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Local Compositions and the Square-Well Fluid[1]

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Many applied thermodynamic models are based on the local composition concept, that is, that the composition of neighboring molecules around a central molecule is different from the bulk fluid composition. In this paper we consider the rigorous calculation of local compositions for a model mixture of square-well molecules via statistical mechanics using Monte Carlo simulations and integral equation theory. The results show that the currently available models do not correctly describe the density and composition dependence of the local structure.

KEY WORDS: density; local composition; Monte Carlo method; square-well fluid; statistical mechanics.

1. INTRODUCTION

The concept of local composition has been the subject of considerable interest in the analysis and development of applied thermodynamic models [1–3] such as equation-of-state mixing rules. In order to understand fully the molecular basis of these models it is useful to apply them to model systems for which the local intermolecular structure can be obtained in a rigorous and unambiguous fashion via the methods of statistical mechanics.

One system which is especially useful for this purpose is a fluid mixture in which the molecules interact with square-well potentials. In this paper we present a study of the local compositions in square-well fluid mixtures using two statistical mechanical techniques. First, we have performed Monte Carlo simulations of square-well mixtures in which the radial

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distribution functions in the fluid can be calculated in an essentially exact manner. However, since these simulations are expensive and time-consuming, it is worthwhile investigating the possibility of finding a more economical method for calculating the distribution functions. Such a method should, of course, have a rigorous foundation in statistical mechanics. To this end we have carried out calculations of the structure and thermodynamic properties of square-well mixtures using the mean spherical approximation (MSA) integral equation [4]. This theory has been shown to give reliable results for pure fluids [5]. The present work demonstrates that this is also true for mixtures.

The remainder of the paper is organized as follows. In the next section we briefly outline the concept of local compositions and review the basis of some of the widely used models. In Section III we describe our simulation and integral equation calculations. Finally, in Section IV we describe our results and make comparisons with the predictions of commonly used local composition models. In particular, we focus on the accuracy of the models in predicting the density dependence of the local compositions and, additionally, the composition dependence of the total coordination number at constant density or pressure.

2. LOCAL COMPOSITION MODELS FOR MIXTURES

In our previous work on the generalized van der Waals partition function [1, 2], we have shown that the quantity of fundamental interest is the configurational contribution to the internal energy $E^{\mathrm{CONF}}(N_1, N_2, ..., V, T)$ given by

$$E^{\mathrm{CONF}}(N_1, N_2, ..., V, T) = \sum_i \sum_j E_{ij}^{\mathrm{CONF}}(N_1, N_2, ..., V, T) \tag{1}$$

where

$$E_{ij}^{\mathrm{CONF}}(N_1, N_2, ..., V, T) = \frac{N^2}{2V} x_i x_j \int u_{ij}(r)\, g_{ij}(N_1, N_2, ..., V, T; r)\, d\mathbf{r} \tag{2}$$

In this equation E_{ij}^{CONF} is the configuration energy for i molecules around a central j molecule, $u_{ij}(r)$ and $g_{ij}(r)$ are the interaction energy and pair correlation functions for the i–j interaction, x_i and N_i are the mole fraction and mole number of species i, V is the volume, T is the temperature, and r is the radial separation distance. From the configurational energy and the use of either the Gibbs–Helmholtz relation or the generalized van der Waals partition function, the Helmholtz free energy and the fundamental equation of state of the mixture can be obtained.

Rather than the configurational energy, many recent studies have concentrated on the local compositions or local mole fractions. However, it is only for the square-well fluid

$$u_{ij}(r)=\begin{cases}\infty & r<\sigma_{ij}\\ -\varepsilon_{ij} & \sigma_{ij}<r<R\sigma_{ij}\\ 0 & R\sigma_{ij}<r\end{cases}$$

for which

$$E_{ij}^{\text{CONF}}=\frac{-N^2}{2V}x_i x_j \varepsilon_{ij}\int_{\sigma_{ij}}^{R\sigma_{ij}} g_{ij}(r)\,d\mathbf{r}=\frac{-Nx_j}{2}\varepsilon_{ij}N_{ij} \tag{3}$$

that (i) the local composition is unambiguously defined since there is no uncertainty about the nearest-neighbor cutoff distance and that (ii) the number of i molecules around a j molecule

$$N_{ij}=\frac{N}{V}x_i\int_{\sigma_{ij}}^{R\sigma_{ij}} g_{ij}(r)\,d\mathbf{r} \tag{4}$$

contains the same information as E_{ij}^{CONF}. In this communication, we concentrate, for the square-well fluid, on the species–species coordination numbers N_{ij} and the local mole fractions

$$x_{ij}=\frac{N_{ij}}{\sum_k N_{kj}} \tag{5}$$

as these are what have been considered recently [6–8].

There are two general classes of local composition models. The first involves a model for each of the N_{ij}. The second class is based on models for the ratio N_{ij}/N_{jj} (or equivalently, x_{ij}/x_{jj}) and requires another, and quite separate, assumption for the temperature, density, and composition dependence of the total coordination number

$$N_{cj}=\sum_k N_{kj} \tag{6}$$

In recent studies [1, 3] we have presented an analysis of local composition models in terms of the generalized van der Waals partition function. With this analysis it is possible to identify assumptions about the density and composition dependence of the local compositions and the total coordination number implicit in these models. The forms of the local compositions for various models are briefly summarized in Table I.

Table I. Local Composition Models and the Equation-of-State Mixing Rule to Which They Lead

Local composition and coordination number model	Equation-of-state mixing rule
(a) $N_{ij}=\frac{N_i}{V}C, \qquad i, j=1, 2$	vdW 1-fluid
(b) $N_{ij}=\frac{N_i}{V}C_{ij}, \qquad i, j=1, 2$	vdW 1-fluid
(c) $N_{ij}=\frac{N_i}{V}C_{ij}e^{\varepsilon_{ij}/kT}, \qquad i, j=1, 2$	vdW 1-fluid
(d) $N_{ij}=C_{ij}\frac{N_i}{V}\exp(\alpha\varepsilon_{ij}/kT), \qquad i, j=1, 2$ $\alpha=0.60-0.58\left(\rho\sum x_i\sigma_{ii}{}^3\right)^{0.1865}$	Hu et al. [15]
(e) $\frac{N_{ij}}{N_{jj}}=\frac{N_i}{N_j}\frac{v_j}{v_j}$ $N_{cj}=N_{ij}+N_{jj}=\frac{N}{V}C_j$	$a=\left(\sum x_i v_i\right)\sum\sum\phi_i\phi_j\frac{a_{ij}}{v_j}$, where $\phi_i=x_i v_i\Big/\sum x_j v_j$
(f) $\frac{N_{ij}}{N_{jj}}=\frac{N_i}{N_j}\frac{v_i}{v_j}e^{(\varepsilon_{ij}-\varepsilon_{jj})/kT}$ (Wilson model) $N_{cj}=N_{ij}+N_{jj}=\frac{N}{V}C_j$	As above
(g) $\frac{N_{ij}}{N_{jj}}=\frac{N_i}{N_j}\frac{C_{ij}}{C_{jj}}e^{(\varepsilon_{ij}-\varepsilon_{jj})N_c/kT}$ $N_c=\frac{N}{V}C$	Whiting and Prausnitz [14]

Having identified these assumptions we can test them by making accurate calculations of the local structure in the fluid mixture using rigorous statistical mechanics. In the next section we describe these calculations.

3. STATISTICAL MECHANICAL TOOLS

3.1. Computer Simulations

We have performed a number of computer simulations using the Monte Carlo method, for a range of binary square-well mixtures with various diameter and well-depth ratios. The details of the simulations are described in detail elsewhere [2]. The quantities calculated in these simulations were the radial distribution functions and the species coordination numbers. Table II shows the interaction parameters and state points used.

3.2. Mean Spherical Approximation

The mean spherical approximation (MSA) was suggested as a closure to the Ornstein–Zernike [9] equation by Lebowitz and Percus [4]. For a mixture the Ornstein–Zernike equation may be written

$$h_{ik}(r) = c_{ik}(r) + \sum_{j} \sum_{j} \int h_{ij}(|\mathbf{r} - \mathbf{r}'|)\, c_{jk}(|\mathbf{r}'|)\, d\mathbf{r}' \tag{7}$$

where $h_{ij}(r) = g_{ij}(r) - 1$ is the total correlation function, and $c_{ij}(r)$ is the direct correlation function. The subscripts denote the different types of correlations between the species in the mixture. In the MSA Eq. (6) is supplemented with the conditions

$$h_{ij}(r) = -1, \qquad r < \sigma_{ij} \tag{8}$$

$$c_{ij}(r) = \frac{-u_{ij}(r)}{kT}, \qquad r > \sigma_{ij} \tag{9}$$

Equation (8) is an exact result which follows from the inpenetrability of the hard-sphere cores, while Eq. (9) is an approximation. Equations (7)–(9)

Table II. Mixture Square-Well Parameters and State Points Used in the Monte Carlo Simulations and MSA Integral Equation Calculations

Square-well parameters	
Set 1	$\varepsilon_{11}/kT = 0.4, \quad \varepsilon_{22}/kT = 0.8$
	$\sigma_{11} = \sigma_{22}, \quad R_{11} = R_{22} = 1.5$
Set 2	$\varepsilon_{11}/kT = \varepsilon_{22}/kT = 0.4$
	$\sigma_{22} = 1.5\,\sigma_{11}, \quad R_{11} = R_{22} = 1.5$
State points	
MSA	$x_1 = 0.125$ to 0.875 in increments of 0.125
	$\rho\bar{\sigma}^3 = 0.1$ to 0.7 in increments of 0.1
MC	$x_1 = 0.25$ to 0.75 in increments of 0.25
	$\rho\bar{\sigma}^3 = 0.1$ to 0.7 in increments of 0.2
	$\bar{\sigma}^3 = x_1 \sigma_{11}{}^3 + x_2 \sigma_{22}{}^3$

may be solved simultaneously to obtain the total and direct correlation functions at a given temperature and density. To do this we have used the efficient and stable method developed by Gillan [10] and extended to mixtures by Abernethy and Gillan [11]. In these numerical solutions we have used a grid size of $0.05\sigma_{11}$ and a maximum value of r of $6.4\sigma_{11}$.

Once the distribution functions have been obtained, the coordination numbers may be calculated, as well as other thermodynamic properties. Due to the approximate nature of the MSA, the values of thermodynamic properties obtained via different routes are not consistent with each other. For pure square-well fluids, Smith et al. have found that the energy equation route is the most satisfactory and gives excellent agreement with computer simulation results except at low densities. Additionally, of course, this is the route which is thermodynamically consistent with the calculations of coordination numbers from the distribution functions. Hoye and Stell [12] have shown that all the energy equation thermodynamic

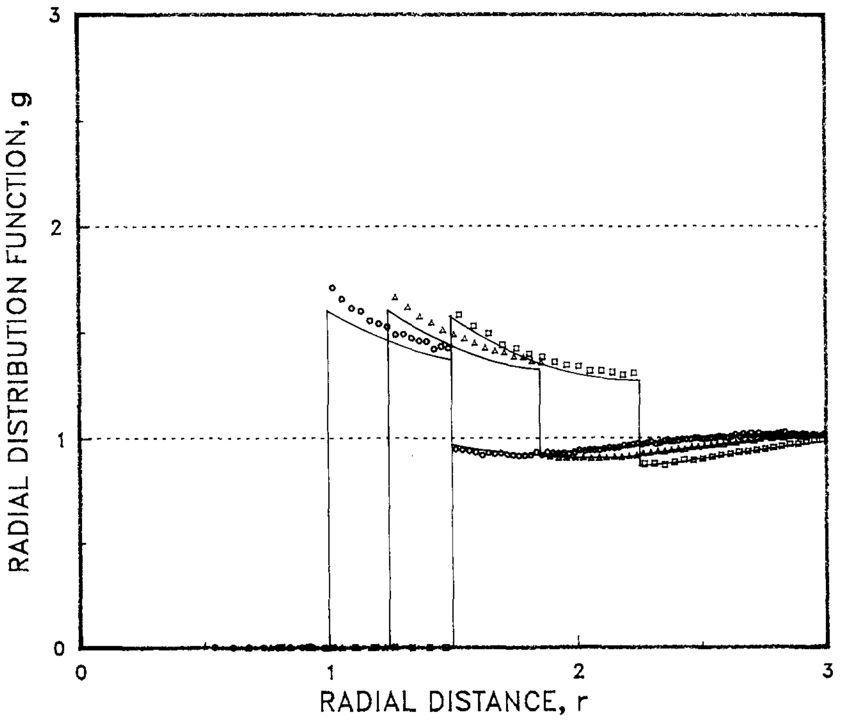

Fig. 1. The radial distribution function for a square-well mixture in which $\sigma_1 = 1.5$, $\sigma_2 = 1.0$, $\varepsilon_{11} = \varepsilon_{22} = 0.4$, $\rho\sigma^3 = 0.3$, and $x_1 = 0.5$. The lines are the result of MSA and the points ○, △, and □ are the Monte Carlo results for g_{11}, g_{12}, and g_{22}, respectively.

properties in the MSA may be obtained directly from the distribution functions without recourse to numerical thermodynamic integration or differentiations. Therefore, thermodynamic properties from the MSA used in this paper were obtained using the energy equation.

4. RESULTS

As mentioned above, there are two aspects to the present paper. First, we wish to demonstrate the efficiency of using the MSA as an economical and accurate probe of the local structure in these mixtures, which can then be used in more extensive investigations. Second, we wish to use results from both the simulations and the MSA to investigate the accuracy of key assumptions inherent in the local composition models used currently.

Figures 1 and 2 show the representative comparisons of the distribution functions in square-well mixtures calculated from the MSA with those from the Monte Carlo simulations. The agreement is excellent,

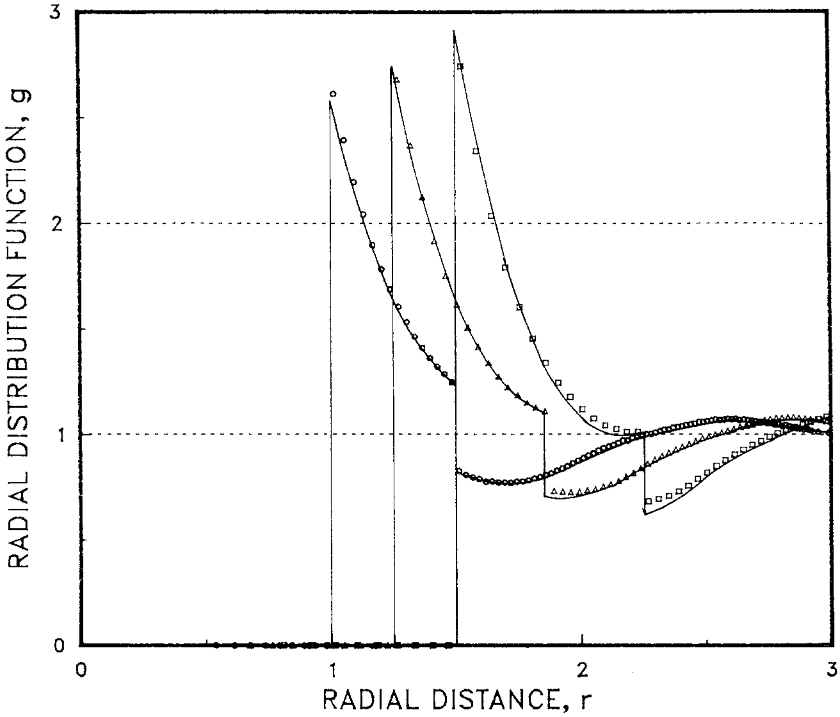

Fig. 2. The radial distribution function for the same square-well mixture with $\rho\sigma^3 = 0.7$. Legend as for Fig. 1.

especially at a high density, which is impressive since the MSA calculations are very quick and inexpensive. Having thus established the accuracy of the MSA, many of the comparisons which follow will be with the MSA results. It should be noted, however, that the MSA is not correct in the limit of zero density and, therefore, contains some error at low densities as well.

From the radial distribution functions the spcial-species coordination numbers, N_{ij}, can be calculated from Eq. (4), and the total coordination number from Eq. (6). Figure 3 is a plot of the ratios as a function of reduced density $\rho\overline{\sigma}^3$ and composition. Shown are the results of Monte Carlo simulation, MSA theory, and the various local composition models in Table I. From Fig. 3 we see the general agreement between the Monte Carlo and the MSA results for this very sensitive ratio and the lack of agreement of all the local composition models with the data derived from statistical mechanics. We believe that the small systematic discrepancy between the Monte Carlo and the MSA results is related to the incorrect low-density behavior of the MSA.

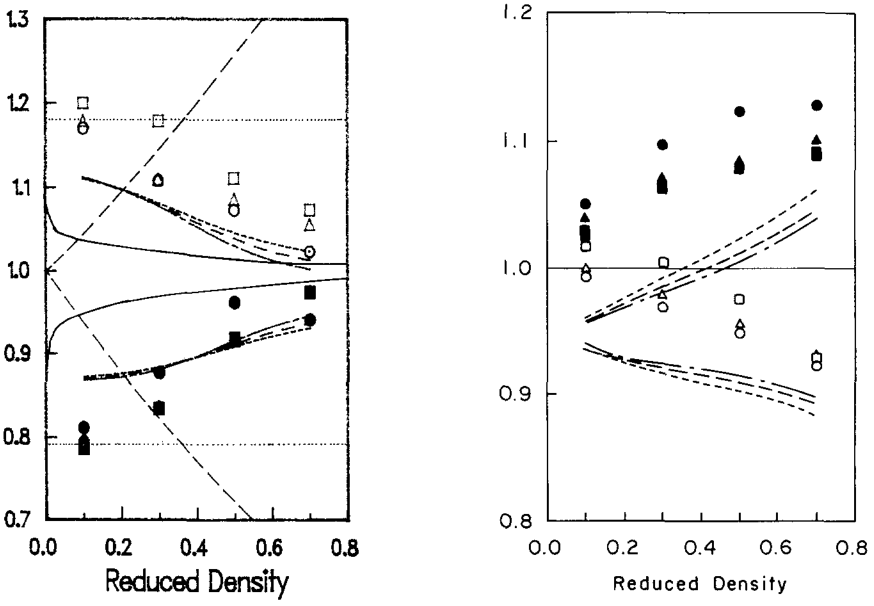

Fig. 3. The local composition ratios $N_{21}N_1\sigma_{11}^3/N_{11}N_2\sigma_{22}^3$ (top) and $N_{12}N_2\sigma_{22}^3/N_{22}N_1\sigma_{12}^3$ (bottom) as a function of density for (a) $\sigma_{11}=\sigma_{22}=1$, $\varepsilon_{11}/kT=0.4$, and $\varepsilon_{22}/kT=0.8$ and (b) $\sigma_{11}=1$, $\sigma_{22}=1.5$, and $\varepsilon_{11}/kT=\varepsilon_{22}/kT=0.4$. These ratios would be unity in a completely random mixture. The points ■ and □, ▲ and △, and ● and ○ results from Monte Carlo simulation at $x_1=0.25$, 0.5, and 0.75, respectively. The lines —·—, — —, and ---- are from MSA at the same compositions. The remaining lines, ····, ----, and —— result from the models of Wilson [13], Whiting and Prausnitz [14], and Hu et al. [15] in (a).

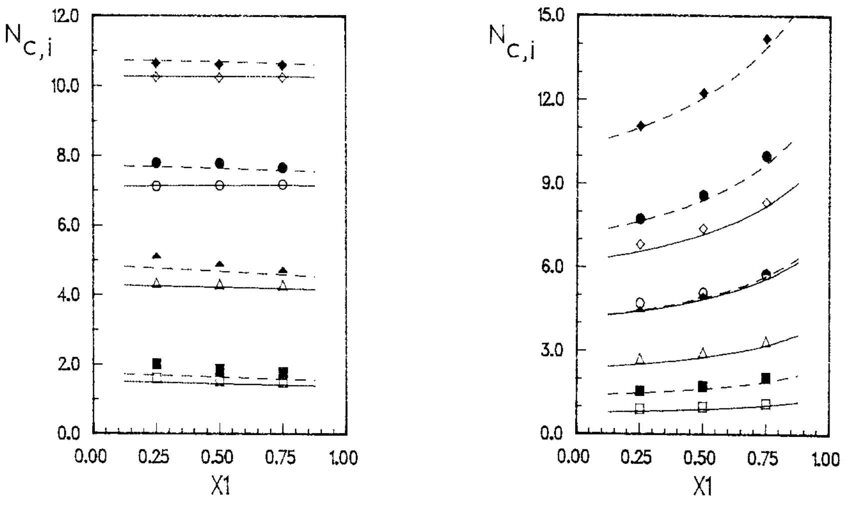

Fig. 4. The total coordination numbers N_{c1} and N_{c2} as a function of composition at a constant reduced density. The points □, △, ○, and ◇ and the lines —— results form the MSA and Monte Carlo simulation for the reduced densities $\rho\sigma^3$ of 0.1, 0.3, 0.5, and 0.7 for N_{c1}, while the points ■, ▲, ●, and ◆ and the lines ---- are for N_{c2}. (a) For mixture $\sigma_{11} = \sigma_{22} = 1.0$, $\varepsilon_{11}/kT = 0.4$, and $\varepsilon_{11}/kT = 0.8$; (b) for $\sigma_{11} = 1.0$, $\sigma_{22} = 1.5$, and $\varepsilon_{11}/kT = \varepsilon_{22}/kT = 0.4$.

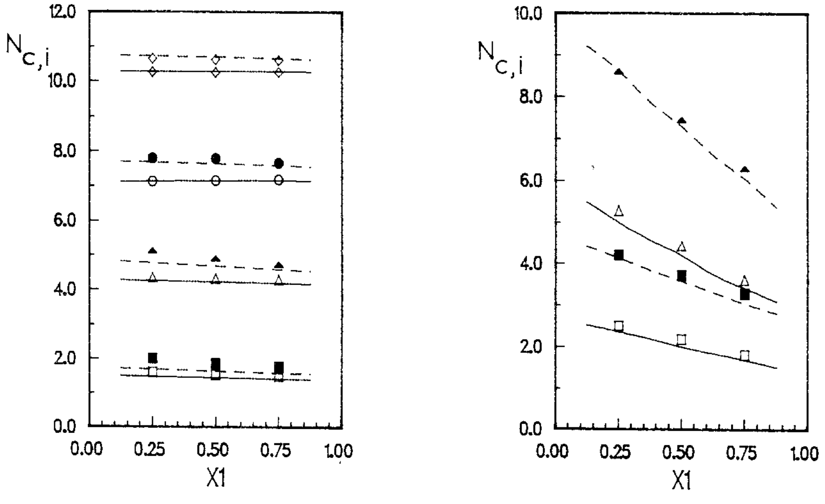

Fig. 5. The total coordination numbers N_{c1} and N_{c2} as a function of composition at constant number density. Legend as for Fig. 4 except for densities ρ of 0.1, 0.3, 0.5, and 0.7.

The second assumption imbedded in some local composition models (models e, f, and g in Table I) is that the total coordination number is constant as a function of the mole fraction. This assumption is tested in Figs. 4–7, where we examine the composition dependence of the total coordination numbers as a function of the mole fraction at constant density, constant reduced density $\rho\overline{\sigma^3}$, and constant pressure. In Fig. 4 we see that, at a constant reduced density, the total coordination number is approximately constant with composition for equal-size molecules but increases for both the large and the small molecules with the mole fraction of the small molecule in the equal-well-depth, unequal-size mixture.

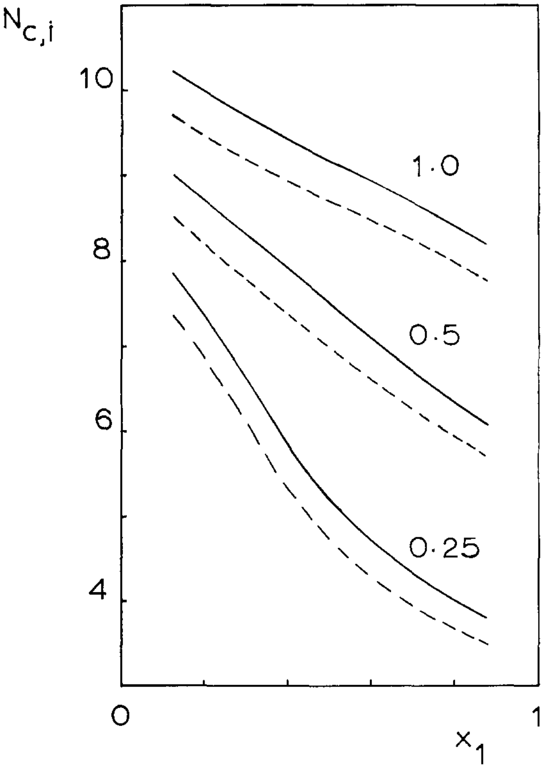

Fig. 6. The total coordination number for each species in a mixture of equal-size square-well molecules versus composition at constant pressure. The interaction parameters are $\varepsilon_{11}/kT = 0.4$ and $\varepsilon_{22}/kT = 0.8$. The solid line gives the results for component 2, and the dashed line that for component 1. Results for three pressures are shown, and the curves are marked with the value of P/kT.

Figure 5 shows that as the mole fraction of the small molecule increases, the total coordination number for both the large and the small molecules decreases at a constant reduced density. (Note that for the equal-size mixture constant density and constant number density are identical.) Finally, in Figs. 6 and 7 we see that for compositional changes at constant

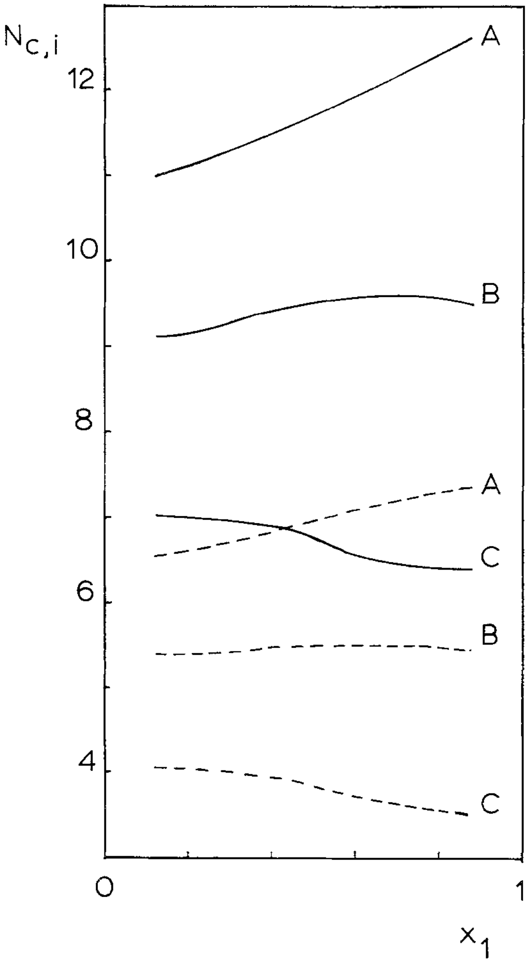

Fig. 7. The total coordination number for each species in a mixture of different-size square-well molecules versus composition at constant pressure. The interaction parameter are $\sigma_{11} = 1.0$, $\sigma_{22} = 1.5$, and $\varepsilon_{11}/kT = \varepsilon_{22}/kT = 4$. The solid line gives the results for component 2, and the dashed line that for component 1. The letters marking each curve denote the value of P/kT: (A) 1.0; (B) 0.5; (C) 0.25.

pressure in the unequal-size mixture, the total coordination numbers of both the large and the small molecules decrease with increasing mole fraction of the smaller species at low pressure, are approxmately constant at moderate pressures, and increase at high pressures.

5. CONCLUSIONS

In this communication we have shown, by comparison with the results of Monte Carlo simulation, that at moderate and high densities ($\rho\overline{\sigma^3} \geqslant 0.3$) the mean spherical approximation is a computationally efficient method of obtaining accurate structural and local composition information about mixtures of square-well molecules. Presumably, other integral equation methods would also be useful for this kind of study with more general potential models.

Next, we have shown in Fig. 3 that local compositions different from the bulk compositions do exist, but none of the local composition models for the ratios N_{ij}/N_{jj} currently used are in agreement with statistical mechanical calculations. Since such local composition models are the basis for equation-of-state mixing rules and activity coefficient equations, further study of local compositions (or more correctly, the configurational energies E_{ij}^{CONF}) is clearly justified.

Also imbedded into some local composition models, such as that of Wilson [13] and of Whiting and Prausnitz [14], is the lattice model assumption that the total coordination number around a molecule is independent of the mole fraction. We have shown here that except for the case of equal-size molecules, this assumption is incorrect. In particular, for the unequal-size molecular mixture studied here, with increasing mole fraction of the smaller molecule, the total coordination numbers of both species increase at constant density, decrease at constant reduced density, and, depending on the system pressure, either increase or decrease at constant pressure.

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