Equations of state for a binary mixture of hard spheres

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A new thermodynamic approach based on the exclusion factor is applied to the binary mixture of hard spheres with the size ratio 0.2 and the mole fraction of larger spheres 0.064 to derive a precise equation of state adjusted to computer simulation data.

A new theory of an equation of state based on an excluded volume has been formulated recently and used for deriving equations of state for a gaseous region.[1–4] Later, by considering higher approximations of the theory, equations of state were deduced for the entire density range[5] and compared with computer simulation data. The general equation of state for a system of hard spheres in the *n*th approximation ($n \geq 3$) can be written as

$$Z^{(n)} = \frac{1}{(1-k\varphi)^{n-1}}\left\{1 - \frac{2k(n-1)-2b_2}{(n-1)(n-2)k^2\varphi}\left[(1-k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\}, \quad (1)$$

where Z is the compressibility factor, b_2 is the second virial coefficient, φ is the packing fraction, and k is a constant that was used as a fitting parameter with respect to the computer simulation database. Equation (1) was successfully tested for a fluid of hard spheres of one size.[5] However, the theory formulated is of general character and should be applicable to a multicomponent system. Therefore, it is of interest to complement the test by applying equation (1) to a mixture of hard spheres. This was the aim of this work.

An appropriate database has been found in the literature[6] as five points of the compressibility factor isotherm computed by the Monte Carlo simulation for the binary mixture of hard spheres with the mole fraction $x \equiv x_1 = 0.064$ at the radius ratio $\lambda \equiv r_2/r_1 = 0.2$ (two first columns in Table 1). One can think that the properties of the binary system can be only slightly different from those of the pure second component at such a small value of the mole fraction of larger spheres. However, the real situation is opposite. To verify this, we have to consider the composition dependence of the second virial coefficient for a hard-sphere fluid given by the expression[2,4]

$$b_2 = \frac{4x^2 + (1+\lambda)^3 x(1-x) + 4\lambda^3(1-x)^2}{x + \lambda^3(1-x)}. \quad (2)$$

Figure 1 exhibits a deep minimum of b_2 at $x \approx 0.082$, which is close to 0.064. Therefore, we can expect the second virial coefficient for the mixture under consideration to be quite different as compared with the case of a fluid of hard spheres of one size. Indeed, the direct calculation using equation (2) at $x = 0.064$ and $\lambda = 0.2$ yields $b_2 \approx 2.069$ against the value $b_2 = 4$ for $x = 0$. This makes the test system interesting for the sake of testing equation (1).

By setting $b_2 = 2.069$ in equation (1) and using constant k as a fitting parameter with respect to the above database for various n, it was found that the best fit was attained in the fourth approximation ($n = 4$) with $k = 1.117$ and the coefficient of determination 0.999677. The fit for the fifth approximation yields a bit worse result, and this can be explained by using only a single fitting parameter for all approximations.

Table 1 Numerical representation of equation (3) as compared with computer simulation data.[6]

φ	Z (ref. 6)	$Z^{(4)}$	%
0.1729	1.516	1.509	0.46
0.1891	1.583	1.579	0.27
0.2039	1.652	1.647	0.30
0.2425	1.852	1.850	0.08
0.3006	2.241	2.245	0.18

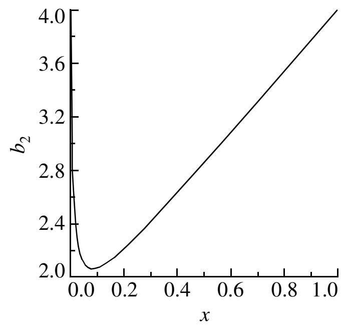

Figure 1 The dependence of the dimensionless second virial coefficient on the composition of a binary mixture of hard spheres with the size ratio 0.2 (x is the mole fraction of larger spheres).

With the above values of b_2 and k, the equation of state in the fourth approximation acquires the numerical form

$$Z^{(4)} = \frac{1-(3k-b_2)\varphi + k(k-b_2/3)\varphi^2}{(1-k\varphi)^3} \approx \frac{1-1.283\varphi + 0.478\varphi^2}{(1-1.117\varphi)^3}. \quad (3)$$

Equation (3) has been tabulated in the third column of Table 2. The deviations (%) of the compressibility factor values given by equation (3) from the computer simulation database are displayed in the fourth column. The mean deviation of about 0.26% gives evidence of a sufficiently high precision of equation (3). Therefore, we may conclude that the new theory of an equation of state based on the exclusion factor also yields an adequate description of a mixed hard-sphere fluid.

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