

One - fluid Conformal Solution Theory for Lennard - Jones Liquid Mixtures

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Lennard - Jones 유체 혼합물의 열역학적 연구

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요 약

Lennard - Jones 유체 혹은 거의 구형에 가까운 분자들의 혼합물의 열역학적 성질을 예측하기 위한 용액이론이 유도되었다. 이 이론에는 에너지와 분자직경에 대한 두 개의 변수가 존재하며, 강구(hard sphere)를 중심으로 하여 동경함수(pair distribution function)를 확장시키는 교반이론(perturbation theory)에서 $1/kT$ 에 대한 일차와 이차계수의 관계로부터 얻어지는 혼합법칙을 이용하는 HSE이론과 달리 Orstein-Zernike결과와 일치되는 분자직경 변수를 먼저 구한 다음, 일차계수와 함께 얻어진 혼합법칙이 유도되었다.

이 방법으로 위 유체들의 혼합물에 적용시켰을 때, 원래의 HSE나 vdW-1의 방법보다 좋은 결과의 열역학적 성질을 예측할 수 있었다.

Introduction

There has been considerably increased effort during the past decade in the extension of rigorous theories for the prediction of pure fluid properties to mixture properties.

One approach is to make use of the molecular theory based on perturbation theory and thereby provides a more rigorous description of the composition dependence in calculating thermodynamic properties of mixture. The pseudo - experimental data such

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as Monte Carlo (MC) and molecular dynamics (MD) make it possible to verify the validity of the theoretical models proposed.

The purpose of this work is to calculate thermodynamic properties of Lennard-Jones and real simple fluid mixtures by a newly-derived conformal solution theory and to compare the results with those of other methods and MC data, which are conventionally considered to be 'experimental'.

Theory

The statistical-mechanical theories of liquids and their mixtures such as perturbation and variational method provide relations between the thermodynamic functions of a system and the interaction energy $u(r)$, which involves the distribution functions of sets of molecules. The pair distribution function (PDF), $g(r)$, is the probability of finding two molecules i and j simultaneously at a given relative distance r . The compressibility factor of a mixture (z_m) using $u_{ij}(r)$ and $g_{ij}(r)$ is given by

$$z_m = 1 - \left(\frac{2\pi\beta\rho}{3} \right) \sum_i \sum_j x_i x_j \int r^3 \left(\frac{du_{ij}}{dr} \right) g_{ij}(r) dr \quad (1)$$

Where β is $1/kT$ and ρ represents the mixture density.

The perturbation theory requires the separation of the properties into a contribution

arising from molecular repulsion and other contributions resulting from molecular attraction :

$$u_{ij}(r) = u_{ij}^+ + \epsilon_{ij} f^-(r/d_{ij}) \quad (2)$$

where u_{ij}^+ is the hard sphere potential and the other is attraction contribution term in which the conformal solution theory is employed. Mansoori and Leland (1972) proposed the mean density approximation (MDA) to relate the pair distribution function of a pair in a mixture to that of a hypothetical pure reference fluid. For spherical molecules, the MDA assumes

$$g_{ij}(r) = g_o(r/d_{ij}, kT/\epsilon_{ij}, \rho\bar{d}^3) \quad (3)$$

Expand the pair distribution function in powers of ϵ_{ij}/kT around the pair distribution function for the hard sphere reference

$$g_o(r) = g^{hs}(r/d_{ij}, \rho\bar{d}^3) + \sum_{n=1}^{\infty} (\epsilon_{ij}/kT)^n F_n(r/d_{ij}, \rho\bar{d}^3) \quad (4)$$

In eqn (4), F_n is a universal function which depends on the dimensionless groups $\rho\bar{d}^3$ and r/d_{ij} .

Substituting eqns (2) and (4) into eqn (1) and rearranging gives

$$z_m = z_{hsm} - z_m^- \quad (5)$$

where

$$z_{hsm} = \int (du^+ / dy) g^{hs}(y) y^3 dy \quad (6)$$

$$\begin{aligned} z_m^- &= 1/kT \sum \sum x_i x_j \epsilon_{ij} d_{ij}^3 \\ &\int (df^- / dy) F_1(y) y^3 dy \\ &+ (1/kT)^2 \sum \sum x_i x_j \epsilon_{ij}^2 \\ &d_{ij}^3 (df^- / dy) F_2(y) y^3 dy \quad (7) \\ &+ \sum_{n=3}^{\infty} (1/kT)^n \sum \sum x_i x_j \epsilon_{ij}^n \\ &d_{ij}^3 \int (df^- / dy) F_n(y) y^3 dy \end{aligned}$$

In eqn (5), the superscript '-' and subscript 'hsm' denote the attraction part and hard sphere mixture. Also, z_{hsm} is evaluated from an equation of state of the mixture.

The same type of equation of state as eqn (6) is also developed for a hypothetical pure reference fluid in terms of the properly determined pseudo-parameters $\bar{\epsilon}$ and \bar{d}^3

$$z_r \cong z_{hsr} - z_r^- \quad (8)$$

$$\begin{aligned} z_r &= (1/kT) \bar{\epsilon} \bar{d}^3 \int (df^- / dy) g^{hs} \\ &(y) y^3 dy \\ &+ (1/kT)^2 \bar{\epsilon}^2 \bar{d}^3 \int (df^- / dy) F_1 \\ &(y) y^3 dy \\ &+ \sum_{n=3}^{\infty} (1/kT)^n \bar{\epsilon}^n \bar{d}^3 \int (df^- / dy) \\ &F_n(y) y^3 dy \quad (9) \end{aligned}$$

where z_{hsr} represents the compressibility factor for the hard sphere reference.

The corresponding states principle (CSP) is applied to get the attraction part of mixture from that of the reference fluid. Subtracting eqn (7) from eqn (9) gives:

$$\begin{aligned} z_m^- - z_r^- &= (1/kT) (\sum \sum x_i x_j \epsilon_{ij} d_{ij}^3 - \\ &\bar{\epsilon} \bar{d}^3) \int (df^- / dy) g^{hs}(y) y^3 dy \\ &+ (1/kT)^2 (\sum \sum x_i x_j \epsilon_{ij}^2 d_{ij}^3 - \\ &\bar{\epsilon}^2 \bar{d}^3) \int (df^- / dy) F_1(y) y^3 dy \\ &+ \sum_{n=3}^{\infty} (1/kT)^n (\sum \sum x_i x_j \epsilon_{ij}^n d_{ij}^3 - \\ &\bar{\epsilon}^n \bar{d}^3) \int (df^- / dy) F_n(y) y^3 dy \\ &= 0 \quad (10) \end{aligned}$$

Equating the coefficient of the first order of $1/kT$ yields

$$\bar{\epsilon} \bar{d}^3 = \sum \sum x_i x_j \epsilon_{ij} d_{ij}^3 \quad (11)$$

The original HSE theory of Mansoori and Leland (1972) is derived from equating the first and second leading terms. But Tan (1986) pointed out that by use of the following definition of diameter in eqn (12) the Ornstein-Zernike (OZ) equation for pure hard spheres can exactly represent the OZ equation for a pair in a hard sphere mixture.

$$\bar{d}^3 = \sum x_i d_{ij}^3 \quad (12)$$

In this work, equations (11) and (12) are used to evaluate the pseudo-parameters. The unlike-pair term d_{ij} in the pseudo-parameters can be related to the

pure fluid properties i and j so that the Ornstein - Zernike equation should be met :

$$d_{ij} = (d_{ii} d_{jj})^{1/2} \quad (13)$$

Also ϵ_{ij} is defined as

$$\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2} \quad (14)$$

Eqn (13) is different from the Lorentz - Berthelot (LB) rule, i.e.,

$$d_{ij} = (d_{ii} + d_{jj}) / 2 \quad (15)$$

This work like the HSE theory can not be complete unless a consistent method is found to evaluate the effective hard sphere diameter. The effective hard sphere diameters for known potentials can be determined by perturbation method. The separation of isotropic pair potential into repulsion and attraction part is not unique because it is related to the rate of convergence of perturbation expansion and accuracy of results.

Many approaches to calculate these diameters have been reported in the literature. The Verlet and Weis' work (1972) modifying the Weeks and his coworkers' perturbation method (1971) is known better than others and thus their so-called 'blip function method' for the determination of hard sphere diameter was employed in this work. The hard

sphere diameter is given by

$$\frac{d_{ij}}{\sigma_{ij}} = \frac{0.3837 + 1.068 (\epsilon_{ij}' / KT)}{0.4293 + (\epsilon_{ij}' / KT)} \quad (16)$$

In eqn (16), σ_{ij} and ϵ_{ij}' are the Lennard - Jones size and energy parameters, respectively. On the other hand, the energy parameter ϵ_{ij} in this study can be determined from the Lennard - Jones parameters ϵ_{ij}' and σ_{ij} combined with d_{ij} as in the Chang's VW - HSE method (1984).

$$\epsilon_{ij} = \epsilon_{ij}' (\sigma_{ij} / d_{ij})^6 \quad (17)$$

The equation of state of the mixture can be evaluated from

$$z_m = z_{hs m}(\rho, x_1, x_2, \dots, d_1, d_2, \dots) + z(\bar{\epsilon} / kT, \rho \bar{d}^3) - z_{hs}(\rho \bar{d}^3) \quad (18)$$

The excess volume property, V^E , is defined as

$$V^E = V_m - \sum x_i v_i^0 \quad (19)$$

where v_i^0 denotes the volume of a pure fluid i and V_m is the mixture volume.

The calculation procedure by the above information is summarized as follows :

- 1) Assume the mixture density.
- 2) Calculate the hard sphere diameter and energy parameters using eqns (16) and (17).
- 3) Evaluate the pseudo - parameters in eqns (11) and (12).

- 4) Calculate the total z from an appropriate equation of state.
- 5) Calculate the hard sphere properties for mixture and pure reference at pseudo-parameter conditions.
- 6) Computer z_m in eqn (18) and the corresponding pressure of mixture.
- 7) Check the convergence on pressure., If not, go back to step 1).
- 8) Find the excess property from eqn (19).

Results and Discussions

The equation of state with 32 terms (Nicolas et al., 1979) for the Lennard-Jones fluids was used to evaluate the total thermodynamic properties in eqn (18). For the hard sphere terms the MCSL equation of state (Mansoori et al., 1971) was also employed.

Table 1 compares the calculated results by means of this method on the excess volume

Table 1, Excess volume (V^E) of equimolar Lennard-Jones fluid mixture at $P=0$, $T=97K$, $\epsilon_{12}/k=1$ 33.5K, $\sigma_{12}=3.596 \text{ \AA}$. (V^E in $\text{cm}^3/\text{g-mole}$)

σ_{12}/σ_{11}	$\epsilon_{12}/\epsilon_{11}$	MC	vdW-1	HSE	VW-HSE	This work
1.03	0.810	-1.080	-1.110	-1.161	-1.101	-1.135
	0.900	-0.300	-0.331	-0.360	-0.290	-0.321
	1.000	0.010	-0.051	-0.010	0.000	0.043
	1.111	-0.610	-1.200	-0.040	-1.300	-0.319
	1.235	-0.800	-0.810	-1.500	-0.650	-0.880
1.06	0.810	-1.290	-1.390	-1.270	-1.212	-1.294
	0.900	-0.410	-0.542	-0.471	-0.393	-0.406
	1.000	0.020	-0.181	-0.011	-0.022	-0.026
	1.111	-0.100	-0.273	-0.260	-0.060	-0.121
	1.235	-0.680	-0.811	-0.670	-0.550	-0.692
1.09	0.810	-1.500	-1.760	—	-1.531	-1.439
	0.900	-0.530	-0.841	—	-0.593	-0.459
	1.000	-0.050	-0.410	—	-0.062	-0.001
	1.111	-0.060	-0.431	—	-0.090	-0.016
	1.235	-0.550	-0.901	—	-0.473	-0.502
1.12	0.810	-1.760	-2.231	—	-1.790	-1.665
	0.900	-0.660	-1.210	—	-0.743	-0.495
	1.000	-0.100	-0.722	—	-0.203	-0.040
	1.111	-0.020	-0.681	—	-0.082	-0.065
	1.235	-0.450	-1.061	—	-0.381	-0.391

property for Lennard - Jones fluids with other methods such as VdW -1 (Leland et al. 1968), HSE, VW -HS and the Monte Carlo data (Singer and Signer, 1970). In general, this method is better than the original HSE and VdW -1 methods and comparable to the VW -HSE theory.

In the VW -HSE method by Chang (1984), he employed the Verlet and Weis method for the determination of hard sphere diameter into the HSE. This work is different from the HSE and VW -HSE methods in deriving the pseudo - parameters and d_{ij} in eqn (12), by which the OZ equation can be met as mentioned before.

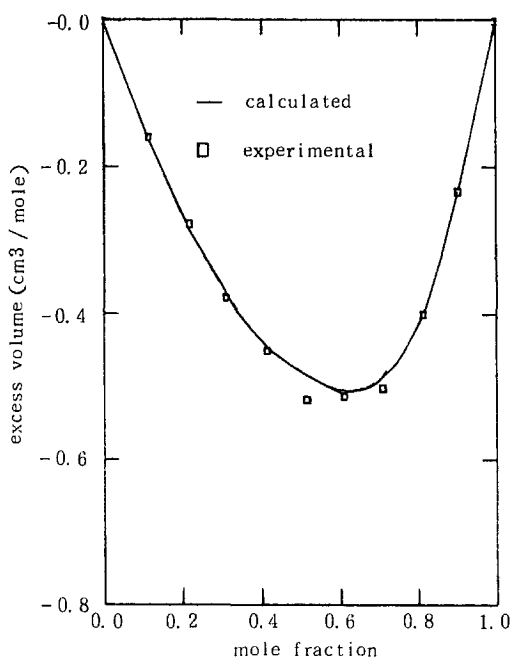


Figure 1. Comparison of calculated and experimental excess volumes for the argon - krypton mixture as a function of composition.

By applying the Lennard - Jones parameters to the real simple fluids like argon, krypton, and methane, the excess volume properties were calculated. Figure 1 shows the results for a system of argon - krypton at $T=115.77K$ and $P=0$ as a function of composition. The results by this work agree very well with experimental results (Davies et al., 1966).

Ely (1984) derived the modified MDA (MMDA) to improve the PDF for mixture. The results executed by this method on thermodynamic excess functions, however, are not better than those with the original MDA. This is mainly due to the fact that the MDA predict the structural integral well owing to error cancelation even though the MDA underestimates the PDF.

The MDA employed in this derivation is known to fail to predict the pair distribution function of mixtures with large size difference correctly, so new conformal solution theory should be developed for the systems containing molecules with large difference in size ($\sigma_{22}/\sigma_{11} > 1.50$).

Conclusions

This study shows that it is possible to give a better prediction of excess volume properties of simple liquid mixtures with small size differences (up to $\sigma_{12}/\sigma_{11} > 1.12$) using the diameter parameter derived to be forced to agree with the Ornstein - Zernike equation and

first order expansion in powers of ϵ_{ij}/kT . The pure hard sphere diameters are evaluated by the Verlet - Weis method.

From the results by this work, it can be considered that the diameter parameter meeting the Ornstein - Zernike equation is rather important in the derivation of the mixing rule for a conformal solution theory.

It is under way to extend this work to non - conformal solution and will be reported in the near future.

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