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Deriving the equation of state of additive hard-sphere fluid mixtures from that of a pure hard-sphere fluid

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Abstract

We have analyzed the rate of convergence of a series expansion, in terms of the density, of the ratio of the excess compressibility factor of fluid mixtures of additive hard spheres to that of a pure hard-sphere fluid with the same reduced density. The terms in the series can be obtained from the virial coefficients. We have found that the series converges quickly, so that frequently the knowledge of the first two terms of the series, that can be obtained from the second and third virial coefficients which are known analytically, is sufficient to provide an accurate equation of state.

Keywords: Equation of state; Hard spheres; Binary mixtures; Virial coefficients

1. Introduction

For many years, there have been a continued interest in the study of the thermodynamic and structural properties of additive hard-sphere fluid mixtures. Some efforts have been directed towards the determination of these properties by means of computer simulation [1–7]. Other efforts have been devoted to numerical calculation of the virial coefficients [8–15]. Considerable attention has been paid too to derive approximate analytical expressions for higher order virial coefficients [16,17] and to the development of analytical expressions for the equation of state [18–26]. In recent years, a question which has raised great interest [27–29] is the possible existence of a demixing phase transition in additive hard sphere binary mixtures. Up to now, theoretical results have been controversial, because to answer that question with confidence an analytical equation of state, which must be very accurate even for extreme diameter ratios and mole fractions, is needed, and this is at present an unsolved problem.

A way to obtain the exact equation of state of any fluid, at least from a theoretical viewpoint, is the virial expansion. However, in practice only a limited number of the first virial coefficients are known at best, the first five in the case of the additive hard-sphere binary mixtures, for a considerable range of diameter ratios, and not exactly beyond the third. Moreover, the virial expansion converges slowly, so that the truncated virial expansion gives accurate results only at low densities.

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To obtain expressions for the equation of state of hard-body fluids accurate even at high densities on the basis of the knowledge of a small number of virial coefficients, one resorts frequently to *approximants*. These are suitable functions of the density with a number of unknown parameters which are determined from the condition that the series expansion of the function must reproduce the known virial coefficients.

In this work we propose a function of this kind and we will analyze its performance by comparing its predictions with available simulation data. We will introduce the new equation of state in the next section and discuss the results in Section 3.

2. The equation of state

Consider a binary mixture of additive hard spheres (HS) with diameter ratio $R=\sigma_{11}/\sigma_{22}$, where subscript 1 refers to the bigger spheres, mole fractions x_1 and x_2 and reduced density $\rho^*=\rho\sigma_{\text{mix}}^3$, where $\rho=N/V$ is the number density and $\sigma_{\text{mix}}^3=\sum_i x_i\sigma_{ii}^3$. It is obvious that in the limit $R=1$ the compressibility factor $Z_{\text{mix}}^{\text{HS}}$ of the mixture will be equal to Z^{HS}, the compressibility factor of a monodisperse hard-sphere fluid. For values of R close to 1, the ratio $(Z_{\text{mix}}^{\text{HS}}-1)/(Z^{\text{HS}}-1)$ will be close to 1 too. Thus, it seems worthwhile to attempt to relate the excess compressibility factor of the mixture to that of the monodisperse fluid, and express the deviation of the above-mentioned ratio as a series expansion in terms of the density. Therefore, we propose to obtain the equation of state of additive hard spheres in the form

$$Z_{\text{mix}}^{\text{HS}}=1+(Z^{\text{HS}}-1)\sum_{n=0}^{m}a_n\rho*^n \tag{1}$$

and determine the coefficients a_n from the condition that the series expansion of this equation in terms of the reduced density ρ^* must reproduce the known $m+2$ virial coefficients. We expect that the series (1) will converge quickly, because it was shown [24] that the ratio $(Z_{\text{mix}}^{\text{HS}}-1)/(Z^{\text{HS}}-1)$ is, as a good approximation, a linear function of the density, at least for not too extreme values of the size ratio R. The coefficients a_n in the series (1) are given by

$$a_n=\frac{b^{(n+2)}-\sum_{i=0}^{n-1}a_ib_0^{(n+2-i)}}{b_0^{(2)}},\quad n\geqslant 1, \tag{2}$$

with $a_0=b^{(2)}/b_0^{(2)}$, where $b^{(n)}$ is the virial coefficient of order n in the virial expansion of the compressibility factor $Z_{\text{mix}}^{\text{HS}}$ of the mixture in terms of the reduced density ρ^* and $b_0^{(n)}$ that corresponding to the monodisperse fluid.

Therefore, to completely determine the equation of state, first of all we need the virial coefficients of the mixture. The second and third virial coefficients are known analytically [8,30]. In the expansion of $Z_{\text{mix}}^{\text{HS}}$ in terms of the number density ρ, the second virial coefficient can be expressed in the form [31]

$$B^{(2)}=\sum_i\sum_j x_ix_jB_{ij}^{(2)}, \tag{3}$$

where $i,j=1,2$,

$$B_{ij}^{(2)}=4\left(\frac{\pi}{6}\right)\sigma_{ij}^3, \tag{4}$$

and, for additive hard spheres $\sigma_{ij}=(\sigma_{ii}+\sigma_{jj})/2$.

The third virial coefficient can be expressed exactly in the form [31]

$$B^{(3)}=\sum_{i,j,k}x_ix_jx_kB_{ijk}^{(3)}, \tag{5}$$

where $i,j,k=1,2$,

$$B_{iii}^{(3)}=10\left(\frac{\pi}{6}\sigma_{ii}^3\right)^2, \tag{6}$$

and

$$B_{iij}^{(3)}=\frac{2}{3}\left(\frac{\pi}{6}\right)^2\sigma_{ii}^3(\sigma_{ii}^3-18\sigma_{ii}\sigma_{ij}^2+32\sigma_{ij}^3). \tag{7}$$

Note that, with the present notation, $b^{(n)}=B^{(n)}/\sigma_{\text{mix}}^3$.