the value of the pair correlation functions between like species at all conditions.

IV. CONCLUSIONS

An integral equation theory is presented for the structural and thermodynamic properties of the Widom–Rowlinson mixture. The theory incorporates the terms in the density expansion of the direct correlation function that can be evaluated exactly into the closure approximation. The theory is in good agreement with computer simulations for the pair correlation functions and phase diagram although there is room for improvement.

There are several possible ways to improve the performance of the theory with additional computational complexity. Although none of the diagrams in Figs. 1(a) and 1(c) can be evaluated analytically for the WR model, all of them can be evaluated exactly if the f -function were a Gaussian. If $f(r) = \exp(-\alpha r^2)$, for example, the diagrams can be evaluated and α adjusted by requiring $-\int f(\mathbf{r}) d\mathbf{r} = 4\pi\sigma^3/3$. This should provide a more accurate theory for the model. Further improvement could be obtained by imposing internal thermodynamic consistency, i.e. setting $c_{ij}(r) = \lambda c_{ij}^0(r)$ outside the core (where $c_{ij}^0(r)$ are evaluated from the diagrammatic expansion) and choosing λ so that the compressibility and virial pressures are equal. The results of this work suggest that such a program could prove to be fruitful if an accurate theory for the WR model is desired.

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