Thermodynamic Properties of Mixtures of Hard Spheres

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(Received 20 March 1964)

We have investigated the thermodynamic properties of a binary mixture of hard spheres (with special reference to the existence of a phase transition) by using the recently obtained exact solution of the generalized equations of Percus and Yevick for the radial distribution functions of such a mixture. The distribution function obtained from the equations of Percus and Yevick is only an approximation and so yields two different pressures, \( p_1 \) and \( p_2 \), when used, respectively, in the compressibility equation of Ornstein and Zernike and in the equation of state obtained from the virial theorem. Comparisons with machine calculations show that \( p_1 \) is slightly above and \( p_2 \) slightly below the true pressure but that both are close to it. Our results show that the volume change on mixing at constant pressure is negative at all densities and compositions within the fluid phase when it is calculated from \( p_1 \), but that it becomes positive at high densities when calculated from \( p_2 \). In neither case is there a separation into two fluid phases. These results are compared briefly with those obtained from other theories of mixtures.

I. INTRODUCTION

THE statistical mechanical theory of fluid mixtures is at present in a far poorer state than the corresponding theory for single-component fluids. This is not surprising since their properties are much more varied and the labor involved in obtaining them from first principles is correspondingly much larger. Thus even the conceptually simplest case of a binary mixture of hard spheres has three independent parameters, (as compared to one parameter for the one-component case). It was therefore very surprising, and pleasing, that one could obtain an exact, explicit, and simple solution of the generalized Percus–Yevick equation for this “simple” system.

Even more surprising perhaps was the fact that the equation of state obtained from this solution is in very good agreement with “experiment,” i.e., the result of machine computations. It has therefore seemed worthwhile to investigate in detail the implications of this theoretical result with special reference to the question of phase separation. The results of this investigation are presented here.

II. THERMODYNAMIC POTENTIALS

We consider a system consisting of \( m \) components with number densities \( \rho_i \), \( i = 1, \ldots, m \). The particles interact via pair potentials \( \phi_{ij}(r) \) and the structure of the fluid is determined by the radial distribution functions \( g_{ij}(r) \), where \( r \) is the distance between a particle of Species \( i \) and a particle of Species \( j \). The direct correlation functions \( C_{ij}(r) \) are defined in a manner analogous to that in a one-component fluid,\(^1\)

\[
[g_{ij}(r) - 1] = C_{ij}(r) + \sum_{y=1}^{m} \rho_i \int [g_{ij}(r-y) - 1] C_{ij}(y) dy,
\]

\[
C_{ij}(r) = C_{ji}(r).
\] (2.1)

It can be shown, either through a generalization of the Ornstein–Zernike fluctuation theory\(^2\) or from the definition of the direct correlation function as a variational derivative,\(^3\) that

\[
\rho_i \int C_{ij}(r) dr = \delta_{ij} - \beta \rho_i \frac{\partial \mu_i(\rho_1, \ldots, \rho_m)}{\partial \rho_i},
\] (2.2)

where \( \mu_i \) is the chemical potential of the \( i \)th species and \( \beta \) is the reciprocal temperature, \( \beta = (kT)^{-1} \). (We generally do not indicate explicitly the temperature dependence of the functions we consider.) Using thermodynamic relations we obtain from (2.2),

\[
1 - \sum_i \rho_i \int C_{ij}(r) dr = \frac{\beta \rho_i}{\partial \rho_i},
\] (2.3)

where \( \rho \) is the pressure. The left side of (2.2) and (2.3) can be expressed directly in terms of the \( g_{ij} \) by using (2.1). The pressure can also be obtained from the radial distribution functions via the virial theorem.

\[
\beta \rho = \sum_i \rho_i - \frac{3}{2} \sum_{ij} \rho_i \rho_j \int_0^\infty r^2 \phi_{ij}(r) g_{ij}(r) dr.
\] (2.4)

For exact \( g_{ij}(r) \), (2.4) and (2.3) will yield the same equations of state. This will, however, not be true in general when one uses a \( g_{ij}(r) \) obtained from an approximate theory as we are doing in this paper. We shall then denote the pressure and other thermodynamic quantities obtained from (2.2) and (2.3) with a superscript \( \ast \).


\( ^3 \) Supported by the AFOSR under Grant 408–64 and by the AEC under Contract AT(30–1)–1480.

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‡ This work was supported in part by the National Aeronautics and Space Administration Grant NsG–275–62 (4180).
script \( e \) (for compressibility) and those from (2.4) by a superscript \( v \) (for virial). There is reason to believe that the compressibility relations will generally be "more correct" than those obtained from the virial theorem.\(^3\)

The generalization of the Percus–Yevick equation for the radial distribution function to mixtures is straightforward.\(^1\) It can be expressed in the form

\[
g_{ij}(r) \exp[-\beta \nu_{ij}(r)] - 1 = \exp[-\beta \nu_{ij}(r)] C_{ij}(r).
\]

(2.5)

Thus, as in the case of a single-component fluid, the P–Y (Percus–Yevick) approximation for a mixture states that the range of \( C_{ij}(r) \) is equal to the range of \( \nu_{ij}(r) \). In particular for a fluid of hard spheres,

\[
\exp[-\beta \nu_{ij}(r)] = \begin{cases} 
0, & r < R_{ij} = (R_i + R_j) / 2 \\
1, & r > R_{ij},
\end{cases}
\]

(2.6)

where \( R_i \) is the diameter of a particle of the \( i \)th species. Equations (2.5) and (2.6) state that \( C_{ij}(r) \) vanishes for \( r > (R_i + R_j) / 2 \) and \( g_{ij}(r) \) vanishes for \( r < (R_i + R_j) / 2 \). The approximation is, of course, in the first statement, the latter being rigorously true.

Equations (2.1), (2.5), and (2.6) now form a closed set of equations for the \( C \)'s and \( g \)'s which have been solved exactly.\(^1\) The \( C_{ij}(r) \) are given explicitly\(^1\) as simple polynomials in \( r \) (\( r \leq R_{ij} \)) and explicit expressions are obtained for the Laplace transforms of the \( g_{ij} \). Substituting these expressions into (2.2) and (2.3) yields

\[
\beta \mu_i = \ln \left[ \frac{\rho_i b^3}{(2\pi m_i kT)^{1/3}} \right] + \ln (1-\xi) + \frac{\pi}{6} \beta \rho_i R_i^3 \left[ 3Y_1 - 6Y_2 + \frac{R_i^2}{2} \right] \frac{X_1}{(1-\xi)} + \frac{R_i}{(1-\xi)} \left( 3X_1 - 6X_2 + 3X_2^2 \right)
\]

and

\[
\beta \rho_i = \left[ \sum_{j \neq i} \frac{\rho_j b^3}{(2\pi m_j kT)^{1/3}} \right] + (18/\pi) \sum_{i \neq j} \eta_{ij} R_{ij} [2R_{ij} + 2R_i (X)] (1-\xi)^{-3},
\]

(2.8)

where

\[
\eta_i = \frac{\xi \rho_i}{2}, \quad \xi = \sum \eta_i R_i^2, \quad X = \sum \eta_i R_i^2, \quad Y = \sum \eta_i R_i.
\]

The virial pressure is also obtained explicitly from the solution of the P–Y equation since for the case of a mixture of hard spheres (2.4) assumes the form

\[
\beta \rho_i = \sum \rho_j + \frac{2}{3} \pi \sum_{ij} \rho_i R_i^2 \hat{g}_{ij}(R_{ij}),
\]

(2.9)

where \( g_{ij}(R_{ij}) \) is the contact value of the radial distribution function, for which the P–Y equation gives,\(^1\)

\[
g_{ij}(R_{ij}) = \frac{[R_{ij} g_{ij}(R_i) + R_i g_{ij}(R_j)] / 2 R_{ij}}{g_{ii}(R_i)}, \quad \text{and} \quad g_{ii}(R_i) = \{(1-\xi) + \frac{1}{2} R_i X_1 \} (1-\xi)^{-3},
\]

(2.10)

This yields

\[
\beta \rho_i = \beta \rho_i - (18/\pi) \xi X_2 (1-\xi)^{-3}.
\]

(2.12)

From (2.8) and (2.12) we can obtain explicitly the P–Y expression for the Helmholtz free energy of a mixture of hard spheres as a function of \( T, V, N_1, \ldots, N_m \).

We find,

\[
\beta A^* = V \left[ \sum_i \rho_i \mu_i - \beta \rho_i \right],
\]

(2.13)

\[
\beta A^* = \beta A^* + \frac{18}{\pi} \frac{V X_1 (1-\xi)^{-3}}{\xi} \frac{1}{(1-\xi)^2} \ln (1-\xi).
\]

(2.14)

These functions then determine all the thermodynamic properties of this system. In particular the chemical potential of the \( i \)th species obtained from \( A^* \) is given by

\[
\mu_i = \mu_i + \frac{3 R_i X_1}{(1-\xi)^2} \frac{(1-\xi)^{3}}{\xi} \frac{1}{(1-\xi)^2} \ln (1-\xi) - \frac{R_i X_1 (1-\xi) + (1-\xi)^2}{(1-\xi)^3} \frac{1}{\xi} \ln (1-\xi).
\]

(2.15)

We note here an important advantage (in self consistency) of \( \mu \)'s derived from the compressibility relations over those derived from the virial theorem (and hence also of the equations of state). The chemical potential \( \mu_i \) consists physically of two parts:\(^6\)

\[
\mu_i = \mu_i + W_i,
\]

(2.16)

where \( \mu_i = \ln [\rho_i b^3 / (2\pi m_i kT)] \) is the ideal gas (kinetic) part of \( \mu_i \) and \( W_i (\rho_1, \ldots, \rho_i, \ldots, \rho_m, R_1, \ldots, R_m) \) is the work of putting in a particle of Species \( i \) of diameter \( R_i \) into the fluid.\(^5\) Now if we set one of densities, e.g., \( \rho_m \) equal to zero, then

\[
W_m (R_m) = W_m (\rho_1, \ldots, \rho_m = 0, R_1, \ldots, R_m)
\]

is the work of putting in a single particle into an \((m-1)\) component fluids of hard spheres of diameters \( R_1, \ldots, R_{m-1} \) and densities \( \rho_1, \ldots, \rho_{m-1} \). Now if \( R_m \) is made very large then it is clear that

\[
W_m (R_m) = \frac{3}{2} \pi \rho_i (R_m / 2)^3 + o (R_m^3),
\]

(2.17)

where \( o (R_m^3) \) are terms which do not increase as fast as \( R_m^3 \) (surface terms)\(^5,6\) and \( \rho_i \) is the pressure of the \((m-1)\) component fluid. This is indeed the case for

\(^3\) See the end of this section.

\(^4\) Reference 1, Eqs. (37)–(38).
the W's computed from the $\mu^*$ as can be seen directly from (2.7), but not for those computed from $\mu^e$.

III. RELIABILITY OF THE P-Y APPROXIMATION

It is seen from (2.8) and (2.12) that the difference between $p^e$ and $p^r$ is of fourth order in the density. Comparison with exact values of the virial coefficients9 shows indeed that $p^e$ and $p^r$ are exact up to the fourth order in the densities.

For the case of a one-component fluid, which may be obtained by setting all the $R_i$'s equal to $R_i$ (or by setting $p_2=p_3=\cdots=p_m=0$), we find

$$\beta p^r = \beta (1+\xi+\xi^2)/(1-\xi),$$

$$\beta p^e = \beta p^r - \frac{(18/\pi)\rho^2}{(1-\xi)^2}. \tag{3.1} \tag{3.2}$$

This equation of state (3.1) was obtained initially by Reiss, Frisch, and Lebowitz,9 on the basis of an entirely different approximation and later by Wertheim8 and Thiele9 from the solution of the P-Y equation for a one-component hard-sphere fluid. The higher virial coefficients computed from (3.1) and (3.2) are in good agreement with the exact coefficients,8,10 being, respectively, slightly above and slightly below the exact ones. Indeed comparison with the machine computations of Alder and Wainright11 show that $p^r$ and $p^e$ closely bound the actual pressure over the whole range of "liquid" densities, $\xi \leq 0.4$. (It should be noted however that $p^e$ and $p^r$ do not go to infinity at close packing, $\xi = \pi \sqrt{2}/7.0403$, but only at $\xi = 1$.)

An interesting feature of the pressures $p^r$ and $p^e$, (2.8) and (2.12), is that when the diameter of one of the components say $R_m$ is equal to zero, i.e., species one consists of point particles, then

$$\beta p^r = \beta p^e + \left[\rho_m/(1-\xi)\right], \tag{3.3}$$

where $p'$ is the pressure when species one is absent, i.e., $\rho_m = 0$. It is easy to show that the dependence on $\rho_m$ in (3.3) is exact.

We have also made comparisons with the Monte Carlo computations of Smith and Lee18 for a binary mixture in which $R_1 = \frac{1}{2} R_2$, the agreement is good. There is also very good agreement with the recent molecule dynamic computations of Alder13 for $R_1 = \frac{1}{2} R_2$, $\rho_1 = \rho_2$, $\xi \leq 0.4$. Here, too, $p^e$ and $p^r$ bound the exact results.

Summarizing then, we believe that the solutions of the P-Y equation are a good approximation to the exact result (within 4%-5%) for all ratios of $R_1/R_2$ and for $\xi \leq 0.4$, i.e., the range of "fluid" densities.

IV. STABILITY CONDITIONS

For a mixture of hard spheres the specific heat constant volume is equal to $\frac{1}{2} R$, [cf. (2.13); (2.14)]. Hence, the condition of thermodynamic stability reduces simply to the requirement that the matrix $M^{(m)}$, whose elements are

$$M^{(m)}_{ij} = \frac{\partial \mu^e_{ij}}{\partial \rho_{ij}} = \frac{\partial^2}{\partial \rho_{ij}} \left[ A(T, V, N_1, \cdots, N_m) \right]/V = \mu_{i,j} \tag{4.1}$$

be positive definite.14 This is equivalent to the requirement that all the principal minors of the matrix $M^{(m)}$ be positive. It can be verified from (2.7), that when the $\mu^e$ are used in (3.1), then all the diagonal elements of $M^{(m)}$ are positive (the off-diagonal elements vanish in the case of an ideal-gas mixture, $R_i = 0$ for all $i$, but are otherwise also positive). Furthermore, for the case $m=2$,

$$|M^{(2)}_{ij}| = \left| \mu_{i,j} \right| = \left| \mu_{1,1} \right|^2 = \left| \beta p_1 \right|^2$$

Thus, the compressibility relations obtained from the P-Y equation yield no phase transition for a single component or binary mixture of hard spheres. Interestingly enough the determinant of $M^{(2)}$, which is just $M^{(1)}$, is of the same form as (4.1),

$$M^{(1)} = \frac{\partial \mu}{\partial \rho} = (\beta p)^{-1}(1+\xi)^2/(1-\xi)^4 > 0. \tag{4.2} \tag{4.3}$$

We believe that the same form will hold for the determinant of all the $M^{(m)}$, and that the P-Y equation will always show (using the compressibility relations) no phase transition for a mixture of hard spheres.

We can also calculate $|M^{(2)}|$ from the virial free energy $A^v$ by differentiation of the additional terms in $\mu^e$ on the right hand of (2.15). This leads to a positive form if $(R_1/R_2) = 0$, namely

$$|M^{(2)}| = (\beta p_{1,2})^{-2}(1+\xi+3\xi^2)/(1-\xi)^3; \quad R_1 = 0, \tag{4.3}$$

which is smaller and increases more slowly than $|M^{(2)}|$ and is again of the same form as $M^{(1)}$ obtained from the virial equation of state. We have found no similar result if $(R_1/R_2) \neq 0$, but $M^{(2)}$ has been calculated numerically for $(R_1/R_2) = \frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ and for

$$\left(\frac{\rho_1}{\rho_1+\rho_2}\right) = x = 0.1, 0.2, \cdots, 0.9$$

and

$$\eta(R_1) = 0.1, 0.2, \cdots, 1.0.$$
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<td>$V_1/N_{v*}=1.817596$</td>
<td>$V_1/N_{v*}=1.743382$</td>
<td>$V_1/N_{v*}=2.286327$</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.000031</td>
<td>0.000036</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
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<td>0.000085</td>
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<tr>
<td>0.5</td>
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<td>0.000104</td>
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</tr>
<tr>
<td>0.7</td>
<td>-0.000036</td>
<td>0.000040</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>-0.000036</td>
<td>0.000040</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$V_1/N_{v*}=1.519164$</td>
<td>$V_1/N_{v*}=1.436492$</td>
<td>$V_1/N_{v*}=1.943592$</td>
</tr>
<tr>
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<td>-0.000012</td>
<td>0.000028</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
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<td>0.000068</td>
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</tr>
<tr>
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<td>0.000083</td>
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</tr>
<tr>
<td>0.7</td>
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<td>0.000072</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>-0.000014</td>
<td>0.000032</td>
<td></td>
</tr>
</tbody>
</table>
It was found to be positive under all conditions. The determinant \( |M^{(0)}| \) may also be expressed in terms of the Gibbs free energy of the binary mixture \( G = N g(\rho, x, T) \), where \( N \) is total number of particles, \( \rho \) is the pressure, and \( x \) is the mole fraction of Species 1. Utilizing straightforward thermodynamic reasoning gives,

\[
\frac{\partial^2 g(\rho, x, T)}{\partial x^2} = \left[ \frac{\partial^2 (\rho \rho \rho)}{\partial \rho^2} \right] \rho^2 |M^{(0)}|, \quad \rho = \sum \rho_i \tag{4.4}
\]

where the differentiation of \( g \) is carried out at constant \( \rho \). Combining (2.8), (4.1), and (4.4) now yields

\[
\frac{\partial^2 e(\rho, x)}{\partial x^2} = \frac{[x(1-x)]^{-1} [1+2\xi]^2}{[1+2\xi]^2 J(1+2\xi) + K(1-\xi)} - \frac{[1+2\xi]^2}{[1+2\xi]^2 J(1+2\xi) + K(1-\xi)}, \tag{4.5}
\]

where

\[
J = 3x(1-x)(r-1)^2[2r+1+x(r^2-1)(r+1)]
\times[1+x(r^2-1)]^{-1}, \tag{4.6}
\]

\[
K = 3x(1-x)(r-1)^2[1+x(r^2-1)]^2[1+x(r^2-1)]^{-1}, \tag{4.7}
\]

\[
r = R_1/R_2, \tag{4.8}
\]

and the explicit dependence of \( \xi \) on \( x \) is given by

\[
\xi = \frac{2\pi R_2^2 [1+x(r^2-1)]}. \tag{4.9}
\]

The superscript \( c \) in (4.5) again indicates that the compressibility functions were used throughout.

### V. EXCESS VOLUME

The excess thermodynamic properties of a binary mixture of hard spheres are most conveniently expressed in terms of the excess volume

\[
V^e = V - x_1 V^0_1 - x_2 V^0_2, \quad x_i = \rho_i/(\rho_1 + \rho_2), \tag{5.1}
\]

when \( V \), \( V^0_1 \), and \( V^0_2 \) are the volumes of the mixture of Pure Component 1 and Pure Component 2 at a given \( \rho \) and \( T \). There is no energy change on mixing hard spheres and so the excess Gibbs free energy is given at once by

\[
G^e = \int_0^\rho V^e d\rho. \tag{5.2}
\]

The excess volume is negative in the dilute gas, its limit at zero pressure being

\[
V^e = (1/x_1 x_2) (2B_{12} - B_{11} - B_{22})
\]

\[
= -(1/x_1 x_2) (R_1 - R_2)^2(R_1 + R_2) (\pi N/2), \tag{5.3}
\]

where \( B \) is a second virial coefficient. The excess volume at nonzero pressure is found by solving (2.8) or (2.12) for \( v \) at given values of \( (R_1/R_2) \), \( x \), and \( \xi \). These solutions were found by iteration on a computer and the derived values of \( V^e \) are shown in Table I.

The excess volumes are negative under all conditions if the compressibility equation is used. Hence, from (5.2), \( G^e \) is also negative and phase separation does not occur as already seen in (4.1).

If the virial equation is used then \( V^e \) is always negative if \( (R_1/R_2) = 0 \), but becomes positive at very high pressures if the size ratio is not zero. However, graphical integration of (5.2) shows that \( G^e \) is still everywhere negative, and so confirms the conclusion of the last section that phase separation does not occur. The positive values of \( V^e \) calculated from \( \rho^e \) decrease with increasing pressure (at sufficiently high pressures) more rapidly than \( (\rho^e)^{-1} \). Hence, from (5.2), \( G^e \) is bounded and cannot become an infinitely large positive quantity. We conclude from a comparison of the results from \( \rho^e \) and \( \rho^e \) that \( V^e \) is negative at all low and moderate pressures. It is almost zero at very high pressures but then its sign is still uncertain. However, \( G^e \) is almost certainly negative at all pressures and phase separation never occurs.

### VI. COMPARISON WITH OTHER THEORIES

The theoretical treatments with which our results can be most readily compared is that of Buchowski and Bellemans.\(^{12}\) These authors consider the case of a binary mixture of hard spheres in which the diameters differ

by a small amount $\lambda$, $R_2=1$, $R_1=r=1+\lambda$. They then utilize some results of Brown\textsuperscript{46} to obtain a very interesting exact expression for the excess Gibbs free energy $g^E$ to order $\lambda^4$. This expression involves both the thermodynamic properties of the reference system, i.e., Pure Species 2, and also the three-particle correlation function $g_3$ of the reference system. The value of $g_3$ is needed only when the three spheres are in contact, $g_3(1, 1, 2)$. They then use the Reiss, Frisch, Lebowitz\textsuperscript{47} expressions for the thermodynamic properties of the reference system (which, as mentioned in section three, are the same as the P–Y compressibility results for a one-component system) and approximate $g_3(1, 1, 2)$ either by $g^E(1)$ or by the superposition approximation. The first of these approximations to $g_3$ yields a positive $g^E$ for $\rho \geq 0.5$, which increases rapidly and predicts a phase separation at $\rho=1.1$ for $\lambda=0.1$, $x=0.5$. The superposition approximation was carried through by Buchowski and Bellemans only at $\rho=0.77$ where it gave a very small positive $g^E$.

Utilizing (4.5) we obtain for the “compressibility” excess Gibbs free energy and excess volume to order $\lambda^2$,

$$
\frac{\beta G^E}{N} = \beta g^E = -x(1-x)\lambda^2\frac{1}{(1+\frac{2}{3}\lambda \rho)^2} \left[ \frac{1}{(1+\frac{2}{3}\lambda \rho)} \right]^2,
$$

(6.1)

$$
\frac{V^E}{N} = -x(1-x)\lambda^2\frac{1}{(1+\frac{2}{3}\lambda \rho)} \left[ \frac{1}{(1+\frac{2}{3}\lambda \rho)} \right]^3,
$$

(6.2)

which as expected is negative for all values of $\rho$. A virial expansion of (6.1) yields

$$
\beta G^E = -x(1-x)\lambda^2 \left( \frac{1}{(1+\frac{2}{3}\lambda \rho)^2} \right) + 0.656 \left( \frac{2}{3} \lambda \rho \right)^3 + \cdots.
$$

(6.3)

The exact result for the coefficient of $\left( \frac{2}{3} \lambda \rho \right)^3$ given by Buchowski and Bellemans is 0.555. Thus our expression underestimates $g^E$. We believe, however, that within the range of fluid densities $\rho \leq 0.8$ our results are quite good and that $g^E$ for hard spheres is a small negative or positive number at $\rho \approx 0.8$. This would be in approximate agreement with the result, obtained by Buchowski and Bellemans from the superposition approximation which according to Alder\textsuperscript{47} is a good approximation at these densities. For higher densities there is a fluid–solid transition\textsuperscript{11,18} and the use of the Reiss, Frisch, Lebowitz theory for the reference system is not valid. Machine computations for small $\lambda$ are now being carried out by A. Rotenberg at New York University.

Other theories of mixtures are less useful for mixtures of hard spheres. The theory of random mixtures (or “one-fluid” theory) and its extensions to nonrandom mixtures\textsuperscript{18} (“two-fluid” and “three-fluid” theories) introduce singularities into the thermodynamic properties if the molecules are hard spheres. Their use requires the calculation of the change of energy when, if any arbitrary configuration, a molecule of Species $\alpha$ is changed to one of Species $\beta$. If $\alpha$ and $\beta$ are hard spheres of different radii, then these changes can be infinite. Even the qualitative conclusions of these theories are not comparable with the results of this paper. Each of these theories predicts a positive contribution to the Gibbs free energy from differences in size for molecules whose potentials are of the Lennard–Jones $(n, m)$ type. This contribution is dominated by a term of the form,

$$
G^E / x_1 x_2 = -\frac{\alpha(n,n,m)}{U} \left( \frac{R_1 - R_2}{R_1} \right)^2
$$

(6.4)

for a binary mixture, where $U$ is the configuration energy of Component 1. The coefficient $\alpha$ varies from theory to theory, but is of the order of unity. This contribution to $G^E$ is large and positive since $U<0$ and $n, m>6$. Experimental work\textsuperscript{18} confirms the existence of a contribution to $G^E$ of this kind but with small values of $\alpha<0.1$. Clearly the results obtained in this paper for mixtures of hard spheres are not comparable with (6.4).

We conclude that the structure of a fluid mixture of hard spheres is different from that of either pure component. The structure is such that $v^E$ is generally less than zero, and $G^E$ always less than zero. In mixtures of $(n, m)$ fluids it is the attractive forces that impose a similar structure on both the mixture and the pure components, and so lead to positive contributions $G^P$, $H^P$, and $v^P$ that arise from the “overlapping” in the mixtures of repulsive free fields in such structures. Our results, therefore, do little to help improve the accuracy of theories of mixtures of real molecules. These conclusions are similar to those arrived at by Adler.\textsuperscript{18}

ACKNOWLEDGMENTS

One of us (J.L.L.) would like to thank Dr. E. Praestgaard for help with some computations. The other (J.S.R.) thanks Professor J. O. Hirschfelder for the hospitality of the Theoretical Chemistry Institute, University of Wisconsin, and Mrs. Marion Taylor and Mrs. Carol Monash for the computations of $V^F$.


