On the Concentration Fluctuations of a Binary Mixture of Hard Spheres

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We have computed the concentration fluctuations, $S_{cc}(0)$, in a binary mixture of hard spheres on the basis of the Percus-Yevick compressibility (PYC), Percus-Yevick virial (PYV) and Mansoori-Carnahan-Starling (MCS) equations of state. We have also used the Flory-Huggins (FH) model for an athermal solution as a first approximation to the hard sphere description. At fluid packing fraction values, the PYC and MCS theories give similar $S_{cc}(0)$ results, whereas the differences between these and those derived from the PYV equation are more significant. The FH model appears to give rather bad results, which is consistent with the studies of other authors on the entropy of mixing of a binary mixture of hard spheres. The impossibility of a fluid-fluid phase transition in this kind of system is clearly shown by the behaviour of $S_{cc}(0)$ in any of the theories studied.

1. Introduction

The Flory-Huggins (FH) model of solutions [1, 2] is often used to describe the thermodynamic properties of liquid mixtures whose molecules differ greatly in size. For a (non athermal) binary mixture, the FH expression for the Gibbs free energy of mixing reads

$$\Delta G_{\mathrm{FH}} = R\,T(c_1 \ln \phi_1 + c_2 \ln \phi_2) + R\,T\,c_1 \phi_2 W, \qquad (1)$$

where R is the gas constant, ϕ_i the concentration by volume of the species with concentration c_i, and W a parameter defined by $W = \omega/k\,T$, where ω is the interchange energy and k the Boltzmann constant. Originally, the FH model was proposed for treating polymer solutions, but it has proved to be a useful tool for studying the characteristics of more general classes of mixtures. For example, Bhatia et al. [3–5] have used the FH model to describe the properties of binary and pseudobinary liquid alloys with a large size mismatch.

If in (1) ω is assumed independent of T, the entropy of mixing is given by

$$\Delta S_{\mathrm{FH}} = -\,R(c_1 \ln \phi_1 + c_2 \ln \phi_2). \qquad (2)$$

An improvement on (1) is obtained by using for ΔS_{FH} the more general expression corresponding to a hard spheres system, as has been pointed out by Visser et al. [6] and Hoshino [7] (see also Umar et al. [8]). The hard sphere description for the entropy contains physical features (packing, mismatch and excess volume contributions) that the FH expression is incapable of describing. This modified form of (1) has been used to study the thermodynamic properties of liquid mixtures of both conductors [6, 9] and insulators [10, 11]. A model of mixtures of hard spheres of different sizes, between which there are long-range attractive forces, has recently been used by Rowlinson and co-workers [12] to reproduce some of the behaviour of micellar solutions, the micelles being the large spheres and the solvent molecules the smaller ones.

In our recent work [10, 11] on the thermodynamic properties of mixtures of globular organic molecules, we focussed on the concentration-concentration partial structure factor $S_{cc}(0)$. This quantity was originally introduced by Bhatia and Thornton [13], and its usefulness has been discussed in detail elsewhere [5, 14]. In particular, for an ideal solution $S_{cc}(0) = c_1 c_2$. If $S_{cc}(0) < S_{cc}^{\mathrm{id}}(0)$ at a particular composition, unlike-species nearest-neighbour pairs are preferred to like-species pairs, and conversely for $S_{cc}(0) > S_{cc}^{\mathrm{id}}(0)$. Thus $S_{cc}(0)$ provides fundamental information about the

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arrangement of the molecules in the mixture, an effect which depends on both their geometrical structure and the tails of the intermolecular potentials. When studying mixtures of globular molecules, it may be useful to inquire into the effect of size differences on $S_{cc}(0)$ by investigating a hard spheres system, so leaving aside the question of the effect of attractive forces.

The characteristic behaviour of $S_{cc}(0)$ in mixtures of hard convex particles (hard spheres, in particular) has recently been studied by Gallego and Silbert [15] using scale particle theory [16,17]. The results for hard spheres are the same as those that can be derived from the Percus-Yevick compressibility (PYC) equation of state [18]. However, other approximations are available, and it may be worthwhile to compare the results obtained with different theories. In the present paper we present calculations of $S_{cc}(0)$ for a mixture of hard spheres obtained using the Percus-Yevick virial [18] (PYV) and the Mansoori-Carnahan-Starling [19] (MCS) equations of state. The results will be compared with those derived from the PYC equation. We shall also use the FH model for an athermal solution ((1) with $W = 0$), which can be considered as a first approximation to the hard sphere description [6, 7]. Recent computer simulations of mixtures of hard spheres performed by Jackson et al. [20] (see also [21–24]) show that the MCS equation of state is very accurate for mixtures in the fluid range, as it is for pure components [25]. Significant discrepancies only occur at high densities and/or large mismatch [20].

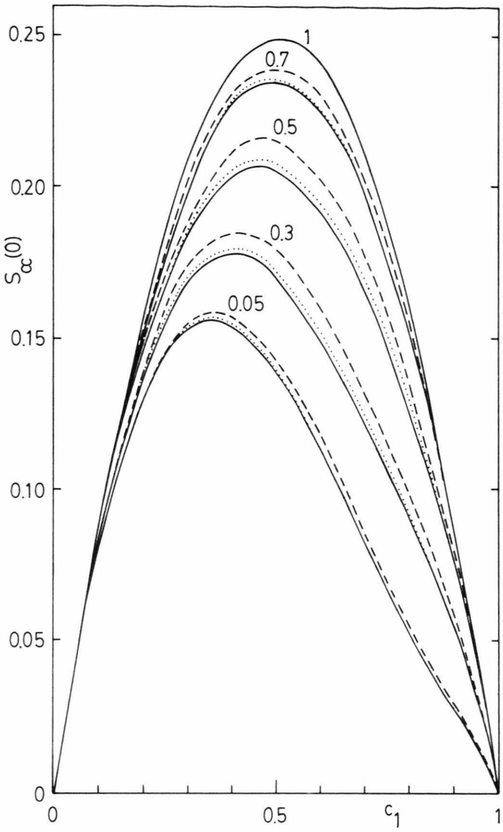

Fig. 1. $S_{cc}(0)$ calculated for mixtures of hard spheres using the PYV (---), MCS (...) and PYC (——) approximations, at $Z = 5$, as a function of the concentration of the smaller component. The numbers labelling the different groups of curves are the values of the diameter ratio $R = R_1/R_2$. The value $R = 1$ leads to the ideal solution curve $S_{cc}^{id}(0) = c_1 c_2$ in all cases.

2. Concentration Fluctuations in Hard Sphere Systems

We have calculated $S_{cc}(0)$ for a binary mixture of hard spheres from the expression [5]

$$S_{cc}(0) = \frac{kT(1-c_1)}{(\partial\mu_1/\partial c_1)_{T,P}}, \tag{3}$$

where μ_1 is the chemical potential of component 1, which we have taken to be the smaller one. The analytical expressions for μ_1 given by the PYC, PYV and MCS approaches may be found elsewhere [18, 26]. According to (3), the evaluation of $S_{cc}(0)$ entails solving both the equation of state [18, 26] (to ensure constant pressure at all concentrations) and the first derivative of μ_1. The results given below are presented in terms of the dimensionless units $Z = P V_2/kT$, where V_2 is the volume of a particle of component 2, and $R = R_1/R_2$, $R_i (i = 1, 2)$ being the diameter of a particle of species i.

Figure 1 shows the results for $Z = 5$, which span fluid packing fraction values, $\eta \le 0.49$ (when $R \neq 1$, crystallization occurs at packing fractions of about 0.50–0.53 [20]; when $R = 1$, at $\eta = 0.49$ [27]). It can be seen that there are only small differences between the $S_{cc}(0)$ values obtained using the PYC and MCS approaches. However, the discrepancies between these and the PYV results are significant. All three theories lead to the ideal solution curve for equal-sized hard spheres. In Fig. 2 we present the results for $Z = 1$, which correspond to low packing fractions ($\eta \le 0.28$). As expected, the differences between the various theories are smaller in this case, the PYC and MCS curves being practically identical.

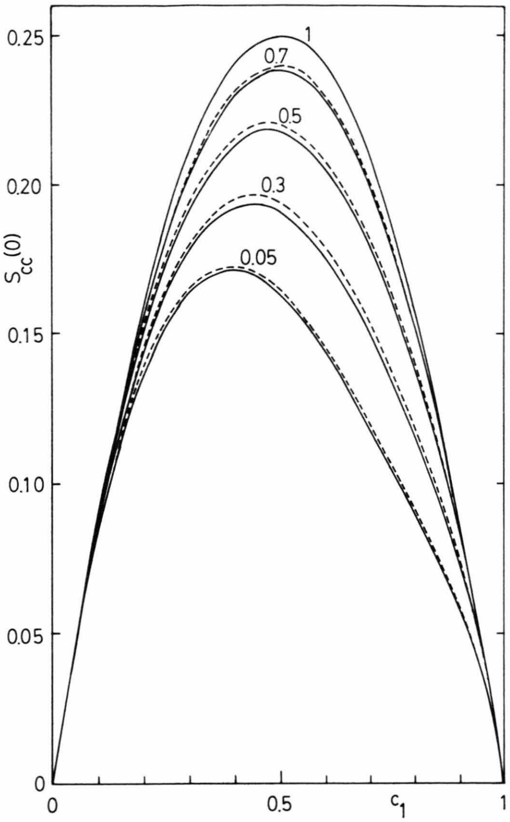

Fig. 2. Same as Fig. 1 but for $Z = 1$. Here (——) corresponds to the PYC and MCS theories, and (– – –) to the PYV approach.

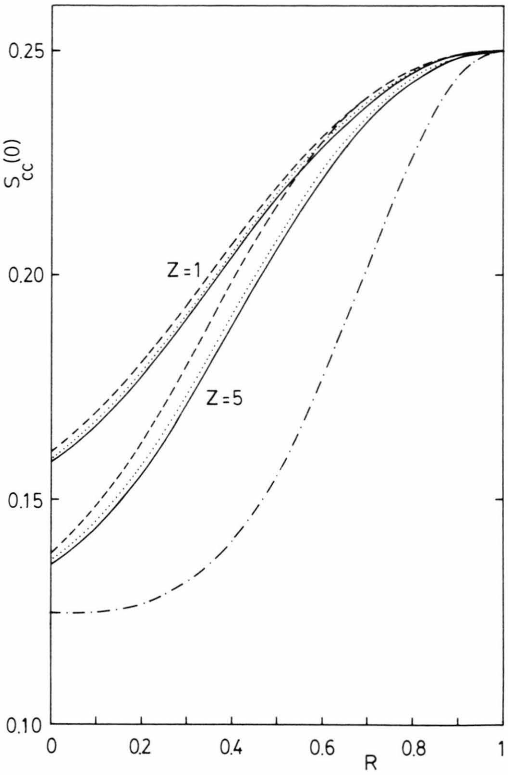

Fig. 3. $S_{cc}(0)$ calculated as a function of the diameter ratio for equimolecular mixtures of hard spheres ($Z = 1$ and $Z = 5$) using the PYV (– – –), MCS (...) and PYC (——) approximations and the FH model for an athermal solution (– · –).

In Fig. 3 we have plotted $S_{cc}(0)$ as a function of the diameter ratio for an equimolecular mixture of hard spheres. In all cases $S_{cc}(0)$ decreases monotonically as $R \to 0$. This result might appear to be in disagreement with the results of Giunta et al. [28]; however, Giunta et al. calculated $S_{cc}(0)$ at constant packing fraction, rather than at constant pressure. Figure 3 also shows the $S_{cc}(0)$ curve obtained using the FH model for an athermal solution, which is given by [5]

$$S_{cc}(0) = c_1 c_2/(1 + c_1 c_2 \delta^2), \quad (4)$$

where

$$\delta = (\beta - 1)/(c_1 \beta + c_2), \quad (5)$$

β being the ratio of the volumes per particle of the pure species. This has been assumed to be equal to the volume ratio of the particles. It can be seen that the FH predictions agree poorly with those of the other theories. This is consistent with the findings of Reatto et al. [29], who found that FH-based values for the entropy of mixing of a binary mixture at constant pressure agreed poorly with those calculated for hard spheres on the basis of the MCS equation.

Figures 1 and 2 show that a hard sphere system always has a tendency to heterocoordination, on account of topological arrangements which are energetically more favourable for this kind of system. No tendency to phase separation or appreciable fluctuations is possible in the absence of attractive forces, which is consistent with the studies of Lebowitz and Rowlinson [18] on the thermodynamic properties of mixtures of hard spheres. The tendency to heterocoordination increases with size mismatch, the $S_{cc}(0)$ curves becoming more asymmetric and their peaks moving towards the bigger-spheres-rich end. These effects are by no means sufficient to explain the observed anomalies in $S_{cc}(0)$ for some real systems [5, 30]; these must therefore be due to the influence of the long range part of the intermolecular potentials, which can either add to or subtract from the hard sphere contribution. (Differences in shape can also affect the behaviour of $S_{cc}(0)$, leading in some limiting cases to the isotropic-anisotropic phase separation [31].)

We may thus conclude that at fluid packing fractions values the PYC results for $S_{cc}(0)$ are similar to those derived from the nearly exact MCS equation, whereas the PYV results differ significantly from both. In all three theories, the tendency of hard spheres systems to heterocoordination as size mismatch increases is clearly reflected in the behaviour of $S_{cc}(0)$, which shows the usefulness of this quantity as a measure of aggregation in liquid mixtures.

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