

Reprinted from:

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 54, NUMBER 4

15 FEBRUARY 1971

Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres

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(Received 18 May 1970)

An equation of state is proposed for the mixture of hard spheres based on an averaging process over the two results of the solution of the Percus-Yevick integral equation for the mixture of hard spheres. Compressibility and other equilibrium properties of the binary mixtures of hard spheres are calculated and they are compared with the related machine-calculated (Monte Carlo and molecular dynamics) data. The comparison shows excellent agreement between the proposed equation of state and the machine calculated data.

While some successful attempts have been made in recent years in the prediction of equilibrium thermodynamic properties of pure fluids by the methods of statistical mechanics, the theories of mixtures are in need of much more improvement than the theories of pure fluids. The relatively successful theories of pure fluids¹⁻³ have put more emphasis on the expansion of the properties of the system around a hard-sphere reference system by a power series, and truncating this power series, by some mathematical technique, to the first few terms. While these approaches theoretically can be used for mixtures, they have not been as successful as for pure fluids, because of additional difficulties which are discussed elsewhere.⁴ One of these difficulties has been the lack of a satisfactory equation of state for hard-sphere mixtures. The need for such a relation is also shown by the development of the "van der Waals"^{5,6} corresponding states method which has been superior to the previous approaches of its kind. This approach shows clearly the importance of an accurate prediction of the hard-sphere contribution to the prediction of thermodynamic properties of real fluid mixtures.

From the solution of the Percus-Yevick (PY) integral equation for the radial distribution function, two routes to an equation of state can be derived. One of these is the compressibility equation derived from fluctuations in the grand canonical ensemble and the other is from differentiation of the logarithm of the configuration integral to give the pressure or "virial equation." Thiele⁷ and Wertheim⁸ independently have solved the PY equation for pure hard spheres; while Lebowitz⁹ has solved it for the mixture of hard spheres. For a hard-sphere mixture of m components, the results are as follows⁹:

$$Z^v = [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi)](1 - \xi)^{-2}, \quad (1)$$

$$Z^c = Z^v - 3\xi^2 y_3 (1 - \xi)^{-2}, \quad (2)$$

where $Z = PV/NkT$ is the compressibility,

$$\xi = \sum_{i=1}^m \xi_i, \quad \xi_i = \frac{1}{2} \pi \rho d_i^3 x_i, \quad \sum_{i=1}^m x_i = 1,$$

ρ is the number density, d_i is the hard sphere diameter of the i th component, and x_i is the mole fraction of

the i th component. The superscripts v and c indicate the virial and compressibility forms, respectively. y_1 , y_2 , and y_3 are defined as follows:

$$y_1 = \sum_{j>i=1}^m \Delta_{ij} (d_i + d_j) (d_i d_j)^{-1/2},$$

$$y_2 = \sum_{j>i=1}^m \Delta_{ij} \sum_{k=1}^m \left(\frac{\xi_k}{\xi} \right) \frac{(d_i d_j)^{1/2}}{d_k},$$

$$y_3 = \left[\sum_{i=1}^m \left(\frac{\xi_i}{\xi} \right)^{2/3} x_i^{1/3} \right]^2,$$

and

$$\Delta_{ij} = [(\xi_i \xi_j)^{1/2} / \xi] [(d_i - d_j)^2 / d_i d_j] (x_i x_j)^{1/2}.$$

TABLE I. Comparison of the compressibility Z for a binary mixture of hard spheres ($x_1 = x_2 = \frac{1}{2}$) with the Monte Carlo (MC) data.^a

	ξ	0.1571	0.2618	0.3665
$d_2/d_1 = 1.1$	Eq. (7)	1.963	3.253	5.688
	MC	1.96	3.17	5.64
$d_2/d_1 = 5/3$	Eq. (7)	1.879	3.041	5.214
	MC	1.87	3.04	5.24

^a References 14 and 15.

In the case of a pure system, Relations (1) and (2) reduce to the relations derived by Thiele⁷ and Wertheim⁸ for the pure hard-sphere system as follows:

$$Z_p^c = (1 + \eta + \eta^2) (1 - \eta)^{-2}, \quad (3)$$

$$Z_p^v = (1 + 2\eta + 3\eta^2) (1 - \eta)^{-2}, \quad (4)$$

where $\eta = \frac{1}{2} \pi \rho d_s^3$ and subscript p stands for pure system.

Carnahan and Starling¹⁰ showed that for the pure hard spheres the compressibility can be calculated from the following equation more accurately than (3) or (4), or even the Padé approximant of Ree and Hoover¹¹:

$$Z_p^{CS} = (1 + \eta + \eta^2 - \eta^3) (1 - \eta)^{-2}, \quad (5)$$

where the superscript CS indicates the Carnahan-

TABLE II. Comparison of the thermodynamic properties of a binary mixture of hard spheres ($x_1 = x_2 = \frac{1}{2}$; $d_2/d_1 = 3$) with the molecular dynamic (MD) data.*

Property	ξ	0.2333	0.2692	0.3106	0.3583	0.3808	0.4393	0.5068
Z	Eq. (7)	2.368	2.772	3.356	4.241	4.764	6.567	9.898
	MD	2.37	2.77	3.36	4.24	4.76	6.57	9.77
$-\Delta Z$	Eq. (8)	0.461	0.616	0.847	1.211	1.431	2.214	3.720
	MD	0.48±0.02	0.63±0.02	0.87±0.03	1.25±0.04	1.48±0.05	2.22±0.06	3.70±0.08
$-S^E/Nk$	Eq. (9)	0.139	0.205	0.306	0.467	0.564	0.898	1.495
	MD	0.14	0.21	0.31	0.48	0.58	0.92	1.52
G^E/NkT	Eq. (10)	1.508	1.977	2.662	3.709	4.327	6.465	10.393
	MD	1.51	1.99	2.67	3.72	4.34	6.49	10.29
$\Delta S^E/Nk$	Eq. (12)	0.130	0.184	0.263	0.382	0.451	0.678	1.061
	MD	0.12	0.18	0.26	0.37	0.44	0.69	1.07
$-\Delta G^E/NkT$	Eq. (13)	0.592	0.800	1.110	1.593	1.881	2.891	4.781
	MD	0.60	0.81	1.13	1.63	1.92	2.91	4.77

* Reference 12.

Starling result. From (3) and (4) it can be shown that for a pure hard-sphere system, Eq. (5) is

$$Z_p^{CS} = \frac{1}{3}(2Z_p^c + Z_p^v). \quad (6)$$

The fact that Z^{CS} is in such good agreement with the machine-calculated data for pure hard spheres indicates that the compressibility relation is more accurate than the virial relation, because of its greater contribution in Equation (6). It should be noted that the machine calculated values for compressibility, for both a pure⁸ and binary mixture¹² of hard spheres, always stand in between the values calculated from c and v relations. The discrepancy between the compressibilities calculated from the c and v relations is, of course, due only to the approximations introduced in the PY integral equation. The superiority of the c form has been proved qualitatively by Lebowitz and Rowlinson¹⁸ with a theoretical approach for mixtures of hard spheres. They show that the excess of the chemical potential of the i th component, which is equal to the work of putting in a particle of species i of diameter d_i into the fluid, can be reproduced better by the c relation than by the v relation for the chemical potential or the equation of state. By considering this point, Relation (6) can be generalized to mixtures of hard spheres, and by joining Relations (1) and (2), according to Relation (6), we should be able to obtain a satisfactory equation of state for mixtures of hard spheres as follows:

$$Z^{cs} = \frac{1}{3}(2Z^c + Z^v) \\ = [(1 + \xi + \xi^2) - 3\xi(\gamma_1 + \gamma_2\xi) - \xi^3\gamma_3](1 - \xi)^{-3}. \quad (7)$$

Although one can obtain the mixture results presented here by means of the linear combination of the two solutions to the PY equation, it is not neces-

sary at all to begin with the PY equation to obtain the mixture results. One can begin with the original derivation of the pure component equation of state presented by Carnahan and Starling¹⁹ which in no way makes use of the PY equation. The mixture results can then be obtained from the contact value of the radial distribution function $g(\sigma)$ which follows from the Carnahan-Starling equation for pure hard spheres by using the same procedure as Lebowitz and Rowlinson¹⁸ who used a $g(\sigma)$ from the PY equation.

In Table I values of compressibility calculated from Eq. (7) are compared with the Monte Carlo (MC) calculations^{14,15} for $d_2/d_1 = 11/10, 5/3$; and $x_1 = x_2 = 0.5$. Table I shows excellent agreement with the Monte Carlo mixture compressibility factor values reported by Smith and Lea¹⁵; however, much poorer agreement was obtained with their compressibility results for a pure component. In general, the agreement between the equation proposed here and the published values is much better for molecular-dynamic results than for Monte Carlo. Also in Table II values of Z from Eq. (7) are compared with the molecular-dynamics²² (MD) data for $d_2/d_1 = 3$ and $x_1 = x_2 = 0.5$.

The pressure drop upon mixing the m components at a constant reduced density can be calculated from the following relation:

$$-\Delta Z = -\Delta(PV/NkT) = Z^{cs} - (1 + \xi + \xi^2 - \xi^3)(1 - \xi)^{-3}, \quad (8)$$

which is a result of Eqs. (5) and (7). In Table II the values of $-\Delta Z$ as calculated from (8) are compared with MD data.

The excess entropy and Gibbs free energy over that of an ideal gas at the same pressure are defined

THERMODYNAMICS OF MIXTURE OF HARD SPHERES

1525

TABLE III. Comparison of the excess volume, entropy, and free energy upon mixing at constant pressure of a binary mixture of hard spheres ($x_1 = x_2 = \frac{1}{2}$; $d_2/d_1 = 3$) with the MD data.*

$P^* = Z\xi_1$	$-\Delta v/v$		$\Delta S^E/Nk$		$-\Delta G^E/NkT$	
	Eq. (7)	MD	Eq. (9)	MD	Eq. (10)	MD
0.03955	0.0267	0.030±0.003	0.0932	0.085	0.159	0.16
0.05342	0.0224	0.024±0.003	0.1135	0.106	0.179	0.17
0.07460	0.0175	0.019±0.002	0.1369	0.130	0.200	0.19
0.10895	0.0123	0.012±0.002	0.1644	0.159	0.228	0.22
0.12950	0.0102	0.011±0.0015	0.1740	0.171	0.224	0.23
0.20623	0.0060	$\begin{cases} -0.068 \\ 0.005 \pm 0.001 \end{cases}$	0.2048	$\begin{cases} 0.600 \\ (0.220) \end{cases}$	0.252	$\begin{cases} 0.15 \\ (0.25) \end{cases}$
0.35369	0.00267	$\begin{cases} -0.083 \\ 0.0025 \pm 0.0004 \end{cases}$	0.2168	$\begin{cases} 0.617 \\ (0.276) \end{cases}$	0.254	$\begin{cases} -0.19 \\ (0.30) \end{cases}$

* Reference 12.

by, respectively,

$$-S^E/Nk = (F - F^{id})/NkT - \ln Z, \quad (9)$$

$$G^E/NkT = Z - 1 - S^E/Nk. \quad (10)$$

By considering Eq. (7) for compressibility, we can show that

$$\begin{aligned} (F - F^{id})/NkT = & -\frac{2}{3}(1 - y_1 + y_2 + y_3) \\ & + (3y_2 + 2y_3)(1 - \xi)^{-1} + \frac{2}{3}(1 - y_1 - y_2 - \frac{1}{3}y_3)(1 - \xi)^{-2} \\ & + (y_3 - 1) \ln(1 - \xi). \quad (11) \end{aligned}$$

In Table II, $-S^E/Nk$ and G^E/NkT calculated by (9) and (10), by considering Relations (7) and (11) for Z and $(F - F^{id})/NkT$, are compared with the MD results for a binary mixture of hard spheres. Also given in Table II are the changes of these excess functions, that is, S^E/Nk and G^E/NkT , on mixing at constant reduced densities, which are shown by $\Delta S^E/Nk$ and $-\Delta G^E/NkT$, respectively,

$$\begin{aligned} \Delta S^E/Nk = S^E/Nk - (3 - 2\xi)(1 - \xi)^{-2} + 3 \\ - \ln[(1 + \xi + \xi^2 - \xi^3)(1 - \xi)^{-3}], \quad (12) \end{aligned}$$

$$\begin{aligned} -\Delta G^E/NkT = \Delta S^E/Nk - Z \\ + (1 + \xi + \xi^2 - \xi^3)(1 - \xi)^{-3}. \quad (13) \end{aligned}$$

In Table III the excess volume, entropy, and free energy upon mixing at constant pressure are compared with the MD results for a binary mixture of hard spheres.

At it is shown by Tables I-III the proposed equation of state in this report, which is shown by Eq. (7) and other thermodynamic functions calculated based on it, reproduce the machine-calculated data for binary mixtures of hard spheres very well and better than all the other equations of state available (see

Refs. 9 and 12-16 for a comparison with other approaches). It is already shown¹⁰ that Eq. (7) is in very good agreement with the machine-calculated data for pure hard-sphere systems. Consequently, it may be claimed that Eq. (7) is the best analytical Equation of state presently available for the multi-component system of hard spheres.

ACKNOWLEDGMENT

This research was supported by grants from the National Science Foundation, GK-2211 at the University of Oklahoma and GK-18176 at Rice University.

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