

Hard-sphere mixture excess free energy at infinite size ratio

Nasiru M. Tukur and Esam Z. Hamad

Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran, 31261, Saudi Arabia

G. Ali Mansoori^{a)}

Chemical Engineering Department, University of Illinois at Chicago, Illinois 60607-7000

(Received 24 July 1998; accepted 10 November 1998)

This article presents the exact limiting value of the derivative of the excess Helmholtz energy, A^E , with respect to molecular size at constant temperature, density and composition for a binary mixture of hard spheres with an infinite size ratio ($\sigma_{11}/\sigma_{22} \rightarrow \infty$); i.e., $\lim_{\sigma_{22} \rightarrow 0} [(\partial A_{hs}^E/RT)/\partial \sigma_{22}]_{T,\rho,x,\sigma_{11}} = (\pi/2)\rho x_1 x_2 \sigma_{11}^2 / (1 - (\pi/6)\rho x_1 \sigma_{11}^3)$. This limiting value is compared with the Mansoori–Carnahan–Starling–Leland (MCSL) and also used to test the limits of some commonly used models in estimating the excess free energy of solvents in mixtures or polymer solutions. The models evaluated include the van Laar, Wilson, Edmond–Ogston, Flory–Huggins, Lacomé–Sanchez, Scott–Magat, and Chen *et al.* It is shown that while the MCSL equation of state produces the same limiting value as the exact value reported here the other mixture models deviate from the exact value. This expression may be utilized to correct the mixture theories at their infinite size ratio limits. © 1999 American Institute of Physics. [S0021-9606(99)50807-6]

I. INTRODUCTION

Properties of hard-sphere mixtures with various size differences between the components are well known.^{1–3} The solutions of the Percus–Yevick equation for hard-sphere mixture resulted in an analytic equation of state for hard spheres.^{1,2} It is also shown that in dense binary mixtures of hard-spheres phase separation occurs when the size ratio, σ_{11}/σ_{22} is less than 0.2 and the partial packing fractions, $(\pi/6)\rho\sigma_{ii}^3$, of the two species are comparable.³ It is the objective of this article to derive an exact limiting value for the excess free energy of hard-sphere mixtures of infinite size difference. This limit is then compared with those derived from the hard-sphere equation of state and the limits of some commonly used models in estimating the excess free energy of mixtures or polymer solutions. Availability of such a limiting value may be useful to correct polymer solution theories which usually fail in predicting properties of mixtures with very large size differences between the polymer and solvent.

Two kinds of excess free energy/activity coefficient models have been proposed in the literature. The first kind applies to molecular liquid mixtures (symmetric or asymmetric, polar or nonpolar), while the second set of models was developed purposely for the thermodynamic modeling of macromolecular/polymer solutions. The models that fall in the first group include, but are not limited to, the Mansoori–Carnahan–Starling–Leland (MCSL) hard-sphere equation of state,² the van Laar⁴ and Wilson⁵ equations. The models that apply to macromolecular/polymer solutions include among others: the Edmond and Ogston model,⁶ the Flory–Huggins theory,⁷ the Lacomé and Sanchez⁸ equation of state, the

Scott and Magat theory of polydisperse polymer solutions,⁹ and the Chen *et al.* equation of state.¹⁰ It is the objective of this article to compare the limits of these models for hard-sphere mixtures of infinite size difference with the exact limit obtained from this work.

II. DERIVATION OF THE LIMIT

The limiting value of the excess Helmholtz free energy will be derived from the mixture pair correlation integrals. From the definition of the mixture pair correlation integrals it is demonstrated that the following expression exists for the partial derivative of the canonical partition function with respect to the molecular size parameter of component two:^{11,12}

$$\left(\frac{\partial \ln Q}{\partial \sigma_{22}}\right)_{T,\rho,x,\sigma_{11}} = -2N\pi\rho(x_2^2\sigma_{22}^2g_{22} + x_1x_2\sigma_{12}^2g_{12}). \quad (1)$$

Now considering the definition of partition function Q ,

$$\ln Q = -A/kT \quad (2)$$

by combining Eqs. (1) and (2) the following expression for the partial derivative of the Helmholtz free energy with respect to σ_{22} , the molecular size parameter of component 2 results in

$$\left(\frac{\partial A/RT}{\partial \sigma_{22}}\right)_{T,\rho,x,\sigma_{11}} = 2\pi\rho(x_2^2\sigma_{22}^2g_{22} + x_1x_2\sigma_{12}^2g_{12}). \quad (3)$$

Considering Eq. (3) and taking its asymptotic limit as σ_{22} approaches zero ($\sigma_{22} \rightarrow 0$) we get

$$\therefore \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A/RT}{\partial \sigma_{22}}\right)_{T,\rho,x,\sigma_{11}} = 2\pi\rho x_1 x_2 \left(\frac{\sigma_{11}}{2}\right)^2 \lim_{\sigma_{22} \rightarrow 0} g_{12}. \quad (4)$$

^{a)} Author to whom correspondence should be addressed; electronic mail: mansoori@uic.edu

For a hard-sphere mixture the $\sigma_{22} \rightarrow 0$ limiting value of the pair correlation function is already available and it is given in Ref. 13 as

$$\lim_{\sigma_{22} \rightarrow 0} g_{12}^{hs} = \frac{1}{1 - \frac{\pi}{6} \rho x_1 \sigma_{11}^3}. \quad (5)$$

Then, by combining Eqs. (4) and (5) for a hard-sphere mixture we get

$$\begin{aligned} \therefore \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A_{hs}/RT}{2\sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} \\ = \frac{\pi}{2} \rho x_1 x_2 \sigma_{11}^2 \left/ \left(1 - \frac{\pi}{6} \rho x_1 \sigma_{11}^3 \right) \right. \end{aligned} \quad (6)$$

The next few steps will be to relate the above limit to that of the excess Helmholtz free energy, A^E . The excess Helmholtz free energy of a mixture over that of an ideal solution is defined by

$$A^E = \Delta A - \sum x_i \Delta A_i, \quad (7)$$

where

$$\Delta A = A_{\text{mix}}(T, \rho) - A_{\text{mix}}^{ig}(T, \rho)$$

and

$$\Delta A_i = A_i(T, \rho) - A_i^{ig}(T, \rho).$$

Differentiating Eq. (7) for a binary hard-sphere mixture with respect to σ_{22} at constant T , ρ , σ_{11} and composition yields

$$\left(\frac{\partial A^E}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} = \left(\frac{\partial \Delta A}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} - x_2 \left(\frac{\partial \Delta A_2}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}}. \quad (8)$$

A_1 does not depend on σ_{22} , which is the molecular diameter of the second component of the binary mixture. Taking the limit of the partial derivative of A^E , given by Eq. (8) with respect to σ_{22} as $\sigma_{22} \rightarrow 0$ leads to

$$\lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A^E}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} = \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial \Delta A}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}}. \quad (9)$$

The second term of Eq. (8) will drop upon taking the limit as shown below. Now considering the expression for the Helmholtz free energy of pure component 2

$$\Delta A_2 = A_2 - A_2^{ig} = f \left(\frac{\pi}{6} \rho \sigma_{22}^3, T \right), \quad (10)$$

one can get

$$\left(\frac{\partial \Delta A_2}{\partial \sigma_{22}} \right)_{T,\rho} = f \left(\frac{\pi}{2} \rho \sigma_{22}^2, T \right). \quad (11)$$

It can be shown that taking the limit of Eq. (11) as $\sigma_{22} \rightarrow 0$ yields

$$\lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial \Delta A_2}{\partial \sigma_{22}} \right)_{T,\rho} = 0. \quad (12)$$

Now, dividing Eq. (9) by RT gives:

$$\lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A^E/RT}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} = \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial \Delta A/RT}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}}. \quad (13)$$

By joining Eqs. (6) and (13) the following limiting value for the partial derivative of the excess Helmholtz free energy of a hard-sphere mixture will be derived:

$$\begin{aligned} \therefore \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A_{hs}^E/RT}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} \\ = \frac{\pi}{2} \rho x_1 x_2 \sigma_{11}^2 \left/ \left(1 - \frac{\pi}{6} \rho x_1 \sigma_{11}^3 \right) \right. = \frac{3x_2 y_1}{\sigma_{11}(1-y_1)}. \end{aligned} \quad (14)$$

where:

$$y_1 = \frac{\pi}{6} \rho x_1 \sigma_{11}^3 \quad (15)$$

is defined as the packing fraction of component one in the mixture. Equation (14) is exact and it is applicable for calculation of the limiting excess Helmholtz free energy when the size difference between the components of the hard-sphere mixture goes to infinity. In the next section the same limiting value is calculated for various mixture theories and they are compared with the above exact value.

III. COMPARISONS AND CONCLUSIONS

Differentiating the excess Helmholtz free energy of the MCSL equation of state² with respect to σ_{22} at constant temperature and reduced density (y), and taking the limit as $\sigma_{22} \rightarrow 0$ gave a limiting value that is exactly identical to the one arrived at in this work [(Eq. 14)]

$$\therefore \lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A_{hs}^E/RT}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}} = \frac{3x_2 y_1}{\sigma_{11}(1-y_1)}.$$

TABLE I. Comparison of the exact value with the existing mixture models.

Models	$\lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial A_{hs}^E/RT}{\partial \sigma_{22}} \right)_{T,\rho,x,\sigma_{11}}$
Exact value as reported by Eq. (14)	$\frac{3x_2 y_1}{\sigma_{11}(1-y_1)}$
Van Laar (Ref. 4)	0
Wilson (Ref. 5)	∞
Edmond-Ogston (Ref. 6)	0
Flory-Huggins (Ref. 7)	0
Lacome-Sanchez (Ref. 8)	0
Scott-Magat (Ref. 9)	0
Chen-Fredenslund-Rasmussen (Ref. 10)	0
MCSL hard-sphere equation of state ²	$\frac{3x_2 y_1}{\sigma_{11}(1-y_1)}$

However, differentiating the excess Gibbs free energy of the MCSL equation with respect to σ_{22} at constant temperature, volume, and composition and taking the limit as $\sigma_{22} \rightarrow 0$ gave an additional term as the limiting value.

$$\lim_{\sigma_{22} \rightarrow 0} \left(\frac{\partial G_{hs}^E / RT}{\partial \sigma_{22}} \right)_{T, \rho, x, \sigma_{11}} = \frac{3x_2y_1}{\sigma_{11}(1-y_1)} + \frac{3x_2y_1}{\sigma_{11}(1-y_1)^2}.$$

It is generally known that for liquids one can safely assume $G^E(\text{at constant } T \& P) = A^E(\text{at constant } T \& V)$. Therefore, for the purpose of comparison, the partial derivative of the excess Gibbs free energy with respect to σ_{22} in the limit as $\sigma_{22} \rightarrow 0$ of some models commonly used in estimating activity coefficients were obtained. The results are compared with the limiting value obtained in this work for the derivative of excess Helmholtz free energy. The values of 0 and ∞ obtained from the models were quite different from the exact limit, Eq. (14). Table I shows the limits arrived at from these models for the hard-sphere mixtures of infinite size ratio. According to Table I all the available models for molecular mixtures and macromolecular/polymer solutions deviate from the exact limiting value of the derivative of the excess Helmholtz free energy, Eq. (14), at infinite size and temperature ratios. The MCSL hard-sphere equation of state reproduces the exact limiting value. The exact equation reported here, Eq. (14), may be utilized to correct the inaccurate limiting value of mixture theories at infinite size ratio.

ACKNOWLEDGMENTS

The authors thank Ali Eliassi for his help in some of the model calculations. This research is supported in part by the U.S. National Science Foundation, Grant No. DE-FG02-84ER13229.

APPENDIX: NOMENCLATURE

Symbols

Q	= Partition function,
G	= Gibbs energy,
A	= Helmholtz energy,
V	= Molar volume,
P	= Pressure,
R	= Universal gas constant,
x	= molar fraction,
y	= reduced density,
k	= Boltzmann's constant,
g_{ij}	= Pair correlation function of molecules of type i and j .

Superscripts

E	= excess property,
ig	= ideal gas.

Subscripts

i	= component i ,
mix	= mixture.

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