Two-fluid theory and thermodynamic properties of liquid mixtures. Application to hard-sphere mixtures

(statistical thermodynamics/fluids/phase equilibria/molecular size ratio/hard spheres)

V. BRANDANI AND J. M. PRAUSNITZ

Chemical Engineering Department and Molecular and Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Contributed by J. M. Prausnitz, February 22, 1982

ABSTRACT This paper is the second of three describing a two-fluid theory of binary liquid mixtures. The general theory presented in the preceding paper is used to derive a model for calculating thermodynamic properties of hard-sphere mixtures. Calculations indicate that desirable boundary conditions are satisfied.

In the preceding paper (1), we discussed a two-fluid theory for binary mixtures, formulated in terms of the short-range structure of two hypothetical fluids. Each hypothetical fluid is characterized by a domain whose properties can be expressed in terms of three variables: the size, the number of nearest neighbors, and a variable that accounts for the composition of the mixture (see section 3 of ref. 1).

In this paper we use the general results of ref. 1 to derive thermodynamic properties for liquids and liquid mixtures of hard spheres. In a subsequent paper (2) the properties of the hard-sphere reference system will be used for calculating those of the real system, taking into account the effect of nonrandomness produced by the attractive contribution of the perturbation potential.

1. One-component hard-sphere system: Equation of state and thermodynamic properties

For a one-component hard-sphere system, equation 2.19 of ref. 1 reduces to

$$\left(\frac{A}{NkT}\right)^{hs} = 0.201 - 3\ln \sigma - 3\ln(\bar{v}^{1/3} - 1) \quad [1.1]$$

From Eq. 1.1, the equation of state is

$$\left(\frac{P}{kT\rho}\right)^{hs} = \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} \quad [1.2]$$

which is an approximate extension to the three-dimensional fluid of the exact result of Tonks (3) for a one-dimensional hard-sphere system.

For a pure, hard-sphere fluid at number density ρ , Fig. 1 compares results from Carnahan and Starling's equation (4) with those from our theory. The packing factor $\eta(=\pi\rho\sigma^3/6)$ is related to the reduced volume $\bar{v}$ by

$$\eta = 0.64/\bar{v} \quad [1.3]$$

where 0.64 is the packing fraction for a randomly close-packed sphere as obtained in experiments with steel balls (5).

For the range of liquid densities, agreement is fairly good;

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

strong discrepancies arise at low and moderate densities. These results indicate that our model can be applied with confidence only to dense (liquid-like) systems.

2. Hard-sphere mixtures: Equation of state and excess thermodynamic properties

From equation 1.4 of ref. 1, the compressibility of a binary mixture is given by

$$Z = \frac{P}{kT\rho} = x_1 Z^{(1)} + x_2 Z^{(2)} \quad [2.1]$$

where, using standard thermodynamics, $Z^{(1)}$ and $Z^{(2)}$ for hard-sphere mixtures are given by

$$Z^{(1)} = \frac{[\bar{v}^{(1)}]^{1/3}}{[\bar{v}^{(1)}]^{1/3} - 1} \quad [2.2]$$

and

$$Z^{(2)} = \frac{[\bar{v}^{(2)}]^{1/3}}{[\bar{v}^{(2)}]^{1/3} - 1}. \quad [2.3]$$

If we define the packing factor for a binary mixture of hard spheres by

$$\eta \equiv \frac{\pi}{6}\rho\sigma_{CS}^3 = \frac{\pi}{6}\rho(x_1\sigma_{11}^3 + x_2\sigma_{22}^3) \quad [2.4]$$

we obtain

$$0.64/\eta = x_1\bar{v}^{(1)}(\langle\sigma^{(1)}\rangle/\sigma_{CS})^3 + x_2\bar{v}^{(2)}(\langle\sigma^{(2)}\rangle/\sigma_{CS})^3 \quad [2.5]$$

where $\langle\sigma^{(1)}\rangle$ and $\langle\sigma^{(2)}\rangle$ are evaluated from equations 3.18 and 3.19 of ref. 1 by using the following equations to express the distribution law for the classes of domains of the two hypothetical fluids:

$$\langle\sigma^{(1)}\rangle = p_1\sigma_{11} + q_1\sigma_{21} \quad [2.6]$$

and

$$\langle\sigma^{(2)}\rangle = p_2\sigma_{22} + q_2\sigma_{12}. \quad [2.7]$$

Here, for the cross parameters, we use the arithmetic mean ($\xi_{12} = 0$)

$$\sigma_{12} = \sigma_{21} = \frac{1}{2}(\sigma_{11} + \sigma_{22})(1 - \xi_{12}). \quad [2.8]$$

Fig. 2 shows a comparison of our model with the Carnahan–Starling equation for binary mixtures with different molecular-size ratios. Agreement between the Carnahan–Starling equation and our model is much better when we calculated properties of domains by using a weighting average to account

FIG. 1. Compressibility factor as a function of reduced density. The domain equation of state provides a good approximation at liquid-like densities.

for differences in molecular size. This may best be seen by comparing the behavior of the curves with the same molecular size ratio but with different size exponent m . In Fig. 2 *Upper*, m was set equal to zero; in Fig. 2 *Lower*, the size exponent is expressed by

$$m = f(\sigma_{22}/\sigma_{11})$$

$$= (0.783 \pm 0.029) + (1.327 \pm 0.096) \left(\frac{\sigma_{22}}{\sigma_{11}} \right)^{-3} \quad [2.9]$$

where $1 \leq (\sigma_{22}/\sigma_{11}) \leq 3$.

Within the uncertainty of the correlation, as the ratio σ_{22}/σ_{11} goes to 1, the limiting value assumed by the size exponent is $m = 2$. This result agrees with that suggested by Kikic *et al.* (6), who proposed that the best representation of the bulk composition for a mixture is obtained in terms of surface fraction.

To evaluate the compressibility factor by our model, it is necessary to solve (by some numerical procedure) an equation for $\bar{v}^{(1)}$ as a function of η . This is obtained by combining 2.2, 2.3, and 2.5. The value of $\bar{v}^{(1)}$ is then utilized for calculating $\bar{v}^{(2)}$; the compressibility factor is finally obtained from Eq. 2.1 after calculation of $Z^{(1)}$ and $Z^{(2)}$ by Eqs. 2.2 and 2.3, respectively.

To reduce the labor required to perform such calculations, it is common practice to follow the suggestion of Prigogine (7)—that is, to assume

$$\bar{v}^{(1)} = \bar{v}^{(2)} = \bar{v} \quad [2.10]$$

where

$$\bar{v} = 3.84/(\pi \rho \sigma_P^3) \quad [2.11]$$

with

$$\sigma_P^3 = x_1 \langle \sigma^{(1)} \rangle^3 + x_2 \langle \sigma^{(2)} \rangle^3. \quad [2.12]$$

With Prigogine's approximation, we obtain an analytical equation for the compressibility factor of a binary mixture of hard spheres:

$$Z = 1/[1 - (\sigma_P/\sigma_{CS})(\eta/0.64)^{1/3}]. \quad [2.13]$$

A comparison between the two-fluid approach and that using the Prigogine approximation is shown in Table 1 for three binary equimolecular mixtures of hard spheres, characterized by different values of the molecular-size ratio. For each model and for each mixture, Table 1 gives the relative percentage standard deviation from the Carnahan-Starling equation for the compressibility factor for 15 values of the reduced density η in the range 0.35–0.49.

Table 1 indicates that we may place some confidence in a calculation of the compressibility factor by the Prigogine approximation when the molecular-size ratio is < 1.5 . For molecular-size ratios > 1.5 , the Prigogine approximation gives values that are significantly different from those obtained using the two-fluid procedure. (For $\sigma_{22}/\sigma_{11} = 2$ and $\sigma_{22}/\sigma_{11} = 3$, the approximate procedure gives values which are 14% and 27%

FIG. 2. Compressibility factor as a function of reduced density for binary mixtures with different molecular-size ratios. Left-hand ordinate, for $\sigma_{22}/\sigma_{11} = 1.2$; right-hand ordinate, for $\sigma_{22}/\sigma_{11} = 2.0$. (Upper) Ensemble averaging with size exponent $m = 0$. (Lower) Ensemble averaging with size exponent $m = f(\sigma_{22}/\sigma_{11})$ as explained in text.

greater, respectively, than those obtained from the two-fluid procedure.)

Table 1 also shows results obtained from the one-fluid theory of hard-sphere mixtures—i.e., Flory's equation. As expected, when differences in molecular size are appreciable, the two-fluid theory gives marked improvement over the one-fluid theory.

To provide another semiquantitative test, we compare the

experimental value of the excess entropy for an equimolecular mixture of *n*-hexane and *n*-hexadecane with that calculated by our model for hard-sphere mixtures. McGlashan (8) found that at about 64°C this mixture is athermal. By linear extrapolation of experimental data (9) for excess Gibbs energy at 50°C and 60°C, the excess entropy at 64°C is $S^E/R = 0.030$ (experimental). It is daring to apply a model for spherical molecules to an equimolar mixture of large paraffins. Nevertheless, using our

Table 1. Relative percentage standard deviations from the Carnahan–Starling equation for the compressibility factor of binary equimolar mixtures with $m = f(\sigma_{22}/\sigma_{11})$ and with η in the range 0.35–0.49.

Model* σ_{22}/σ_{11}	1.2	2.0	3.0
a	3.0	5.0	6.3
b	3.1	5.7	8.0
c	4.6	21.7	37.8

* a, Our model; b, Prigogine's approximation; c, one-fluid model (Flory's equation).

two-fluid model

$$S^E/R = 3x_1 \left\{ \ln \frac{\langle \sigma^{(1)} \rangle}{\sigma_{11}} + \ln \frac{[\bar{v}^{(1)}]^{1/3} - 1}{\bar{v}_1^{1/3} - 1} \right\} + 3x_2 \left\{ \ln \frac{\langle \sigma^{(2)} \rangle}{\sigma_{22}} + \ln \frac{[\bar{v}^{(2)}]^{1/3} - 1}{\bar{v}_2^{1/3} - 1} \right\}, \quad [2.14]$$

assuming σ_{11} proportional to $V_{w1}^{1/3}$ and σ_{22} proportional to $V_{w2}^{1/3}$, and utilizing data of Holleman (10) for the excess volume of this mixture, we obtain $S^E/R = 0.071 - 0.046 = 0.025$ (calculated with $\xi_{12} = 0$). Here V_w stands for van der Waals volume as calculated by Bondi (11). In performing this calculation, the Prigogine approximation was used because for this mixture the molecular-size ratio is < 1.5 ($\sigma_{22}/\sigma_{11} = 8.420/6.205 = 1.36$). The proportionality factor (1.518) between σ and $V_w^{1/3}$ was determined by using data for methane (11, 12). In the expression above, the first term (0.071) represents the contribution of the first terms in the two brackets of Eq. 2.14. For the combinatorial excess entropy for this mixture, McGlashan (9) reported 0.076, based on Guggenheim's expression (13). Flory's equation for athermal mixtures, which constitutes the upper limit of combinatorial excess entropy, gives 0.101. The calculated excess entropy is sensitive to ξ_{12} ; with $\xi_{12} = 0.0001$, we obtain $S^E/R = 0.071 - 0.041 = 0.030$ (calculated with $\xi_{12} = 10^{-4}$).

3. Conclusions

Two important results were obtained in the application of two-fluid theory to hard-sphere mixtures. First, two-fluid theory avoids calculation of the combinatorial factor for binary liquid mixtures. Second, the bulk composition of a mixture is most conveniently expressed in terms of "effective" surface area fractions, when molecules are different in size. To calculate "effective" surface areas, we use a size exponent which is correlated as a function of the molecular-size ratio.

We have shown that the Prigogine approximation, which assumes equality of the reduced volumes for the two hypothetical fluids, is applicable only for molecular-size ratio < 1.5 . For larger values, we suggest the two-fluid procedure as outlined in Section 2.

Finally, the domain concept, coupled with the two-fluid theory, provides a possibly useful tool for calculating thermodynamic properties of real, nonrandom mixtures as discussed in ref. 2.

For financial support the authors are grateful to the U.S. Department of Energy, to the National Science Foundation, and to the North Atlantic Treaty Organization for the award of a Senior Fellowship to V.B.

1. Brandani, V. & Prausnitz, J. M. (1982) *Proc. Natl. Acad. Sci. USA* **79**, in press.
2. Brandani, V. & Prausnitz, J. M. (1982) *Proc. Natl. Acad. Sci. USA*, **79**, in press.
3. Tonks, L. (1936) *Phys. Rev.* **50**, 955–963.
4. Carnahan, N. F. & Starling, K. E. (1969) *J. Chem. Phys.* **51**, 635–636.
5. Scott, G. D. (1960) *Nature (London)* **188**, 908–909.
6. Kikic, I., Alessi, P., Rasmussen, P. & Fredeslund, A. (1980) *Can. J. Chem. Eng.* **58**, 253–258.
7. Prigogine, I. (1957) *The Molecular Theory of Solutions* (North-Holland, Amsterdam), p. 195.
8. McGlashan, M. L. (1963) *Nature (London)* **198**, 683.
9. McGlashan, M. L. (1961) *Trans. Faraday Soc.* **57**, 588–600.
10. Holleman, Th. (1963) *Physica* **29**, 585–599.
11. Bondi, A. (1968) *Molecular Crystals, Liquids and Glasses* (Wiley, New York), p. 453.
12. Croll, I. M. & Scott, R. L. (1958) *J. Phys. Chem.* **62**, 954–957.
13. Guggenheim, E. A. (1952) *Mixtures* (Clarendon, Oxford), pp. 215–216.