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PARTIAL COORDINATION NUMBERS OF SQUARE-WELL BINARY FLUID MIXTURES

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A coordination number model for single component square-well fluids is generalised here to apply to binary square-well fluids using a one-fluid mean field approach. Based on Monte Carlo computer simulations of this work and of others we test this new predictive model for the species-resolved coordination numbers of square-well binary mixtures. The model is found to be valid for unequal values for the core diameter, interaction range and well-depth in the relative range $\sim \times 2$ for the two components. The predictions of the new model as a function of composition, density and temperature are in exceptional agreement with the Monte Carlo computer simulation results.

KEY WORDS: Monte Carlo computer simulation, coordination numbers, square-well fluid mixtures, Quasi-Chemical Approximation.

1 INTRODUCTION

The square-well fluid combines the essential features (repulsive and attractive forces) of real fluids with an analytic simplicity (collision diameter, σ , well-depth, ϵ and reduced well-width, $\lambda - 1$) which makes it an analytically tractable model fluid for the structural and thermodynamic properties of real molecular fluids. One particular feature which is useful is the unambiguous definition of the local coordination number for the square-well system, which enables the equation of state to be expressed formally and exactly in terms of it. Lattice-based models of fluids, such as the Quasi-Chemical Approximation have made use of this to develop equations of state for mixtures of square-wells based on expressions for the local coordination numbers between the species^{1–3}. Therefore a reasonable local coordination number model specifies the microstructure of the square-well fluids and forms the basis for developing equations of state and other thermodynamic functions. The “local composition” or local mole fraction around each particle can deviate from the average composition and this can be parameterised and empirically introduced into the equation of state^{1–3}. In this study we are interested in mixtures of square wells, concentrating on the preferential association of the two species both directly from simulation and from a proposed expression for the local compositions based on the Quasi-Chemical Approximation. In the past, this has led to density-dependent mixing rules for the mixture parameters in simple cubic equations of state. Although in this study we will concentrate on the coordination numbers.

In this work we build on the foundations of the previous workers. We investigate by Monte Carlo computer simulation, binary mixtures of square-wells over a wide temperature, density and well-range (previous studies have been confined to a well-width equal to half the collision diameter). Making use also of previous simulation data, we generalise, to arbitrary well-width, previous analytic expressions which reproduce the Monte Carlo local coordination data.

2 THEORETICAL BACKGROUND

Consider a square-well potential,

$$\begin{aligned}\phi_{ij}(r) &= \infty, r \leq \sigma_{ij} \\ &= -\varepsilon_{ij}, \sigma_{ij} < r < \lambda_{ij}\sigma_{ij} \\ &= 0, r > \lambda_{ij}\sigma_{ij}\end{aligned}\quad (1)$$

The hard-core diameter, σ_{ij} and interaction energy, ε_{ij} between the two particles is given by the usual Lorentz–Berthelot combining rules

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \quad (2)$$

and

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (3)$$

and for the cut-off radius

$$\lambda_{ij}\sigma_{ij} = (\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj})/2.0. \quad (4)$$

For square-well potentials $\varepsilon_{ij} > 0$ and this finite negative energy interaction region extends between $\sigma_{ij} < r < \lambda_{ij}\sigma_{ij}$. Therefore, the square-well molecule has two length-scales, the core-diameter, σ_{ii} and interaction range, $\lambda_{ii}\sigma_{ii}$ for the self-interactions, and corresponding values for the cross, ij , interactions.

The number of j particles in the shell $r - \Delta/2 < r < r + \Delta/2$ from a central molecule, i , is on average,

$$dn_{ji} = 4\pi\rho_j g_{ji}(r)r^2 dr. \quad (5)$$

Therefore the coordination number of j particles about i are,

$$n_{ji} = 4\pi\rho_j \int_{\sigma_{ii}}^{\lambda_{ii}\sigma_{ii}} g_{ji}(r)r^2 dr. \quad (6)$$

The total coordination number of particles of all species about a central i particle is given by

$$z_i = \sum_j^v n_{ji}, \quad (7)$$

where there are v species. In this study we are considering a binary mixture so $v = 2$ here. Let these species be $i = 1$ and $i = 2$. For the binary mixture let the total number of 12 pairs in the system at a separation, r , be $N_{12}(r)$. Under all circumstances, a 12 interaction must also mean there is a 21 interaction. Therefore, $N_{12}(r)$, must equal, $N_{21}(r)$, the number of 21 pairs at a separation r within the whole system. We have,

$$N_{12}(r) = N_{21}(r). \quad (8)$$

But, in a system of N_1 molecules of species 1 and N_2 molecules of species 2 we have,

$$N_{12}(r) = N_2 n_{12}(r), \quad (9)$$

using the definition of the local coordination number, defined in Eq. (6) and similarly,

$$N_{21}(r) = N_1 n_{21}(r). \quad (10)$$

Consequently from Eq. (8) we have,

$$N_2 n_{12}(r) = N_1 n_{21}(r). \quad (11)$$

Dividing both sides of Eq. (11) by $N = N_1 + N_2$, we have,

$$x_2 n_{12}(r) = x_1 n_{21}(r), \quad (12)$$

where $x_1 = N_1/N$ and $x_2 = N_2/N$, the mole fractions of each species. To reduce Eq. (12) further we define a local mole fraction for species 1 and 2,

$$x_{12} = n_{12}/z_2, \quad (13)$$

and

$$x_{21} = n_{21}/z_1, \quad (14)$$

where $z_1 = n_{21} + n_{11}$ and $z_2 = n_{22} + n_{12}$ from Eq. (7). Substitution of Eq. (13) and (14) into Eq. (11) gives,

$$x_2 z_2 x_{12} = x_1 z_1 x_{21}. \quad (15)$$

If $z_1 = z_2$ then we have the Flemr condition,¹ $x_2 x_{12} = x_1 x_{21}$. Clearly in general $z_1 \neq z_2$ so we cannot expect this balance to hold, but Eq. (15) is exact under all

circumstances. As, $z_2 = n_{12} + n_{22}$, $x_{12} = n_{12}/z_2$ and $x_{22} = n_{22}/z_2$, we have,

$$x_{12} + x_{22} = 1, \quad (16)$$

then substituting Eq. (16) into Eq. (15) we have,

$$x_2 z_2 (1 - x_{22}) = x_1 z_1 x_{21}. \quad (17)$$

Rearrangement of Eq. (17) gives,

$$x_2 z_2 = x_1 z_1 z_{21} + x_2 z_2 x_{22}. \quad (18)$$

This is known as the McDermott–Ashton condition¹. By symmetry we have,

$$x_1 z_1 = x_2 z_2 z_{12} + x_1 z_1 x_{11}, \quad (19)$$

Both the Flemr and McDermott–Ashton conditions are exact and follow from the detailed balance of pairs. Another exact relationship is the sub-species pair radial distribution function condition,

$$g_{12}(r) = g_{21}(r). \quad (20)$$

This is because by definition,

$$g_{12}(r) = VN_{12}(r)/(N_1 N_2 4\pi r^2 \Delta r), \quad (21)$$

$$g_{21}(r) = VN_{21}(r)/(N_1 N_2 4\pi r^2 \Delta r), \quad (22)$$

and as $N_{12}(r) = N_{21}(r)$ for any arbitrary binary mixture then Eq. (20) follows from Eq. (21) and (22).

Thus far we have the following exact “local balance” conditions, which can be derived from the definitions of the component terms,

$$x_{11} + x_{21} = 1. \quad (23)$$

$$x_{12} + x_{22} = 1, \quad (24)$$

$$x_2 z_2 x_{12} = x_1 z_1 x_{21}, \quad (25)$$

$$x_2 z_2 = x_1 z_1 z_{21} + x_2 z_2 x_{22}, \quad (26)$$

$$x_1 z_1 = x_2 z_2 z_{12} + x_1 z_1 x_{11}, \quad (27)$$

Equations (23)–(27) follow from the local mole fraction definitions. Equations (25)–(27) also make use of the requirement that the number of interacting 1–2 pairs

in the whole system must equal the number of 2-1 pairs (*i.e.*, $N_{12}(r) = N_{21}(r)$). In order to specify the local mole fractions exactly, we require another relationship between x_{12} , x_{21} , x_{11} and x_{22} . Unfortunately, no such exact relationship can be derived. We are forced to resort to an alternative approximate approach. We consider a relationship of the form,³

$$\frac{x_{12}x_{21}}{x_{11}x_{22}} = f(N_1, N_2, V, T, \varepsilon_1, \varepsilon_2, \sigma_1, \sigma_2, \lambda_1, \lambda_2 \dots) \quad (28)$$

Together with Eqs. (23) and (24) we have,

$$x_{12} = \frac{(x_1z_1 + x_2z_2) - [(x_1z_1 + x_2z_2)^2 - 4x_1z_1x_2z_2(1 - 1/f)]^{1/2}}{2x_2z_2(1 - 1/f)}, \quad (29)$$

There is no exact analytical expression for the parameter f , which must be included in a semi-empirical fashion. One approach is to use a lattice model for liquids⁴, which considers the interrelationship between x_{12} , x_{21} , x_{11} and x_{22} to be that of a "chemical equilibrium". This is called the Quasi-Chemical Approximation, *QCA*. Consider a lattice of coordination number z upon which is distributed, N_1 , molecules of species-1 and N_2 molecules of species-2. Pairs interacting within, z , are considered to form pair molecules, so that there is an equilibrium of the form,

$$(1 - 1) + (2 - 2) = 2 \times (1 - 2), \quad (30)$$

The equilibrium constant, K , for this "reaction" is by definition,

$$K = \frac{N_{12}^2}{N_{11}N_{22}}, \quad (31)$$

The van't Hoff isochore can be used to specify the temperature dependence of K ,

$$\left(\frac{\partial \ln(K)}{\partial T^{-1}} \right)_V = -\Delta U/R, \quad (32)$$

where $\Delta U/R = (2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22})\beta$, where $\beta = 1/k_B T$, as usual. Integration of Eq. (31) using Eq. (32) gives,

$$\frac{N_{12}^2}{N_{11}N_{22}} = \frac{N_{12}^{*2}}{N_{11}^*N_{22}^*} \exp((2\varepsilon_{12} - (\varepsilon_{11} + \varepsilon_{22}))\beta), \quad (33)$$

Where N_{ij}^* denotes the value of N_{ij} for pure random mixing. A similar formula comes from a treatment of the coordination numbers in the zero density limit. At low density, $\rho \rightarrow 0$, the radial distribution function, $g_{ij}(r)$, follows

$$g_{ij}(r) \rightarrow \exp(-\phi_{ij}\beta) = \exp(-\varepsilon_{ij}\beta), \quad \sigma_{ij} < r < \lambda_{ij}\sigma_{ij}, \quad (34)$$

Therefore

$$n_{ij} \rightarrow \frac{4\pi}{3} (\lambda^3 - 1) \rho_i \sigma_{ij}^3 \exp(-\varepsilon_{ij}\beta), \quad (35)$$

and

$$\frac{x_{12}x_{21}}{x_{11}x_{22}} = \frac{\sigma_{12}^3(\lambda_{12}^3 - 1)\sigma_{21}^3(\lambda_{21}^3 - 1)}{\sigma_{11}^3(\lambda_{11}^3 - 1)\sigma_{22}^3(\lambda_{22}^3 - 1)} \exp(\beta\omega), \quad (36)$$

where $\omega = 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}$. Similarly for,

$$\frac{x_{12}x_2}{x_1x_{22}} = \frac{\sigma_{12}^3(\lambda_{12}^3 - 1)}{\sigma_{22}^3(\lambda_{22}^3 - 1)} \exp(\beta(\varepsilon_{12} - \varepsilon_{22})), \quad (37)$$

and

$$\frac{x_{21}x_1}{x_2x_{11}} = \frac{\sigma_{21}^3(\lambda_{21}^3 - 1)}{\sigma_{11}^3(\lambda_{11}^3 - 1)} \exp(\beta(\varepsilon_{21} - \varepsilon_{11})), \quad (38)$$

Equations (34–38), while adequate at low fluid density, fail to account for the many-body effects that become increasingly important in the dense fluid approaching to fluid close-packing. This is manifest in deviations in local composition ratios from these simple analytical forms. The local composition effects dominated by the influence of the attractive well interactions evident in the local composition ratios of Eqs. (36–38) are most important at low density, becoming less influential at higher densities because of packing constraints in the dense fluid. Nevertheless, Eqs. (36–38) do provide useful reference formulae for the coordination number that can form the basis for modification in the high density limit. Any modifications to the ratios of Eqs. (36–38) must reduce to these equations as $\rho \rightarrow 0$.

In this study we concentrate on an analytical expression for coordination number of binary mixtures using density-dependent mixing rules. Simulation data is used to assess the adequacy of the expressions chosen. The main purpose of this study is to build upon the previous work performed on this subject to take into account the effect of density, mole fraction of each component, diameter ratio and well-depth ratio^{1–6} on the species local coordination numbers. This formidable task (given the number of variables to be accommodated in a simple general expression) is founded upon a generalisation to mixtures of a formula proposed by Heyes⁷, and subsequently modified by Heyes and Aston⁸ for the local coordination number of single component square-well fluids which was found successful in these studies.

In the previous work in this series for single component square-well fluids we used the formula for the coordination number⁸,

$$n = c_0\Omega/(1 + \rho(\Omega - 1)), \quad (39)$$

based on the Quasi-Chemical Approximations (QCA). The variable, c_0 is the coordination number based on a random distribution of binary spheres. The remaining part of Eq. (39) is the density-dependent and temperature-dependent adhesive interaction correction to this term. The innovation in the previous study⁸, was to modify the usual expression for c_0 to take better account than before of the local density of the hard-sphere fluid, based on the true hard-sphere pair radial distribution function. In particular, we incorporated the pair radial distribution function at contact, $g(\sigma)$ as a density-dependent parameterisation within the definition for c_0 . This incorporates essentially exact local coordination of the hard-sphere fluid. For c_0 , we have⁸,

$$c_0 = (4\pi/3)(\lambda^3 - 1)\rho^*(1 + \exp(-\alpha_1\rho(\lambda - 1))((1 - \rho/\rho_0)^{-2} - 1)), \quad (40)$$

where $\rho_0 = 1.625\sigma^{-3}$ is the reference density introduced by Heyes and Woodcock⁹. The term, c_0 , becomes exact as $\lambda \rightarrow 1$. In fact as $\lambda \rightarrow 1$ we find the last term in Eq. (30) reducing to $g(\sigma)$ the pair distribution function at contact. To a very good approximation, for hard-spheres⁹,

$$g(\sigma) = 1/(1 - \rho/\rho_0)^2. \quad (41)$$

Now

$$\Omega = \exp(\alpha\varepsilon\beta) \quad (42)$$

where

$$\alpha = 1 - \alpha_2\rho/\lambda, \quad (43)$$

where from the previous work: $\alpha_1 = 5.2708$, $\alpha_2 = 0.491$ and $\rho_0 = 1.625$. The term, α in Eq. (42) goes some way towards incorporating in the model the diminishing role of temperature on the coordination number as density increases, and also the effect of λ , while ensuring the analytically correct $\rho \rightarrow 0$ limit for c . Both the denominator in Eq. (39) and the density dependent term in Eq. (39) are incorporated to reduce the temperature and density dependence of the coordination number as density increases towards the dense fluid-solid transition.

Now we propose a generalisation of the above treatment for binary square-well mixtures using the one-fluid generalisation rules found successful in other works¹⁻⁴. (There are several variations on the combination rules used to apply single-component formulae to multi-component systems. The one we have chosen conforms to one of the more successful and popular of choices.) Equation (40), the hard-sphere component to the coordination number is generalised to account for (a) a general increase in the number density introduced by a one-fluid equivalent number density, $\bar{\rho}$, but nevertheless (b) for each species pair, ij , it must return to the specific parameters accounting for the core size and interaction range of that particular pair. Following broadly the same combination rules used in previous treatments, to go from the

single component to the multi-component system, Eq. (30) then becomes,

$$c_{ij0} = (4\pi/3)(\lambda_{ij}^3 - 1)r_{ij}\bar{\rho}(1 + \exp(-\alpha_1 r_{ij}\bar{\rho}(\lambda_{ij} - 1))((1 - r_{ij}\bar{\rho}/\rho_0)^{-2} - 1)), \quad (44)$$

$$\Omega = \sum \sum x_i x_j \exp(\alpha_{ij} \varepsilon_{ij} \beta), \quad (45)$$

where

$$\alpha_{ij} = 1 - \alpha_2 r_{ij} \sum \sum x_i x_j \bar{\rho} / \lambda_{ij}, \quad (46)$$

$$r_{ij} = \sigma_{ij}^3 / \bar{\sigma}^3, \quad (47)$$

$$n_{ij} = c_{ij0} \Omega / (1 + r_{ij} \bar{\rho} (\Omega - 1)), \quad (48)$$

and

$$\bar{\sigma}^3 = \sum x_i \sigma_{ii}^3 \quad (49)$$

$$\bar{\rho} = N \bar{\sigma}^3 / V, \quad (50)$$

The mixing rules in this model predict random mixing in the high-density limit and Boltzmann factor non-randomness at low density. The model predicts the local pair dependent coordination numbers in Eq. (48). This can then be used to calculate the local mole fractions (*e.g.*, Eqs. (13) and (14)) and the derived ratios (Eqs. (46–48)) that probe the extent of non-ideality of mixing as a function of the density, temperature, mole fractions and the other molecular parameters. In contrast, it does not predict the density of the mixture, only the local coordination numbers. The number densities, $N_1 \sigma_{11}^3 / V$ and $N_2 \sigma_{11}^3 / V$ are parameters that must be introduced into the model. It cannot give information about the equation of state, without additional assumptions.

3 RESULTS AND DISCUSSION

We performed *SW* simulations with $N = 256$ over most of the fluid part of the phase diagram for over 2000 ρ , β , λ combinations. This was combined with data from references (2,3,5) and (10). With so many variables it is a formidable task to assess or even represent the adequacy of any model. All that can be realistically achieved is for the model to be tested at a selection of representative state points where non-ideality is most likely to be manifest. Therefore, we consider state points at temperatures just below or just above the critical temperature of the mixture. Although this is not known, it can be estimated from the following empirical formula,

$$T_{c,mix} = x_1 T_{c,1} + x_2 T_{c,2}, \quad (51)$$

The critical temperature of the pure phase, $T_{c,i}$ is estimated by a fit to the data from¹¹.

For each species, with its own λ value, the critical temperature can be estimated as¹¹,

$$T_c/\varepsilon = (\lambda - 0.4)^2. \quad (52)$$

For the states considered below we consider, $T/\varepsilon_{11} = 2.0$ and 3.0 , which are either above or just below the estimated critical temperature. Therefore at most of the states considered we are in a single supercritical fluid phase, not in the liquid-vapour two-phase region. For those states just within the co-existence envelope (*i.e.*, intermediate density and $T/\varepsilon_{11} = 2.0$ and $\lambda_i = 1.75$) we are only in the spinodal region at worst. Within a finite- N simulation cell of several hundred particles this will not manifest two-phase co-existence. All it will do is manifest enhanced clustering, evident in Figure 2.

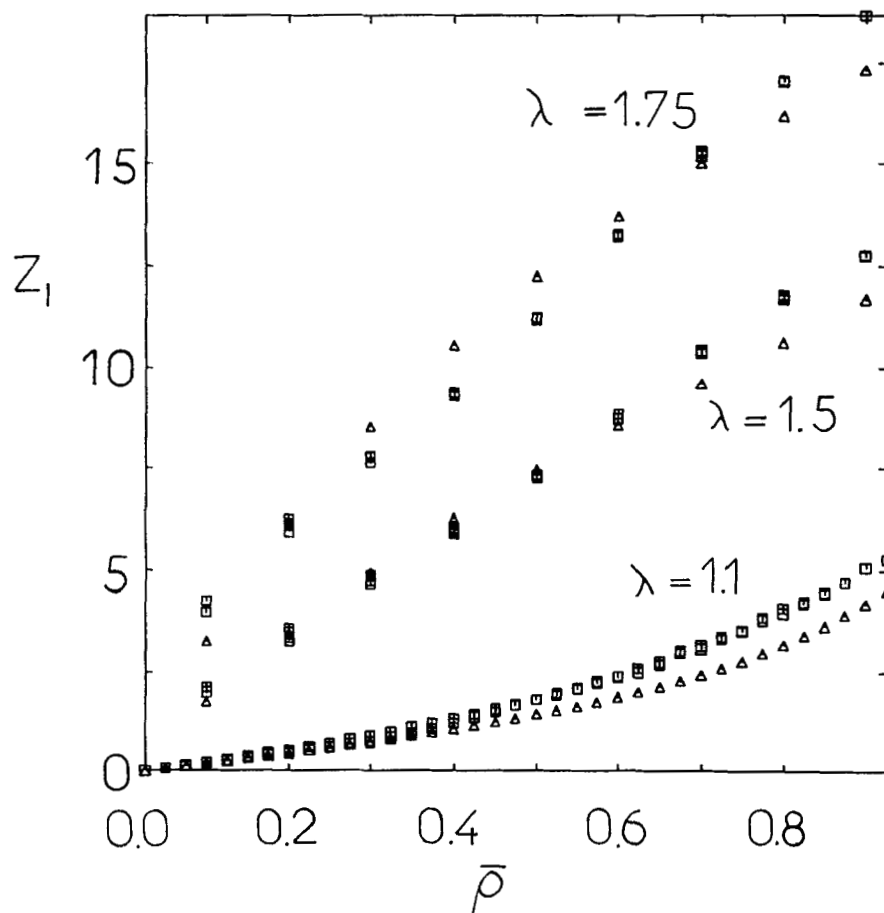


Figure 1 Total local coordination number, z_1 by MC simulation for three values of λ , given on the figure. The band of state points is prescribed by: $x_1 = x_2 = 0.5$, $\varepsilon_{22}/\varepsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 1.0$, $T/\varepsilon_{11} = 2.0$ and $\lambda_{11} = \lambda_{22} = 1.1, 1.5$ and 1.75 . Key: \square , simulation, and \triangle , Model results based on Eq. (38).

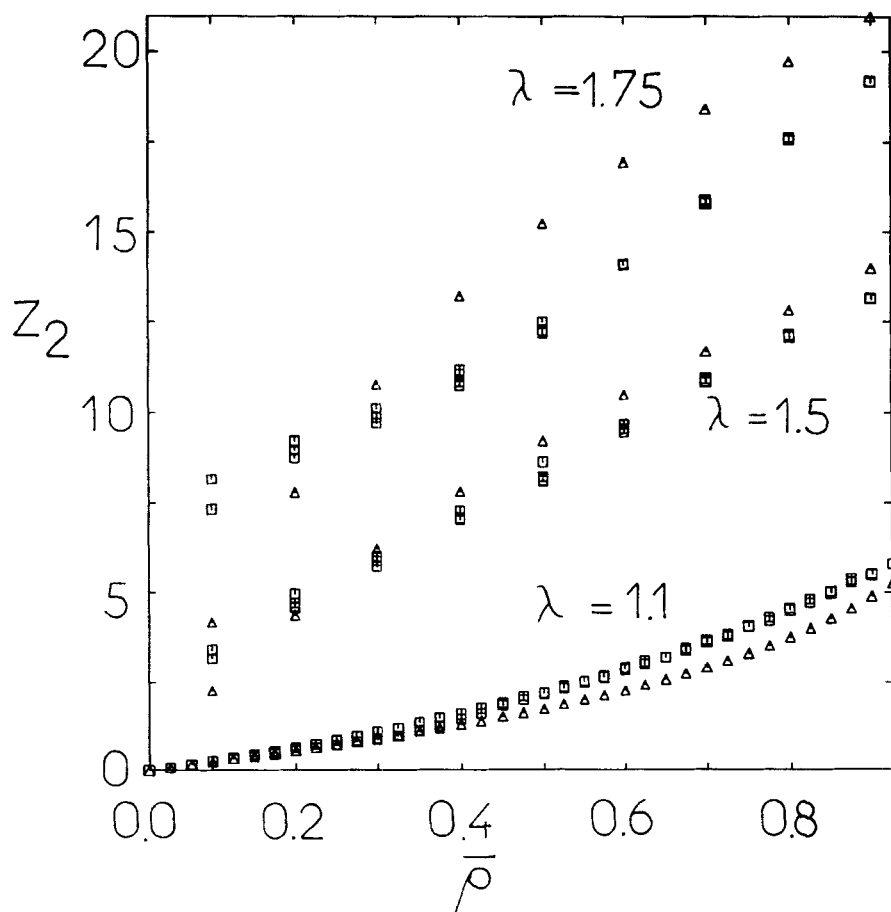


Figure 2 As for Figure 1, except that the corresponding values for z_2 are presented.

The simulations reported here were conducted with $x_1 = x_2 = 0.5$ because the equimolar mixtures show the largest deviations from ideality. In Figure 1, we show the MC and model local coordination numbers for component-1, z_1 , and in Figure 2 the corresponding, z_2 , are shown. We chose, $\varepsilon_{22}/\varepsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 1.0$, $T/\varepsilon_{11} = 2.0$ and $\lambda_{11} = \lambda_{22} = 1.1, 1.5$ and 1.75 . At any number density, the coordination number increases with λ because more particles can enter within the interaction range of an arbitrarily chosen central particle. Therefore as the relevant λ_{ij} increase then for any specific value of $\bar{\rho}$ the average coordination number will increase. This is observed in Figures 1 and 2. For $\lambda_{ij} \rightarrow 1$ the $n_{ij}(\lambda_{ij}\sigma_{ij})$ versus $\bar{\rho}$ curve is concave. As the interaction range increases we find that the coordination number becomes saturated as it includes the whole of first coordination shell.

The model fits for the z_i are reasonably good over the whole of the studied region. In Figure 3 and 4 we present the corresponding z_1 and z_2 for the fixed parameter combinations $x_1 = x_2 = 0.5$, $\varepsilon_{22}/\varepsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 0.5$, $T/\varepsilon_{11} = 3.0$ and $\lambda_{11} = 1.2$

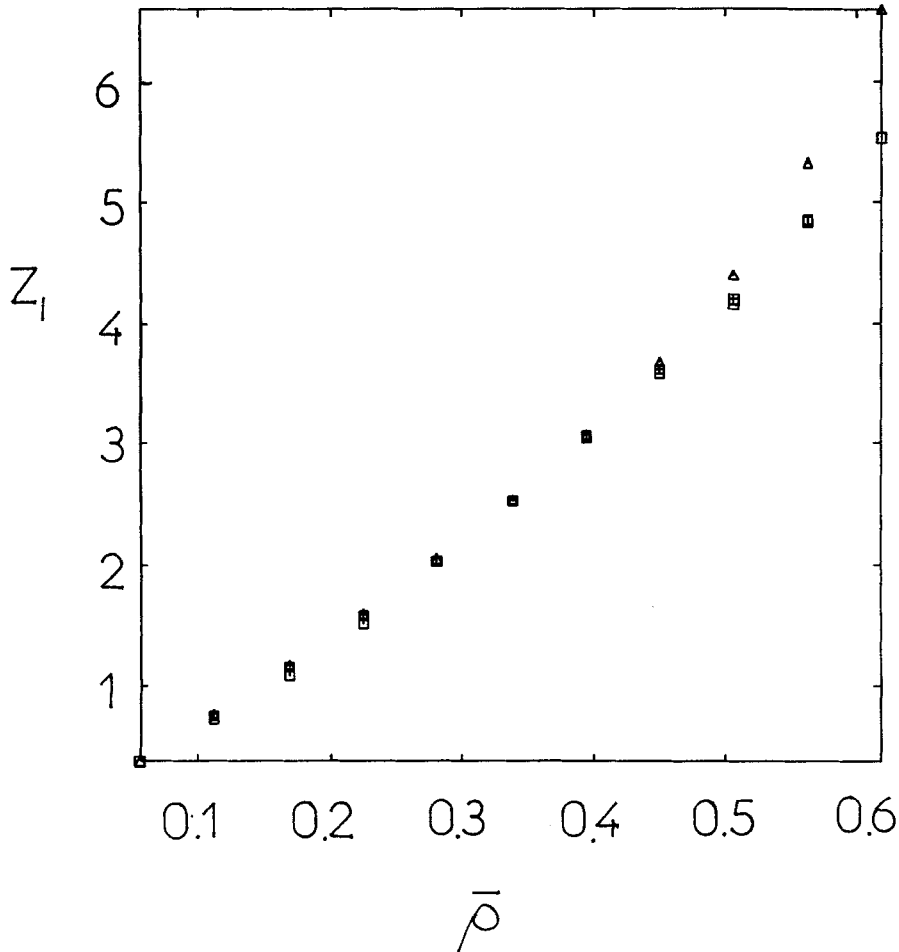


Figure 3 As for Figure 1, except that $x_1 = x_2 = 0.5$, $\varepsilon_{22}/\varepsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 0.5$, $T/\varepsilon_{11} = 3.0$ and $\lambda_{11} = 1.2$ and $\lambda_{22} = 1.4$. Key: \square , simulation, and \triangle , Model results based on Eq. (39).

and $\lambda_{22} = 1.4$. Again for this particularly asymmetric combination of parameters the match between *MC* and the model of Eq. (48) is exceptional, vindicating the underlying quasi-one-fluid approach.

In the tables we illustrate the trends in the local coordination numbers and their ratios. Table 1 has the simulation and model values for x_{11} and x_{22} . We consider two sequences of simulation. The first series, Series A, has $x_1 = x_2 = 0.5$, $\varepsilon_{22}/\varepsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 1.0$, $T/\varepsilon_{11} = 2.0$ and $\lambda_{11} = \lambda_{22} = 1.1, 1.5$ and 1.75 . This shows for x_{11} in the low density limit a value for $x_{11} < x_1$. Conversely, at the same state points we have $x_{22} > x_2$. This indicates that the local fractional density of species-1 about species-1 within their mutual interaction distances is lower than the mean mole fraction. Also the local fractional density of species-2 about species-2 within their mutual interaction distances is greater than the mean mole fraction. Species-2 attracts species-2 (and

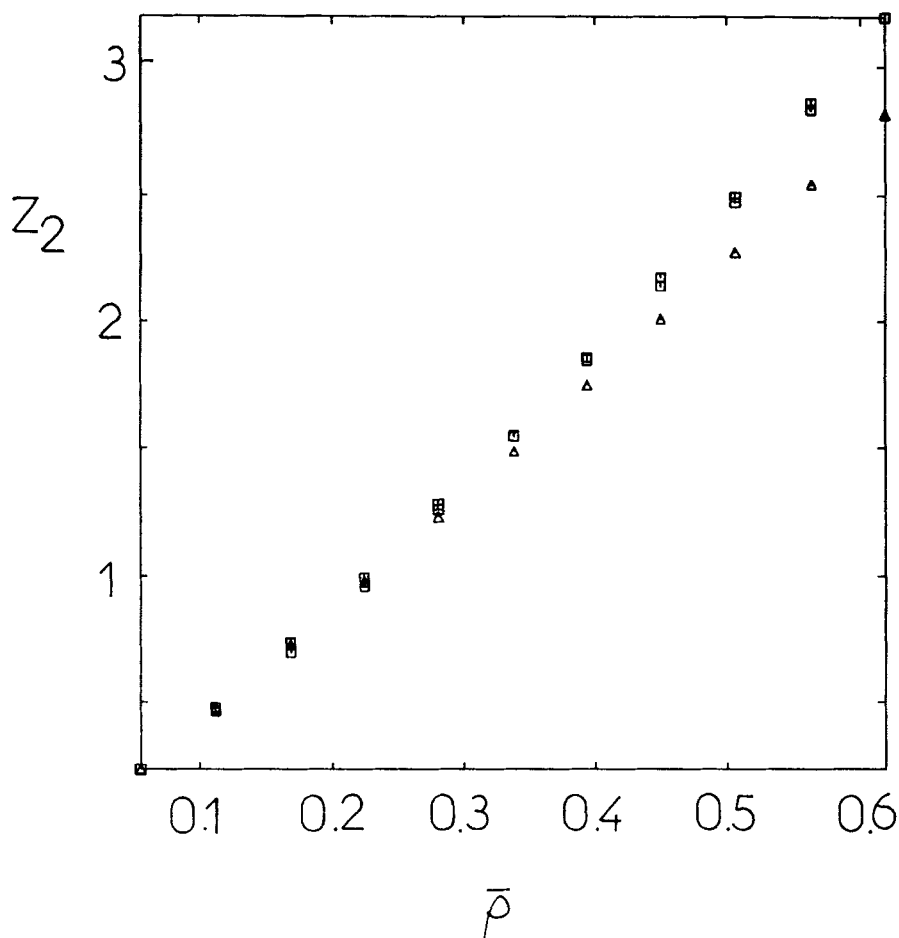


Figure 4 As for Figure 3, except that z_2 are shown.

also species-1) more strongly than species-1 attracts itself because in this case, $\epsilon_{22}/\epsilon_{11} = 2.0$. Therefore species-1 has fractionally fewer of its own kind in the first coordination shell than on average. It is possible for $x_{ii} \neq x_i$ because the square-well interaction range $\lambda_{ii}\sigma_{ii}$ is finite. (Clearly, as $\lambda_{ii} \rightarrow \infty$, $x_{ii} \rightarrow x_i$). This effect diminishes as density increases because of the increasing importance of excluded volume effects. The $x_{ii} \rightarrow x_i$ trend as $\bar{\rho} \rightarrow \rho_{\max} = 0.9428\bar{\sigma}^3$, is strongest for the species-1, the species-2 maintains its relative excess of its own kind to much higher volume fractions. These trends are well-reproduced quantitatively by the mean-field model proposed above. Also in Table 1 we consider the situation where particle-2 has half the core diameter of species-1. The parameter combination for this second series of calculations, called Series B, is, $x_1 = x_2 = 0.5$, $\epsilon_{22}/\epsilon_{11} = 2.0$, $\sigma_{22}/\sigma_{11} = 0.5$, $T/\epsilon_{11} = 3.0$ and $\lambda_{11} = 1.2$ and $\lambda_{22} = 1.4$. Here the same trends with density are apparent as for Series A, but

Table 1 Local mole fractions, x_{ii} , calculated directly from simulation (MC) and from the QCA model (MOD). Key: $x_1 = x_2 = 0.5$.

σ_2/σ_1	$\varepsilon_2/\varepsilon_1$	$\bar{\rho}$	T/ε_{11}	λ_1	λ_2	$x_{11,MD}$	$x_{11,MOD}$	$x_{22,MD}$	$x_{22,MOD}$
1.000	2.000	0.100	2.000	1.100	1.100	0.450	0.451	0.562	0.570
1.000	2.000	0.500	2.000	1.100	1.100	0.460	0.460	0.551	0.557
1.000	2.000	0.600	2.000	1.100	1.100	0.460	0.462	0.543	0.553
1.000	2.000	0.900	2.000	1.100	1.100	0.511	0.469	0.546	0.544
1.000	2.000	0.925	2.000	1.100	1.100	0.503	0.470	0.546	0.543
1.000	2.000	0.100	2.000	1.500	1.500	0.420	0.450	0.632	0.570
1.000	2.000	0.900	2.000	1.500	1.500	0.502	0.464	0.517	0.551
1.000	2.000	0.100	2.000	1.750	1.750	0.420	0.450	0.686	0.571
1.000	2.000	0.900	2.000	1.750	1.750	0.521	0.461	0.533	0.555
0.500	2.000	0.112	3.000	1.200	1.400	0.595	0.604	0.373	0.373
0.500	2.000	0.225	3.000	1.200	1.400	0.599	0.614	0.368	0.370
0.500	2.000	0.281	3.000	1.200	1.400	0.608	0.620	0.369	0.368
0.500	2.000	0.338	3.000	1.200	1.400	0.608	0.628	0.360	0.367
0.500	2.000	0.619	3.000	1.200	1.400	0.635	0.728	0.368	0.361

superimposed on top of the purely geometric effect arising from the difference in the particle core-diameters and their interaction ranges, $= \lambda_{ii}\sigma_{ii}$.

Series B has $x_{11} > x_1$ and $x_{22} < x_2$, the reverse trend to that evident for series A. This is intuitively reasonable because as species-1 gets larger than species-2, then the particles of species-2 are forced to live in the interstices of a network or "lattice" formed by the molecules of species-1, which is largely undistorted locally as a result. More of larger particles can fall within their own coordination spheres than the mean value would indicate. Conversely, as the small particles are forced to occupy the spaces of the larger particles, they are on average further from one another and have fewer neighbours of their own kind than the mean mole fraction would indicate. There is a favouring of the number of 11 contacts as opposed to the number of 22 contacts, explaining the values: $x_{11} \sim 0.6$ and $x_{22} \sim 0.4$. At fixed mole fraction, the n_{11} increases with decreasing σ_{22}/σ_{11} . As species-2 becomes smaller its molecules exert a reduced screening influence on the species-1 particles. This allows more species-1 molecules to come within the interaction range of one-another and also fewer of species-2 to interact with species-2. The total coordination number of species, z_1 increases as the ratio σ_{22}/σ_{11} decreases, and vice versa¹². Density does not have as pronounced effect on the Series B, x_{ii} , as for the Series A, x_{ii} . Note that the mean-field model fits exceptionally well to the simulation data.

In Table 2 we present the corresponding data for the cross-species local mole fractions, x_{12} and x_{21} . Recall that the convention is that 12 is to be interpreted as species-1 about a single particle of species-2, and vice versa. For Series A, we note that x_{12} is lower than x_1 , the value for random mixing. We interpret this as arising from the definition $x_{12} = n_{12}/z_2$. The total coordination number of species-2 is higher than that of species-1 due to its deeper attractive well. The increase in the magnitude of the denominator causes $x_{12} < x_1$. Conversely, $x_{21} > x_2$ because of the decrease in z_1 compared to z_2 . This is a valid conclusion as $n_{12} = n_{21}$ for the case when

Table 2 Local mole fractions, x_{ij} , calculated directly from simulation (MC) and from the QCA model (MOD). Key: $x_1 = x_2 = 0.5$.

σ_2/σ_1	$\varepsilon_2/\varepsilon_1$	$\bar{\rho}$	T/ε_{11}	λ_1	λ_2	$x_{12,MD}$	$x_{12,MOD}$	$x_{21,MD}$	$x_{21,MOD}$
1.000	2.000	0.100	2.000	1.100	1.100	0.438	0.430	0.550	0.549
1.000	2.000	0.300	2.000	1.100	1.100	0.451	0.437	0.533	0.545
1.000	2.000	0.600	2.000	1.100	1.100	0.457	0.447	0.540	0.538
1.000	2.000	0.900	2.000	1.100	1.100	0.454	0.456	0.489	0.531
1.000	2.000	0.100	2.000	1.500	1.500	0.368	0.430	0.580	0.550
1.000	2.000	0.400	2.000	1.500	1.500	0.434	0.437	0.523	0.545
1.000	2.000	0.900	2.000	1.500	1.500	0.483	0.449	0.498	0.536
1.000	2.000	0.100	2.000	1.750	1.750	0.314	0.429	0.580	0.550
1.000	2.000	0.500	2.000	1.750	1.750	0.446	0.437	0.498	0.544
1.000	2.000	0.900	2.000	1.750	1.750	0.467	0.445	0.479	0.539
0.500	2.00	0.112	3.000	1.200	1.400	0.627	0.627	0.405	0.396
0.500	2.000	0.281	3.000	1.200	1.400	0.631	0.632	0.392	0.380
0.500	2.000	0.450	3.000	1.200	1.400	0.636	0.635	0.381	0.347
0.500	2.000	0.619	3.000	1.200	1.400	0.632	0.639	0.365	0.272

Table 3 Local mole fraction ratios, $r_1 = x_{21}x_1/x_2x_{11}$ and $r_2 = x_{12}x_2/x_{22}x_1$ calculated directly from simulation (MC) and from the QCA model (MOD). Key: $x_1 = x_2 = 0.5$.

σ_2/σ_1	$\varepsilon_2/\varepsilon_1$	$\bar{\rho}$	T/ε_{11}	λ_1	λ_2	$r_{1,MD}$	$r_{1,MOD}$	$r_{2,MD}$	$r_{2,MOD}$
1.000	2.000	0.100	2.000	1.100	1.100	1.221	1.219	0.780	0.756
1.000	2.000	0.200	2.000	1.100	1.100	1.204	1.208	0.801	0.766
1.000	2.000	0.300	2.000	1.100	1.100	1.144	1.196	0.822	0.776
1.000	2.000	0.400	2.000	1.100	1.100	1.130	1.185	0.786	0.786
1.000	2.000	0.500	2.000	1.100	1.100	1.174	1.175	0.814	0.797
1.000	2.000	0.600	2.000	1.100	1.100	1.175	1.164	0.842	0.807
1.000	2.000	0.700	2.000	1.100	1.100	1.084	1.153	0.814	0.818
1.000	2.000	0.800	2.000	1.100	1.100	1.124	1.142	0.867	0.828
1.000	2.000	0.925	2.000	1.100	1.100	0.987	1.129	0.831	0.842
1.000	2.000	0.900	2.000	1.100	1.100	0.991	1.132	0.854	0.839
1.000	2.000	0.100	2.000	1.500	1.500	1.379	1.222	0.583	0.753
1.000	2.000	0.400	2.000	1.500	1.500	1.095	1.197	0.766	0.775
1.000	2.000	0.700	2.000	1.500	1.500	0.945	1.173	0.872	0.798
1.000	2.000	0.900	2.000	1.500	1.500	0.993	1.157	0.934	0.813
1.000	2.000	0.100	2.000	1.750	1.750	1.379	1.223	0.457	0.752
1.000	2.000	0.300	2.000	1.750	1.750	1.130	1.209	0.668	0.765
1.000	2.000	0.500	2.000	1.750	1.750	0.991	1.195	0.804	0.777
1.000	2.000	0.700	2.000	1.750	1.750	0.960	1.181	0.894	0.790
1.000	2.000	0.900	2.000	1.750	1.750	0.920	1.167	0.875	0.803
0.500	2.000	0.056	3.000	1.200	1.400	0.692	0.669	1.685	1.663
0.500	2.000	0.169	3.000	1.200	1.400	0.677	0.642	1.701	1.694
0.500	2.000	0.281	3.000	1.200	1.400	0.646	0.612	1.709	1.716
0.500	2.000	0.394	3.000	1.200	1.400	0.622	0.565	1.714	1.735
0.500	2.000	0.506	3.000	1.200	1.400	0.604	0.490	1.736	1.753
0.500	2.000	0.619	3.000	1.200	1.400	0.575	0.375	1.716	1.773

$x_1 = x_2$, as it is in all of these cases. Therefore, the difference in the z_i values must be the only cause for the difference in the x_{12} and x_{21} values. For Series B, Table 2 reveals that for the unequal-sized molecules we have $x_{12} > x_1$ and $x_{21} < x_2$, where $x_1 = x_2 = 0.5$ due to the larger total coordination number of species-1 as opposed to species-2 because its interaction volume is larger. Species-1 is larger than species-2, so $z_1 > z_2$. The mean-field model treatment again is capable of reproducing these values remarkably well.

In Table 3 we consider the local composition ratios, $r_1 = x_{21}x_1/x_2x_{11}$ and $r_2 = x_{12}x_2/x_{22}x_1$. These ratios are also measures of the extent of non-random mixing or local composition effects. In the $\bar{\rho} \rightarrow 0$ limit for equi-sized equimolar binary mixtures we have,

$$r_1 = \frac{x_{21}x_1}{x_2x_{11}} = \exp(\beta(\varepsilon_{21} - \varepsilon_{11})), \quad (53)$$

$$r_2 = \frac{x_{12}x_2}{x_1x_{22}} = \exp(\beta(\varepsilon_{12} - \varepsilon_{22})), \quad (54)$$

Table 4 Local mole fraction ratio, $r_3 = x_{21}x_{12}/x_{22}x_{11}$, calculated directly from simulation (MC) and from the QCA model (MOD). Key: $x_1 = x_2 = 0.5$.

σ_2/σ_1	$\varepsilon_2/\varepsilon_1$	$\bar{\rho}$	T/ε_{11}	λ_1	λ_2	$r_{3,MD}$	$r_{3,MOD}$
1.000	2.000	0.100	2.000	1.100	1.100	0.952	0.921
1.000	2.000	0.200	2.000	1.100	1.100	0.964	0.925
1.000	2.000	0.400	2.000	1.100	1.100	0.888	0.932
1.000	2.000	0.500	2.000	1.100	1.100	0.956	0.936
1.000	2.000	0.800	2.000	1.100	1.100	0.974	0.946
1.000	2.000	0.900	2.000	1.100	1.100	0.794	0.950
1.000	2.000	0.100	2.000	1.500	1.500	0.804	0.920
1.000	2.000	0.200	2.000	1.500	1.500	0.743	0.923
1.000	2.000	0.300	2.000	1.500	1.500	0.837	0.926
1.000	2.000	0.400	2.000	1.500	1.500	0.839	0.928
1.000	2.000	0.500	2.000	1.500	1.500	0.789	0.931
1.000	2.000	0.600	2.000	1.500	1.500	0.773	0.933
1.000	2.000	0.700	2.000	1.500	1.500	0.823	0.936
1.000	2.000	0.800	2.000	1.500	1.500	0.898	0.939
1.000	2.000	0.900	2.000	1.500	1.500	0.927	0.941
1.000	2.000	0.100	2.000	1.750	1.750	0.631	0.920
1.000	2.000	0.300	2.000	1.750	1.750	0.755	0.924
1.000	2.000	0.500	2.000	1.750	1.750	0.797	0.929
1.000	2.000	0.700	2.000	1.750	1.750	0.859	0.933
1.000	2.000	0.900	2.000	1.750	1.750	0.806	0.938
1.000	2.000	0.700	2.000	1.750	1.750	1.066	0.933
0.500	2.000	0.056	3.000	1.200	1.400	1.166	1.114
0.500	2.000	0.169	3.000	1.200	1.400	1.152	1.088
0.500	2.000	0.281	3.000	1.200	1.400	1.103	1.050
0.500	2.000	0.394	3.000	1.200	1.400	1.066	0.980
0.500	2.000	0.506	3.000	1.200	1.400	1.049	0.859
0.500	2.000	0.619	3.000	1.200	1.400	0.986	0.664

In the $\bar{\rho} \rightarrow 0$ limit the model formulae (which reduces to Eqs. (53) and (54)) should agree exactly with the simulation data. Agreement with this and the density dependence produced by Lee, Sandler and Patel³ is achieved: the simulated ratio, r_1 starts at ~ 1.2 at $\bar{\rho} \rightarrow 0$. Also, $r_2 \sim 0.8$ at $\bar{\rho} \rightarrow 0$, the same as the model predictions, within statistics. For the least attractive species, the ratio goes to unity in the close-packed limit, whereas the species-2 ratio r_2 remains significantly below unity throughout the whole fluid range. This demonstrates that r_2 acts as a good probe of non-ideality. The local composition effects due to the attractive interaction are most apparent at low densities, becoming insignificant at higher densities for the least attractive component of Series A. Nonideality diminishes more rapidly with increasing density as λ the reduced range of the interaction increases, as the mean field limit is approached¹¹. For Series B shows greater nonideality, persisting to much higher densities than for series A. Again the model from Eq. (38) gives an exceptionally good representation of these ratios.

In Table 4 we present data for the ratio, $r_3 = x_{21}x_{12}/x_{22}x_{11}$. Despite containing four local coordination numbers, this ratio departs less from unity than the ratios, r_1 and r_2 for both Series A and Series B. Largely, because of cancellation from within the two subcomponent ratios x_{21}/x_{11} and x_{12}/x_{22} .

4 CONCLUSIONS

In this work, we have investigated square-well fluid mixtures over a wide range of core diameters, interaction ranges, well-depths and temperatures. We used both Monte Carlo simulation methods and a new model for the local coordinations of the components that satisfies the low density limit (known exactly), and also the detailed balance conditions for the total number of pairs. From the local coordination number ratios we have observed that the extent of local composition non-ideality due to core-size and well-depth ratios up to ~ 2 is fairly small (typically less than 20%), varying monotonically with average number density throughout the fluid range. The local coordination number model proposed here gives an excellent representation of the machine calculation data.

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