

A NEW MIXING RULE FOR MIXTURES OF HARD-SPHERES

*Mohsen-Nia, Mohsen and Modarress, Hamid**

Department of Chemical Engineering, Amir-Kabir University of Technology, Tehran, I.R. Iran

Mansoori, Gholam Ali

Department of Chemical Engineering, University of Illinois at Chicago, USA

ABSTRACT: A mixing rule for the mixtures of hard-spheres is presented which can be reduced to the standard van der Waals mixing rule at low densities. The effectiveness of the mixing rule for the size and energy parameters of Lennard-Jones fluids are examined by combining them with an equation of state to calculate thermodynamic properties. The results of calculation are compared with the molecular dynamic simulation data and the superiority of the present mixing rule over the standard van der Waals mixing rule is demonstrated.

KEY WORDS: Equation of state, Mixing rule, van der Waals, Corresponding state theory.

INTRODUCTION

According to of the molecular corresponding state theory [1-3] the interaction of a molecular pair can be expressed in terms of a universal function F_ϵ which can be represented by the following equation:

$$u/\epsilon = F_\epsilon(r/\sigma)$$

where u is the molecular pair interaction potential function and σ and ϵ are the pair size and energy parameters in the potential function.

In application of the corresponding state theory to the fluid mixtures, it is necessary to assume the same functionality F_ϵ for each pair of molecules and by considering the mixture as a hypothetical pure

fluid, the size and energy parameters (σ_m and ϵ_m) for the mixture can be expressed in terms of parameters for pure components using appropriate mixing rules.

Several mixing rules have been presented [4,5] among which the standard van der Waals mixing rule derived by Leland et al. [6,7] based on statistical mechanical concepts, has been widely used for the calculation of thermodynamic properties [8-12]. However, the van der Waals mixing rule is unable to produce satisfactory results due to the limited validity of inherent assumptions as shown by several workers [13,14]. In our previous work on thermodynamic properties calculations of real fluids it was shown that

* To whom correspondence should be addressed.

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van der Waals mixing rule fails especially at high reduced densities where the molecular diameter ratios of the components are large [15].

In this work, a new mixing rule for the size parameter is presented which can be reduced to the standard van der Waals mixing rule at low densities. The effectiveness of the proposed mixing rule is examined by comparing the calculated thermodynamic properties with the simulation data for the same properties for the Lennard-Jones fluids.

THEORY

The standard van der Waals mixing rule can be obtained if one considers the second virial coefficient of a mixture, which from statistical mechanical theories is derived as [16]:

$$B_m = \sum_i^n \sum_j^n x_i x_j B_{ij}(T) \quad (1)$$

where x_i and x_j represent the mole fraction of components i and j . For a pure hard-sphere fluid the second virial coefficient is expressed as [16]:

$$B(T) = 2\pi\sigma^3/3 \quad (2)$$

From Eqs. (1) and (2), a mixture size parameter can be derived in the following form [5,12]:

$$\sigma_m^3 = \sum_i^n \sum_j^n x_i x_j \sigma_{ij}^3 \quad (3)$$

where, σ_{ij} is defined as:

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (4)$$

In Eq. (4), σ_i and σ_j , respectively are the molecular diameters of components i and j , considered as hard-spheres.

In the previous work [17], based on structural considerations as well as the concepts of partial segregation theory [15] it was shown that it is reasonable to propose an effective diameter σ_e for a pure hard-spheres fluid in the following form:

$$\sigma_e^3 = \sigma^3 (1 + \alpha y) \quad (5)$$

where, σ is the actual hard sphere diameter, y is a packing fraction which takes the structural considerations into account and α is an adjustable parameter, (for $\alpha=0$, $\sigma_e^3 = \sigma^3$ and hard-sphere assumption is acceptable). The packing fraction, y can be expressed

in terms of ρ the actual density as [18]:

$$y = \rho \pi \sigma^3 / 6 \quad (6)$$

From Eqs. (3) and (5) and considering the mixture of hard-spheres as a hypothetical pure fluid, the effective size parameter can be written as:

$$\sigma_{me}^3 = \sum_i^n \sum_j^n x_i x_j \sigma_{ij}^3 (1 + \alpha y) \quad (7)$$

where y is the packing fraction for the mixture of hard-spheres and is expressed in the following form:

$$y = \sum_{i=1}^n (\pi/6) \rho \sigma_i^3 x_i \quad (8)$$

To apply the mixing rule presented in Eq. (7), the adjustable parameter α should be evaluated by an exact equation of state for the mixture of hard-spheres.

Mansoori et al. [18] presented the following equation for the residual Helmholtz free energy for the mixture of hard-spheres:

$$\frac{A_r}{NkT} = \frac{3}{2} (1 - Y_1 + Y_2 + Y_3) + (3Y_2 + 2Y_3)(1 - y_m) - 1 + \frac{3}{2} (1 - Y_1 - Y_2 - \frac{1}{3} Y_3)(1 - y_m) - 2(Y_3 - 1) \ln(1 - y_m) \quad (9)$$

where, y is defined the same as in Eq. (8) and Y_1 , Y_2 and Y_3 are functions of packing fractions [18]. For the pure hard-spheres fluid, Eq. (9) can be reduced to:

$$\frac{A_r}{NkT} = y_m (4 - 3y_m) / (1 - y_m)^2 \quad (10)$$

According to the idea of the effective diameter for the hard-spheres presented in this work, the actual packing fraction y_m , in Eq. (10) should be replaced by an effective packing fraction y_e , which is obtained from Eqs. (5) and (6) as:

$$y_e = (\pi/6) \rho \sigma^3 (1 + \alpha y) \quad (11)$$

Then for the mixture of hard-spheres, one will have:

$$y_{me} = (\pi/6) \rho \sigma_m^3 (1 + \alpha y_m) \quad (12)$$

To calculate α , we consider the mixture as a hypothetical pure hard-sphere fluid and calculate y_{me} from Eq. (12). Then, y_{me} is used in Eq. (10) to calculate the residual Helmholtz free energy, A_r , for the hypothetical pure hard-spheres fluid. The calcu-

lated A_r is used in Eq. (10), to drive an equation for α . The derivation is not explicit, however, an approximate equation for α can be presented as [15]:

$$\alpha = \sum_i^n \sum_{j<i}^n x_i x_j [(\sigma_i - \sigma_j)/\sigma_{ij}]^2 (\sigma_i/\sigma_j) \quad (13)$$

On substituting for α from Eq. (13) in (7) and using Eq. (8), the following mixing rule can be obtained for the size parameter of the hard-spheres mixture.

$$\sigma_{me}^3 = \sum_i^n \sum_{j<i}^n x_i x_j \sigma_{ij}^3 \left\{ 1 + \sum_i^n (\pi/6) x_i \rho \sigma_i^3 \right\} \sum_{j<i}^n x_i x_j [(\sigma_i - \sigma_j)/\sigma_{ij}]^2 (\sigma_i/\sigma_j) \quad (14)$$

To calculate thermodynamic properties, the proposed mixing rule can be combined with an appropriate equation of state for the pure hard-spheres fluid. In the next section this point will be discussed in details.

Hard-spheres mixture calculations

The compressibility factor of pure hard-spheres as proposed by Carnahan and Starling [19], can be expressed in the following form:

$$Z = (1 + y + y^2 + y^3)/(1 - y)^3 \quad (15)$$

Combining the mixing rule as proposed in Eq. (14), with the Carnahan-Starling equation of state, the following equation for the hard-spheres mixture can be obtained:

$$Z = (1 + y_{me} + y_{me}^2 - y_{me}^3)/(1 - y_{me}^3) + (4 - 2y_{me})/(1 - y_{me})^3 \left[\left(\frac{\pi \rho \sigma_m^3}{6} \right) (\alpha y / y_{me}) \right] \quad (16)$$

Table 1 shows the compressibility factor for an equimolar binary mixture of hard-spheres compared with the results of molecular dynamic (MD) simulation [20,21] and those of equation of state by Mansoori et al. (MCSL) [18]. According to this table the compressibility factor using the proposed mixing rule is predicted with the same accuracy as those of MD and MCSL. It is worth noting that the MCSL is an accurate but complicated equation of state for hard-spheres mixture. Therefore, the simplicity and accuracy of the proposed mixing rule is an attribute for promoting its applications over the MCSL for thermodynamic properties calculations of hard-sphere fluids.

Table 1: The compressibility factor for a binary mixture of hard-spheres for ($x_1 = x_2 = 0.5$)

Method	y= 0.1571	y= 0.2618	y= 0.3665
$\sigma_2/\sigma_1 = 1.1$			
MD	1.96	3.17	5.64
MCSL	1.96	2.25	5.69
This work	1.96	3.25	5.68
$\sigma_2/\sigma_1 = 5/3$			
MD	1.87	3.04	5.24
MCSL	1.88	3.04	5.21
This work	1.88	3.04	5.18

Table 2 indicates the comparison between the calculated thermodynamic properties of an equimolar binary mixture of hard-spheres by the proposed mixing rule and the MCSL equation of state [18], and the results are compared with the MD data [20,21] where the applicability and simplicity of the proposed mixing rule is clearly demonstrated.

Fig. 1 shows the calculated compressibility factor of the mixture with ($\sigma_2/\sigma_1 = \text{infinity}$) by the proposed mixing rule and the MCSL equation. This figure indicates the accuracy of presented mixing rule for systems with large diameter ratios and high densities.

In Figs. 2-5 the calculated excess properties of the binary mixtures of hard-spheres for the entire range

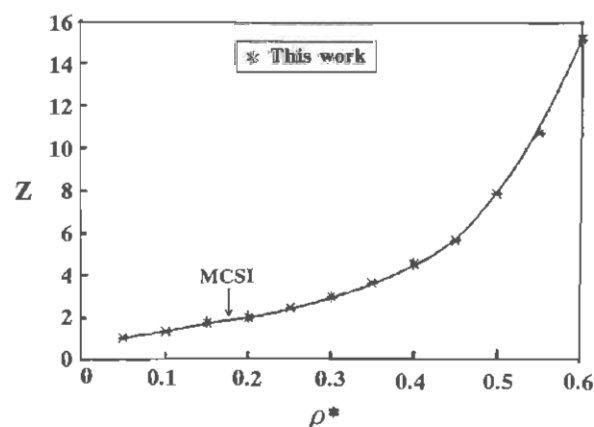


Fig. 1: Calculated compressibility factor (Z), of the mixture ($\sigma_2/\sigma_1 = \text{infinity}$) vs. reduced density (ρ^*), by the proposed mixing rule and MCSL equation.

Table 2: Comparison of calculated thermodynamic properties of binary mixture of hard spheres ($x_1 = x_2 = 0.5$, $\sigma_2/\sigma_1 = 3$) by this work, MCSL equation of state and molecular dynamic (MD) data.

Properties	Method	y= 0.233	y= 0.358	y= 0.500
Z	MD	2.37	3.36	9.77
	MCSL	2.37	3.36	9.90
	This work	2.38	3.37	9.68
$-\Delta Z$	MD	0.46	0.84	3.62
	MCSL	0.46	0.85	3.72
	This work	0.46	0.83	3.95
$-S^E/NK$	MD	0.14	0.31	1.52
	MCSL	0.14	0.31	1.52
	This work	0.14	0.31	1.52
$\Delta S^E/NK$	MD	0.12	0.26	1.07
	MCSL	0.13	0.26	1.06
	This work	0.13	0.26	1.04
G^E/NK	MD	1.51	2.67	10.29
	MCSL	1.51	2.66	10.39
	This work	1.51	2.69	10.19
$-\Delta G^E/NK$	MD	0.60	1.13	4.77
	MCSL	0.59	1.11	4.78
	This work	0.57	1.08	4.98

of mole fractions are compared with the results of van der Waal (vdW) mixing rule. It is worth noting that for $\alpha=0$, the proposed mixing rule is reduced to vdW mixing rule. These figures show that the presented mixing rule has better accuracy than the vdW mixing rule.

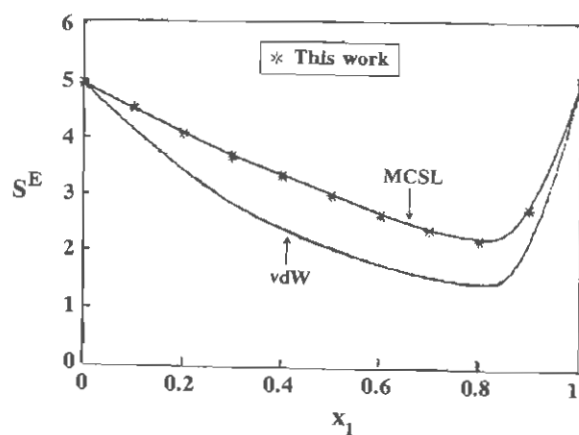


Fig. 2: Comparison of calculated excess entropy (S^E), for the binary mixtures ($\sigma_2/\sigma_1 = 3$) of hard-spheres vs. mole fractions of component 1, (x_1).

Lennard-Jones mixtures calculations

For hard-spheres fluids only the repulsive term in the potential energy function is considered. To apply the proposed mixing rule to the real fluids an energy parameter mixing rule based on a potential function containing both attractive and repulsive terms is required.

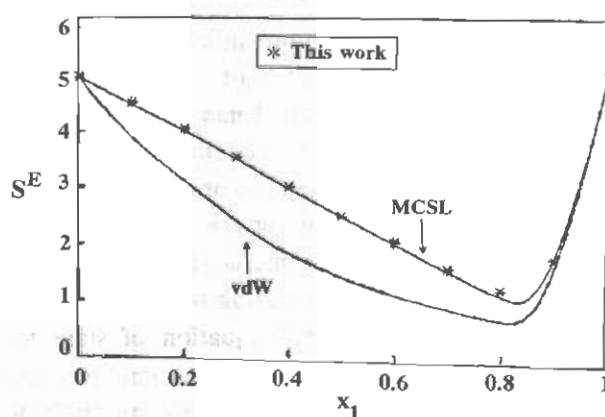


Fig. 3: Comparison of calculated excess entropy (S^E), for the binary mixtures ($\sigma_2/\sigma_1 = 6$) of hard-spheres vs. mole fractions of component 1, (x_1).

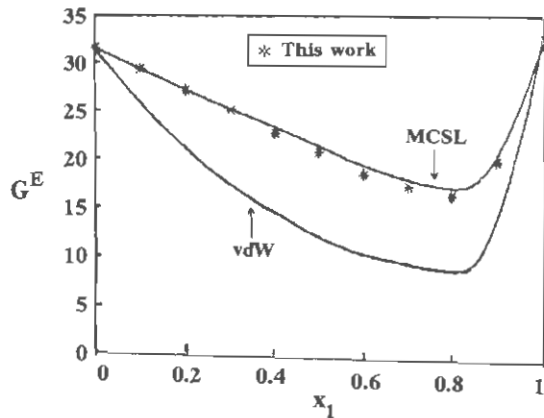


Fig. 4: Comparison of calculated excess Gibbs free energy, (G^E) for the binary mixtures ($\sigma_2/\sigma_1 = 6$) of hard-spheres vs. mole fractions of component 1, (x_1).

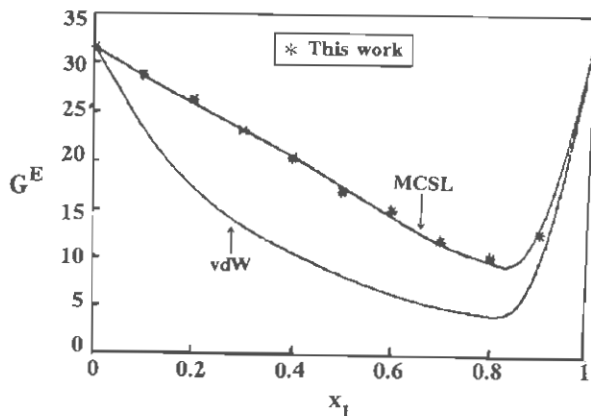


Fig. 5: Comparison of calculated excess Gibbs free energy, (G^E) for the binary mixtures ($\sigma_2/\sigma_1 = 3$) of hard-spheres vs. mole fractions of component 1, (x_1).

The potential energy function which is used here is the Lennard-Jones function [22,23]:

$$u = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (17)$$

where, σ and ε are size and energy parameters respectively.

The standard van der Waals mixing rule for energy parameter has been presented as [5]:

$$\varepsilon_x \sigma_x^3 = \sum_i^m \sum_j^m x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \quad (18)$$

where:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad \text{and} \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$$

On combining Eqs. (14) and (18) the energy parameter ε_m for a mixture of hard-spheres will be

obtained as:

$$\varepsilon_m = \frac{\sum_i^n \sum_j^n x_i x_j \varepsilon_{ij} \sigma_{ij}^3}{\sum_i^n \sum_j^n x_i x_j \sigma_{ij}^3} \left\{ 1 + \left(\sum_i^n \frac{\pi}{6} \rho x_i \sigma_i^3 \right) \sum_{i=1}^n \sum_{i>j}^n x_i x_j [(\sigma_i - \sigma_j) / \sigma_{ij}]^2 (\sigma_i / \sigma_j) \right\} \quad (19)$$

Here again an equation of state is needed in order to calculate the thermodynamic properties. Nicolas et al. [24] proposed an equation of state which can be fitted to the Lennard-Jones potential function for pure fluids. Therefore we decided to extend the application of Nicolas et al. [24] equation of state to the Lennard-Jones mixtures.

The final form of the equation of state which utilizes the mixing rule presented in Eqs.(14) and (19) is:

$$P^*(T^*, \rho^*) = P_0^*(T^*, \rho^*) + (\rho / \sigma_m^3) (\partial \sigma_m^3 / \partial \rho) [P_0^*(T^*, \rho^*) - \rho^* T^*] \quad (20)$$

where $P^* = P \sigma_m^3 / \varepsilon_m$, $\rho^* = \rho \sigma_m^3$ and $T^* = kT / \varepsilon_m$ are the reduced pressure, density and temperature respectively, and P_0^* refers to the pressure obtained from the Nicolas et al. [24] equation of state for a pure hypothetical fluid.

The Helmholtz function which can be derived for the mixture, from the equation of state, is of the form:

$$A_m = NkT \sum_i x_i \ln x_i + A(kT / \varepsilon_m, \rho \sigma_m^3) \quad (21)$$

where $A(kT / \varepsilon_m, \rho \sigma_m^3)$ is a Helmholtz function expressed in terms of energy and size parameters for the mixture (considered as a hypothetical pure Lennard-Jones fluid).

The residual Helmholtz free energy for the mixture and the residual chemical potential for component(i) are defined respectively as:

$$A_r = A_m - A_m^{id} \quad (22)$$

$$\mu_{ir} = (\mu_i - \mu_i^{id})$$

The residual chemical potential can be obtained from Eqs. (21) and (22) by:

$$\mu_{ir} = (\partial A_r / \partial N_i)_{T, V, N_j} \quad (23)$$

Thus, the final result is:

$$\mu_{ir} = \mu_{mr}^0 + N(\partial \varepsilon_m / \partial N_i)(u_{mr} / \varepsilon_m) + (\partial \sigma_m^3 / \partial N_i) \sigma_m^3 (PV)_{mr} \quad (24)$$

where μ_{mr}^0 refers to the reduced chemical potential of the hypothetical pure component. In the dimensionless form the above equation can be written as:

$$\mu_{ir}^* = \mu_{mr}^* + N(\partial \epsilon_m / \partial N_i)(u_{mr}^* / \epsilon_m) + (P^* / \rho^*)_{mr}(N / \sigma_m^3) (\partial \sigma_m^3 / \partial N_i) \quad (25)$$

where μ_{ir}^* and u_{mr}^* are the dimensionless residual chemical potential and internal energy defined as:

$$\mu_{ir}^* = \mu_{ir} / \epsilon_m \text{ and } u_{mr}^* = u_{ir} / \epsilon_m \quad (26)$$

For a binary mixture, where x_i approaches zero the residual chemical potential can be expressed as [4,20,21]:

$$\lim_{x_i \rightarrow 0} \mu_{ir} / kT = \ln(H_i / \rho kT) \quad (27)$$

where H is the Henry's law constant.

Using the above considerations the Henry's law constant can be obtained for the binary mixture of Lennard-Jones fluid in the following form:

$$\ln(H_i / \rho kT) = \mu_{ir} / kT + N(\partial \epsilon_m / \partial N_i)(u_{jr} / kT \epsilon_{ij}) + (Z_j - 1) (N / \sigma_{ij}^3) (\partial \sigma_m^3 / \partial N_i) \quad (28)$$

Finally after a long but straightforward manipulation the Henry's law constant can be presented as:

$$\ln(H_i / \rho kT) = \mu_{jr} / kT + (u_{jr} / kT) [-2(h-1) - (\pi\rho/6) (\sigma_{ij}-1)^2 + 2(f.h-1)] (Z_j - 1) [2(h-1) + (\pi\rho/6) (\sigma_{ij}-1)^2] \quad (29)$$

where $h = (\sigma_{ij} / \sigma_{jj})^3$ and $f = \epsilon_{ij} / \epsilon_{jj}$.

Figs. (6) and (7) show the calculated dimensionless chemical potential by Eq. (25), for a Lennard-Jones binary mixture with $\epsilon_{11} / \epsilon_{22} = 1$, $\rho(x_1 \sigma_{11}^3 + x_2 \sigma_{22}^3) = 0.7$, $kT / \epsilon_{22} = 1.2$ and $(\sigma_{12} / \sigma_{22})^3 = 1.5$ compared with the MD simulation data. As it is seen the presented mixing rule has a higher accuracy compared to the van der Waals' mixing rule.

Fig. 8 shows the Henry's law constant calculated with $\epsilon_{11} / \epsilon_{22} = 1$, $\rho \sigma_2^3 = 0.7$, $kT / \epsilon_{22} = 1.2$ and $\sigma_{11} / \sigma_{22} = 1$ by Eq. (28) and that obtained from van der Waals mixing rule compared with the MD simulation data. Again it is seen that the proposed mixing rule in this work has a better accuracy.

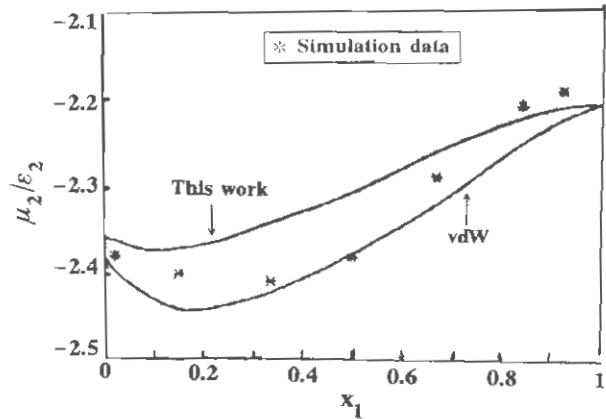


Fig. 6: Comparison of variation of dimensionless chemical potential of component 2, (μ_2/ϵ_2) vs. mole fractions of component 1, (x_1).

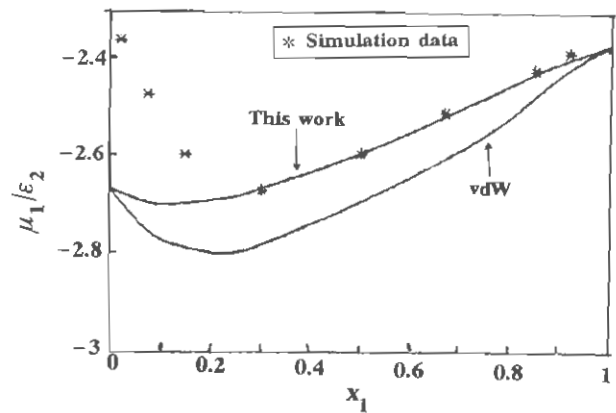


Fig. 7: Comparison of variation of dimensionless chemical potential of component 1, (μ_1/ϵ_1) vs. mole fractions of component 1, (x_1).

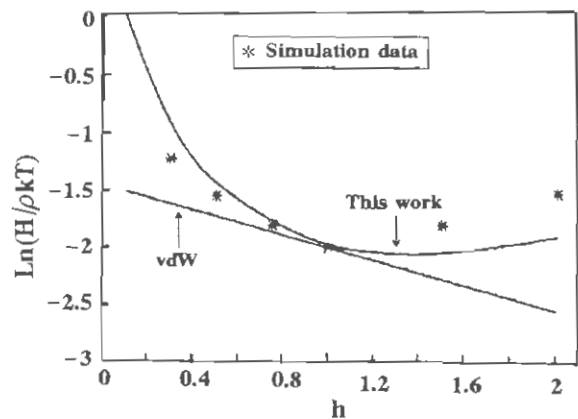


Fig. 8: Comparison of variation of Henry's law constant as $\ln(HV/\rho kT)$ vs. $h = (\sigma_{11}/\sigma_{22})^3$.

Figs. 9 and 10 show the variation of compressibility factor for an equimolar Lennard-Jones mixture

with $\varepsilon_{11}/\varepsilon_{22}=1$ and $\rho^*=0.8$ at $T=270$ K and $T=200$ K respectively. As it is seen the variations have the same trend as the simulation data.

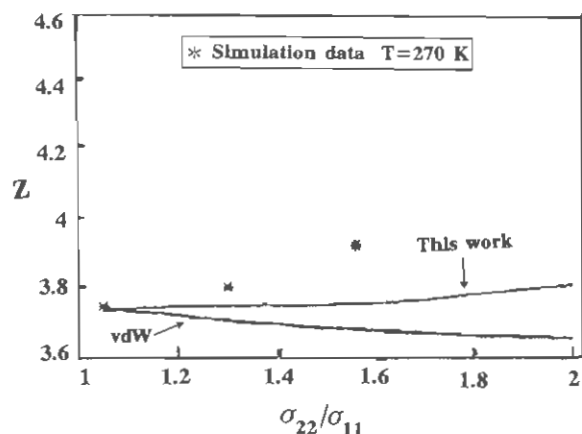


Fig. 9: Comparison of variation of compressibility factor, (Z) vs. σ_{22}/σ_{11} for $\varepsilon_{11} = \varepsilon_{22}$ at $T=270$ K.

CONCLUSION

It was shown that application of the mixing rule based on structural considerations can lead to calculated thermodynamic properties with a better accuracy than the standard van der Waals mixing rule.

Since the mixing rules are derived from parameters of potential function, the accuracy of the calculated thermodynamic properties depend on the capability of the potential function in expressing the molecular interactions. Therefore, using a more realistic potential function can result in an effective mixing rule, hence a more accurate prediction of thermodynamic properties.

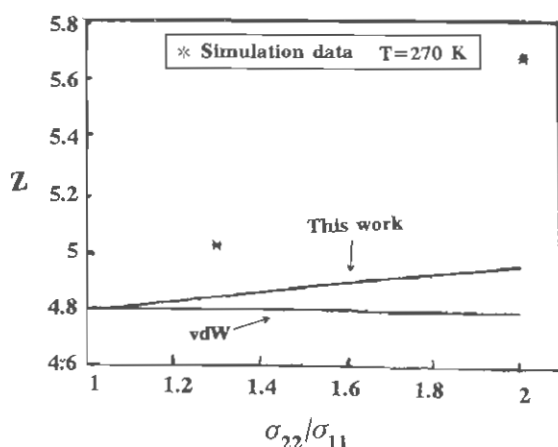


Fig. 10: Comparison of variation of compressibility factor, (Z) vs. σ_{22}/σ_{11} for $\varepsilon_{11} = \varepsilon_{22}$ at $T=200$ K.

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List of symbols and abbreviations

A	Helmholtz energy
B	Second virial coefficient
f	$(\varepsilon_{ij}/\varepsilon_{jj})$
F_ε	Universal potential energy function
H	Henry's law constant
h	$(\sigma_{ij}/\sigma_{jj})^3$
K	Boltzmann constant
MCSL	Mansoori et al. equation of state
P	Pressure
P_0^*	Reduced pressure for Nicolas et al. equation of state
r	Molecular distance
T	Absolute temperature
u	Internal energy
x	Mole fraction
y	Packing fraction
Y_1, Y_2	Functions in MCSL equation of state and Y_3
Z	Compressibility factor

Greek Letters

α	Adjustable parameter
ε	Energy parameter
μ	Chemical potential
ρ	Density
σ	Hard sphere diameter and size parameter

Superscripts

i	Ideal
*	Dimensionless

Subscripts

e	Effective value
i,j	Components i and j
me	Mixture effective value
r	Residual property
0	Hypothetical pure component

REFERENCES

- [1] Hirschfelder J. O., Curtiss, C. F. and Bird R. B., "Molecular Theory of Gases and Liquids", John Wiley and Sons, Inc. New York (1954).

- [2] Prausnitz, J. M., Lichtenthaler R. N. and de Azevedo E. G., "Molecular Thermodynamics of Fluid Phase Equilibria", 2nd Ed., Prentice-Hall, Inc., Engelwood Cliffs, New Jersey (1986).
- [3] Walas S. M., "Phase Equilibria in Chemical Engineering", Butterworth Publishers(1985).
- [4] Mansoori G. A. and Haile J. M., "Molecular-Based Study of Fluids", Advances in Chemistry Series, ACS New York(1983).
- [5] Matteoli E. and Mansoori G. A., "Fluctuation Theory of Mixtures" Advances in Thermodynamics, Volume 2, Taylor and Francis, London (1990).
- [6] Leland T. W. and Chappellear, P. S., Recent Developments in the Theory of Fluid Mixtures, *Ind. Eng. Chem.*, **6**, 15(1968).
- [7] Leland T. W., Rowlinson J. S. and Sather G. A., Statistical Thermodynamics of Mixtures of Molecules of Different size, *Trans. Faraday Soc.*, **64**, 1447(1968).
- [8] Boublik T., Hard-Sphere Equation of State, *J. Chem. Phys.*, **53**, 471(1970).
- [9] Boublik T., Progress in Statistical Thermodynamic Applied to Fluid Phase, *Fluid Phase Equilibria*, **1**, 37(1977).
- [10] Coperman T. N and Mathias P. M., Recent Mixing Rule for Equation of State, An Industrial Perspective, *ACS Symp. Series.*, **300**, 352(1985).
- [11] Dimiterlis D. and Prausnitz J. M., Comparison of Two Hard-Sphere References Systems for Perturbation Theories for Mixtures, *Fluid Phase Equilibria*, **31**, 1(1986).
- [12] Hamad E. Z. and Mansoori G. A., Dense Fluid Theory of Mixtures, *J. Chem. Phys.*, **15**, 6046 (1987).
- [13] Meyer, E. C., A One-Fluid Mixing Rule for Hard-Sphere Mixtures, *Fluid Phase Equilibria*, **41**, 19(1988).
- [14] Mansoori G. A., Mixing Rules for Cubic Equation of State, *ACS Symposium Series*, Washington, D.C., **300**, Part 15, 314(1986).
- [15] Mohsen-Nia, M., "Modification of Equations of State", Ph.D Thesis, Amir Kabir University of Technology, Tehran, Iran (1993).
- [16] Reed T. M. and Bubbins K. E., "Applied Statistical Mechanics, Thermodynamic and Transport Properties of Fluids", McGraw Hill(1973).
- [17] Mohsen-Nia, M., Modarress H. and Mansoori G. A., "Partial Segregation Theory of Fluids.", *The First National Chemical Engineering Meeting*, Tehran, Iran(1994).
- [18] Mansoori, G. A., Carnahan, N. F., Starling, K. E. and Leland T. W., Equilibrium Thermodynamic Properties of the Mixture of Hard-Spheres, *J. Chem. Phys.*, **54**, 1523; see also Carnahan, N. F. and Starling, K. E., Intermolecular Repulsions and the Equation of State for Fluids, *AIChE J.*, **1972**, **18**, 1184(1971).
- [19] Carnahan N. F. and Starling K., Equation of State for Non-attraction Rigid Spheres, *J. Chem. Phys.*, **51**, 2(1969).
- [20] Shing K. S and Gubbins K. E., "The Chemical Potential in Dense Mixtures via Computer Simulation", *Mol. Phys.*, **46**, 1109(1982).
- [21] Shing K. S and Gubbins K. E., The Chemical Potential in Non-Ideal Liquid Mixtures. Computer Simulation and Theory., *Mol. Phys.*, **49**, 1121 (1983).
- [22] Hill T. L., "An Introduction to Statistical Thermodynamics", Addison-Wesely, Reading, Massachusetts(1960).
- [23] Margenau, H. and Kestner N. R., Theory of Intermolecular Forces, *Adv. Quantum Chem.*, **3**, 129(1967).
- [24] Nicolas J. J., Gubbins K. E., Street W. B. and Tildesley D. J., Equation of State for the Lennard-Jones Fluid, *Mol. Phys.*, **37**, 1429(1979).