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Virial coefficients of hard-sphere mixtures

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The fourth and fifth virial coefficients of binary hard-sphere mixtures have been calculated for size ratios $R \geqslant 0.05$ and $R \equiv \sigma_{22}/\sigma_{11}$. The composition independent partial virial coefficients have been expressed in terms of the Mayer diagrams. The corresponding modified star diagrams were evaluated by Monte Carlo integration. The results are compared with predictions of the Boublik [J. Chem. Phys. **53**, 471 (1970)] and Mansoori *et al.* [J. Chem. Phys. **54**, 1531 (1971)] equation of state, and the excellent agreement gives strong support to the validity of that equation of state for very asymmetric mixtures. [S1063-651X(98)09904-8]

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I. INTRODUCTION

The thermodynamics of a fluid can be obtained from a knowledge of the equation of state. One standard approach is the virial expansion of the pressure in powers of the total number density [1] $\rho = N/V$,

$$Z = 1 + B_2\rho + B_3\rho^2 + B_3\rho^3 + B_5\rho^4 + \cdots, \tag{1.1}$$

where $Z = \beta P/\rho$ is the compressibility factor, β is the inverse temperature in units of the Boltzmann constant, and B_n is the nth virial coefficient. For pairwise additive interaction potential, $u(r)$, where r is the center of mass separation of the two particles, these coefficients can be defined in terms of Mayer f functions [2],

$$f(r) = \exp[-\beta u(r)] - 1, \tag{1.2}$$

and the nth virial coefficient can be expressed [3] as

$$B_n = \frac{(1-n)}{n!} \int \cdots \int d\vec{r}_2 d\vec{r}_3 \ldots d\vec{r}_n V_n, \tag{1.3}$$

where V_n is the sum of all products of f functions that doubly connect the n particles involved in the coefficient

$$V_n = \sum_{S_n} \prod_{i>j}^{n} f_{ij}(r), \tag{1.4}$$

where f_{ij} is the f function defined between particles i and j of the cluster, and $r = |\vec{r}_i - \vec{r}_j|$. The sum S_n can be expressed in diagram forms [1], for example in terms of the topologically different diagrams multiplied by their multiplicities (i.e., the number of different sets of products of f functions that can be generated by permutating the labeling of the particles of the diagram), each term of that representation of the sum is called a star diagram [1].

For a binary mixture the virial expansion coefficients are still given by Eq. (1.3), but now each coefficient $\mathbf{B}_n$ contains several summands, weighted according to the number of ways of distributing two molecular species on the n points of the diagram, and the corresponding molar fraction of each component, which can be defined for the component i in terms of its number density: $x_i = \rho_i/\rho$, as

$$\mathbf{B}_n = \sum_{i=0}^{n} \binom{n}{i} x_1^i x_2^{n-i} B(i, n-i), \tag{1.5}$$

where $B(i,n-i)$ is the summand which contributes to the nth virial coefficient whose diagrams contain i and $n-i$ particles of components 1 and 2, respectively. $B(n,0)$ denotes the nth virial coefficient of a pure fluid with particles of component 1. The partial coefficients $B(i,j)$ are composition independent, and can be evaluated through the corresponding extension to binary systems of the V_n sum expressions.

The calculation of the B_4 and B_5 coefficients in a pure fluid requires the evaluation of three and ten different star diagrams, respectively. For a mixture, the extra degree of freedom introduced by the identity of the particles increases the number of topologically different star diagrams. For example, the three equivalent four point ring star diagram of a pure fluid lead to new diagrams and lower multiplicities in the partial sum $V(2,2)$ of a binary mixture [4]. The expressions of $\mathbf{B}_5$ of a binary mixture have been reported [5]. Unfortunately, in the coloring process that followed, several equivalent diagrams of coefficient $V(4,1)$ were drawn, for instance those generated from diagrams VII and IX of $V(5,0)$ shown below in Fig. 1, and more important errors can be observed in the diagrams of $V(3,2)$ [compare Fig. 1(c) with Eq. (5) of Ref. [5]]. The main consequences of these errors are only observed at small values of R. Probably they would not have been perceived if they did not produce the

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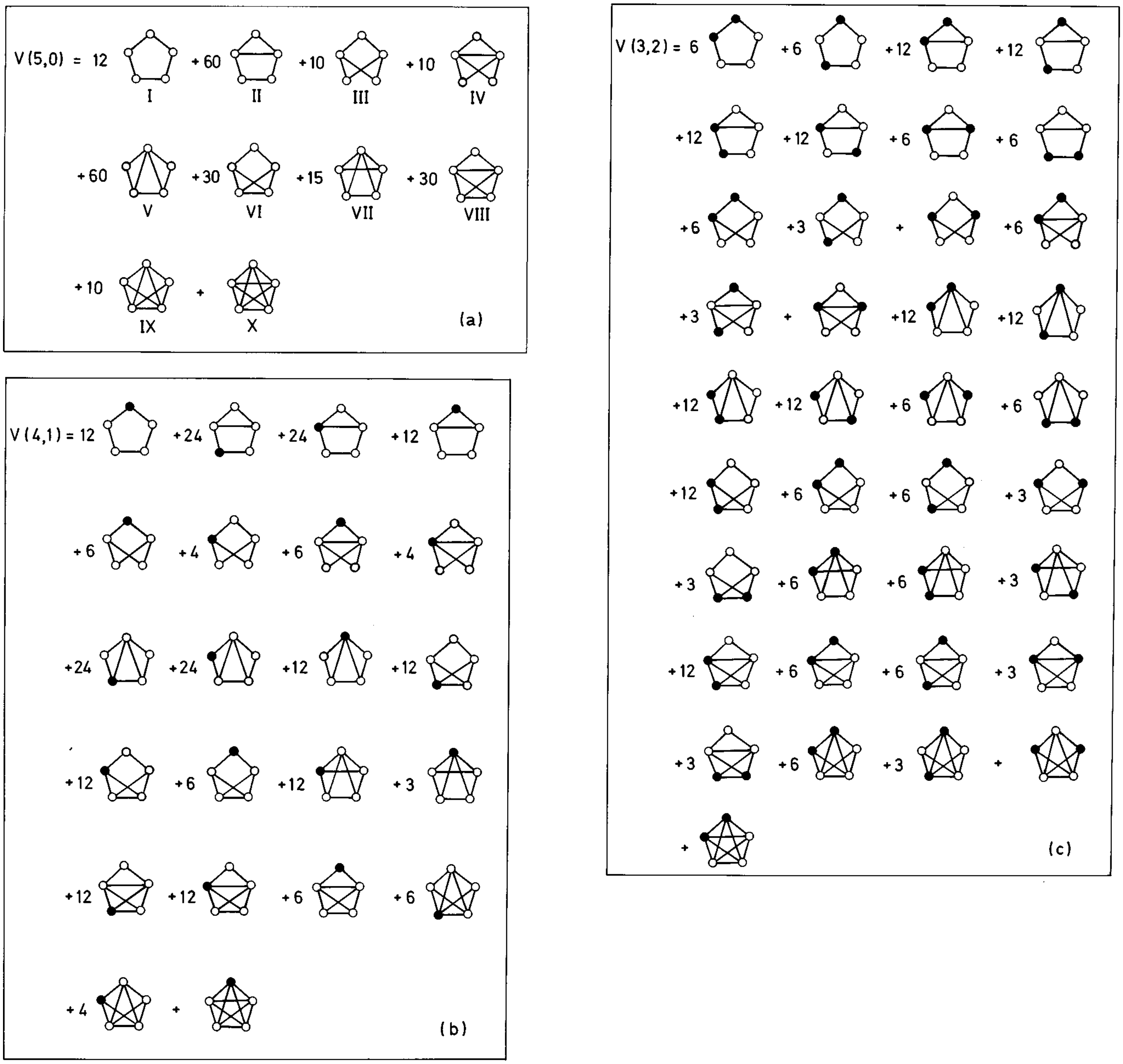

FIG. 1. The Mayer star diagrams contributing to (a) $B(5,0)$, (b) $B(4,1)$, and (c) $B(3,2)$ of a binary mixture. Continuous lines denote an f_{ij} link, and the coefficient of the diagram is its topological multiplicity. Roman numbers label the diagram according to Ref. [9].

following qualitative effects. By using the Borštnik diagrams, Saija, Fiumara and Giaquinta [6] calculated the $\mathbf{B}_5$ coefficient for binary additive hard-sphere and hard-disk mixtures, and observed that the partial coefficient $B(3,2)$ showed negative values for $R \leqslant 0.4$ and $R \leqslant 0.30$, respectively. Such a behavior is opposed to the predictions of the well established extension to hard sphere mixtures of the Carnahan-Starling equation of state, the Boublik and Mansoori *et al.* equation of state (BMCSL EOS) [7]. The negative values of the $B(3,2)$ coefficient produce a reduction of the pressure of the mixtures at certain compositions. Further, given those unexpected results Cousseart and Baus [8] suggested a perturbative correction of the BMCSL EOS to accomplish the Ref. [6] values of $\mathbf{B}_4$ and $\mathbf{B}_5$, and showed how such a correction produces fluid-fluid phase separation for binary mixtures of additive hard spheres with $R=0.15$ and $\frac{1}{3}$. Now, we know that $\mathbf{B}_5$ in such mixtures is always positive, and the reported negative values are a consequence of the errors in the previous $V(3,2)$ diagrams, which invalidate the fluid inmiscibility of such hard sphere mixtures from the perturbated EOS [8]. According to the same argument it is necessary to revise the $\mathbf{B}_5$ coefficient for hard-disk mixtures recently reported [6]. In that stage we decided to recalculate the $\mathbf{B}_4$ and $\mathbf{B}_5$ coefficients for binary hard-sphere mixtures in the asymmetry range $0.05 \leqslant R \leqslant 0.9$.

II. STAR DIAGRAMS

In Fig. 1 we show the topologically different graphs which contribute to the three distinct $\mathbf{V}_5$ sums, $V(5,0)$, $V(4,1)$, and $V(3,2)$. The calculation of the corresponding partial coefficients of $\mathbf{B}_5$ requires the evaluation of 10, 22, and 37 star diagrams, respectively. In order to reduce both the computational effort required to evaluate the Mayer

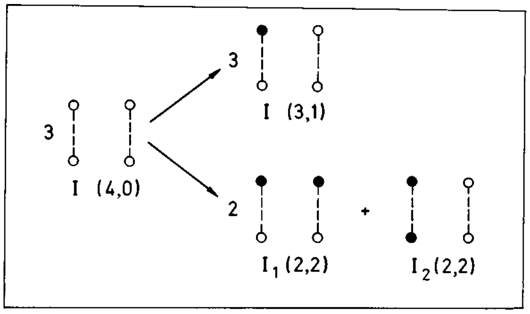

FIG. 2. The modified star diagrams of type I of the $\mathbf{B}_4$ coefficient, for the three partial sums $\widetilde{V}(4,0)$, $\widetilde{V}(3,1)$, and $\widetilde{V}(2,2)$ of a binary mixture. Dashed lines denote an $\widetilde{f}_{ij}$ link, and no drawing means an f_{ij} link.

expressions and numerical errors, we have extended to mixtures the expressions of V_n based in the modified star diagram sums, $\widetilde{S}_n$, of pure fluids developed by Ree and Hoover [3]. The key point of that approach is the dominant effect of the complete star diagram over the rest of the modified diagrams, which represent small contributions to the total value of the coefficient. We define $\widetilde{f}_{ij}=f_{ij}+1$, and introduce that function for every pair of particles no directly connected by a f_{ij} link through the identity $1=\widetilde{f}_{ij}-f_{ij}$. Each diagram with pairs of points not directly connected generates new diagrams with two kinds of links: f_{ij} and $\widetilde{f}_{ij}$ lines. For a pure fluid the three and ten topologically different types of star diagrams which define S_4 and S_5 are reduced to two and five different types of modified stars $\widetilde{S}_4$ and $\widetilde{S}_5$, respectively [3]. For a binary mixture, we only need to introduce the molecular label of the particles, and to consider how the topological multiplicity of each diagram is reduced. For example, if we introduce two particles of a second component on the incomplete modified graph of a pure fluid $I(4,0)$, we observe that such a diagram is decoupled into two new diagrams $I_1(2,2)$ and $I_2(2,2)$ with multiplicities 2 and 1, respectively (see Fig. 2). Of course, by introducing the $\widetilde{f}_{ij}$ link in the partial $\widetilde{\mathbf{V}}_4$ sums [Fig. 3(a)], we recover the expressions of the $\mathbf{B}_4$ coefficients based on the Mayer star diagrams [4]. The same procedure has been followed for obtaining the modified star diagrams of the partial $\widetilde{\mathbf{V}}_5$ [Fig. 3(b)].

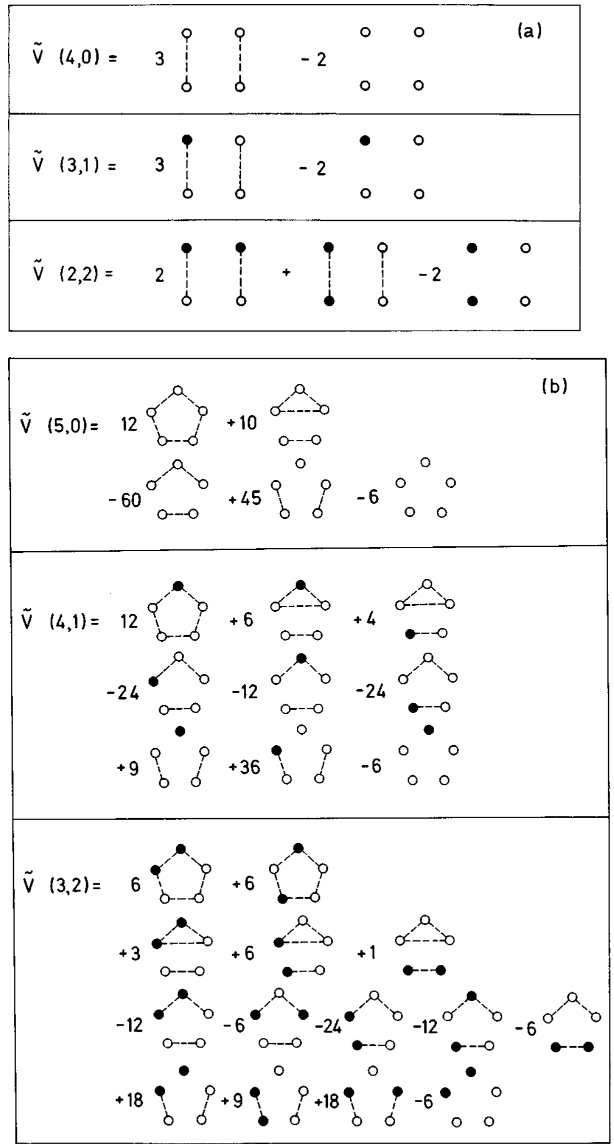

FIG. 3. The modified star diagrams contributing to the composition independent (a) $\mathbf{B}_4$ and (b) $\mathbf{B}_5$ coefficients of a binary mixture. Dashed lines denote an $\widetilde{f}_{ij}$ link, and no drawing means an f_{ij} link.

III. MONTE CARLO CALCULATIONS

The numerical task involved in the evaluation of the diagrams which define $\widetilde{\mathbf{V}}_n$ is reduced considerably for hard core potentials. The first two star diagrams, which define the $\mathbf{B}_2$ and $\mathbf{B}_3$ coefficients, have been obtained analytically [10]. For the rest we can consider the Monte Carlo method [3], which performs the numerical integration of a diagram indirectly, by using the known value of the chain diagram with the same

TABLE I. Partial $\mathbf{B}_4$ virial coefficients of binary mixtures of hard spheres with different diameter ratios R. The coefficients are reduced in terms of the power σ_{11}^9. q denotes the number of independent batches, each of which contains N_t millions of trials. $B(4,0)=2.636$ [1].

$\mathbf{B}_4\sigma_{11}^{-9}$	q/N_t	$B(4,0)$	$B(3,1)$	$B(2,2)$	$B(1,3)$
0.05	60/0.04	2.64(2)	$0.554(5)\times10^{-1}$	$0.431(5)\times10^{-4}$	$0.179(3)\times10^{-7}$
0.2	80/0.04	2.65(2)	0.159(1)	$0.434(2)\times10^{-2}$	$0.849(4)\times10^{-4}$
0.2 [12]	-	-	0.1589(4)	$0.4331(5)\times10^{-2}$	$0.8480(5)\times10^{-4}$
0.6	67/0.05	2.62(2)	0.888(6)	0.287(2)	$0.892(4)\times10^{-1}$
0.6 [4]	-	-	0.912(9)	0.280(3)	$0.891(9)\times10^{-1}$
0.8503	80/0.032	2.65(2)	1.85(1)	1.28(1)	0.889(4)

TABLE II. Partial $\mathbf{B}_5$ virial coefficients of binary mixtures of hard spheres with different diameter ratios R. The coefficients are reduced in terms of the power σ_{11}^{12}. Other symbols have the same meaning as in Table I. $B(5,0)=2.121$ [11].

$\mathbf{B}_5\sigma_{11}^{-12}$	q/N_t	$B(5,0)$	$B(4,1)$	$B(3,2)$	$B(2,3)$	$B(1,4)$
0.05	60/0.80	2.12(3)	$0.266(3)\times10^{-1}$	$0.195(2)\times10^{-4}$	$0.79(1)\times10^{-8}$	$0.224(3)\times10^{-11}$
0.2	80/0.6	2.13(2)	$0.958(6)\times10^{-1}$	$0.234(1)\times10^{-2}$	$0.426(2)\times10^{-4}$	$0.648(4)\times10^{-6}$
0.2 [6]	-	-	$0.96(3)\times10^{-1}$	$-0.240(2)\times10^{-1}$	$0.173(4)\times10^{-3}$	$0.64(2)\times10^{-6}$
0.6	67/1.6	2.10(3)	0.649(6)	0.199(2)	$0.583(4)\times10^{-1}$	$0.166(2)\times10^{-1}$
0.6 [5]	-	-	0.65(2)	0.195(4)	$0.59(3)\times10^{-1}$	$0.18(2)\times10^{-1}$
0.8503	80/0.8	2.14(2)	1.44(1)	0.992(4)	0.670(3)	0.449(2)

number of particles, calculated from the partial $\mathbf{B}_2$ coefficients [3]

$$I_{\rm ch}=\left(\frac{4\pi}{3}\right)^{n-1}\prod_{i=1}^{n-1}\left(\frac{\sigma_i+\sigma_{i+1}}{2}\right)^3. \tag{3.1}$$

A chain configuration is obtained, by placing particle 1 of a diagram at the origin of coordinates, and the remaining points are randomly positioned in the sphere with radius $(\sigma_i+\sigma_{i+1})/2$ centered at the preceding point. Then we count the number of times that the resultant chain conforms the modified star diagrams. After a large number of trials, one obtains an estimation of the diagram value through the relation given by

$$I=(-1)^{n_f}\frac{I_{\rm ch}N_c}{N_t}, \tag{3.2}$$

where n_f is the number of f bonds in the diagram, N_c is the number of occurrences of the diagram, and N_t the number of trials, or generated chains. In a trial we generate a chain for every combination of particle identities. We have performed four different runs, with 20 batches each of $\sim10^4$ chain configurations of four particles; each four point chain is used to generate ~30 five point chains (see Tables I and II for details). We have estimated the error bars as usual in previous studies [3],

$$\text{error}\ \ B(i,j)=2\left[\frac{\sum_{\mu=1}^{q}[B_\mu(i,j)-B(i,j)]^2}{q(q-1)}\right]^{1/2}, \tag{3.3}$$

where $B_\mu(i,j)$ is the average of the μ batch, q is the total number of batches, and $B(i,j)$ is the final average. The diagrams with higher degrees of polydispersity showed smaller error bars, since they have a much larger chance to be generated. In any case, the values accepted in the literature for the pure components [3,11] provided an additional test of the accuracy of our results.

IV. RESULTS

We present the Monte Carlo (MC) results for the composition independent coefficients of $\mathbf{B}_4$ and $\mathbf{B}_5$ in Tables I and II, respectively. The partial $\mathbf{B}_4$ agree with the values reported [12] from evaluation of the Mayer star diagrams. The partial $\mathbf{B}_5$ show discrepancies with Ref. [6]'s values at low values of R. We have included in Table II the values reported by Borštnik for $R=0.6$ [13], the differences are in between the error bar of the numerical integrations. For smaller values of R, we observe the consequences of using Borštnik diagrams, mainly in the $B(3,2)$ and $B(2,3)$ coefficients. Our calculations show positive values in all partial coefficients for all values of R considered in this work. In Fig. 4 a comparison between the calculated coefficients and predictions from the BMCSL EOS is shown. The agreement between both sets of data is excellent.

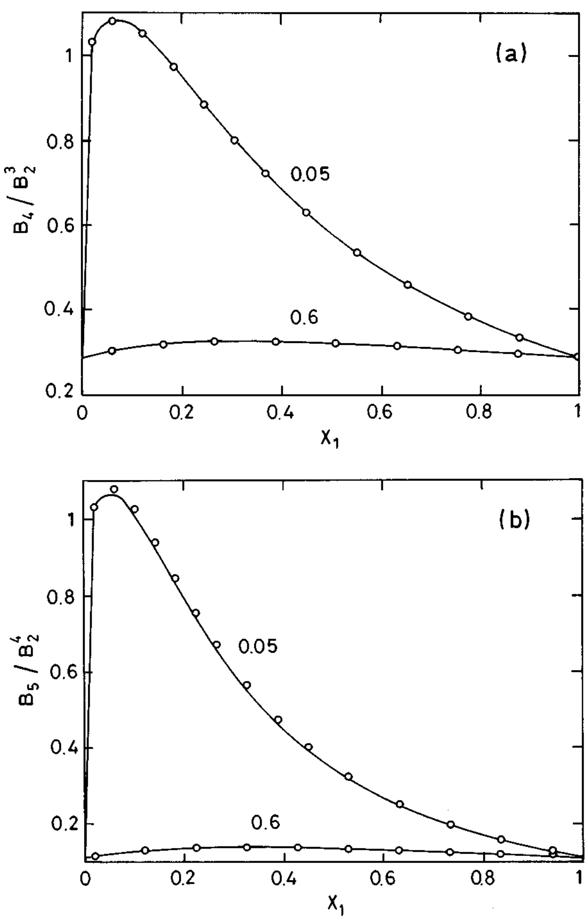

FIG. 4. (a) $\mathbf{B}_4$ and (b) $\mathbf{B}_5$ virial coefficients plotted in reduced units of the $\mathbf{B}_2$ coefficient as a function of the large sphere mole fraction, x_1. Circles are the predictions of the BMCSL EOS (Ref. [7]). The upper plot shows the results for $R=0.05$, and the lower one that for $R=0.6$.

V. CONCLUSIONS

We have obtained Mayer star diagrams which define the composition independent $\mathbf{B}_5$ coefficients of a binary mixture. Also we extended the modified star formalism of Ree and Hoover [3] to binary mixtures, offering a convenient way for numerical evaluation of $\mathbf{B}_4$ and $\mathbf{B}_5$ coefficients. The results show positive values of all partial $\mathbf{B}_5$ of hard sphere mixtures for $R \geqslant 0.05$. The BMCSL EOS is a good description of the thermodynamic properties of highly asymmetric additive hard-sphere mixtures. Recent theoretical schemes [14] have observed composition instabilities in hard-sphere mixtures with $R \sim 0.3$, which were explained as a sign of fluid-fluid phase separation. It would be interesting to test if such approaches can support the results reported here, and the MC calculations of compressibility factor of mixtures with $R = 0.2$ at low molar fractions of the large component [15].

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