Phase equilibria study of Lennard–Jones mixtures by an analytical equation of state

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Abstract

The recently developed equation of state (EOS) for Lennard–Jones mixtures [Y. Tang, B.C.-Y. Lu, Fluid Phase Equilibria 146 (1998) 73.] is further investigated in this work for describing phase equilibria of these mixtures. The investigation covers vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), vapor–liquid–liquid equilibria (VLLE) and vapor–vapor equilibria (VVE) over a wide range of temperatures, pressures and molecular characteristic parameters. Results from the van der Waals one-fluid (VDW1) theory are included for comparison. The newly proposed theory performs very well for VLE and LLE and the performance is better than the VDW1 theory; but both theories yield only qualitative results for VVE. It is also found that one system should exhibit VLLE, which was not noticed in previous investigations. Results from two other perturbation theories are also compared in some cases. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, a new equation of state (EOS) has been developed for the pure Lennard–Jones (LJ) fluid and LJ mixtures [1,2]. The EOS has a number of new features. First, the theory is of second-order and its development is based on an analytical solution of the fundamental Ornstein–Zernike (OZ) equation presented earlier [3]. The underlying radial distribution function (RDF) is well-defined and has been tested satisfactorily against computer simulation results [4,5]. Second, by adopting a two-Yukawa...
function to map the LJ potential, both RDF and EOS expressions are reduced to simple analytical
functions and no integration is required, which is not expected in any other perturbation theories.
Finally, as far as accuracy is concerned, the EOS is found better than the traditional Weeks–Chan-
dler–Anderson (WCA) theory [6] and has at least a comparable performance to the latest 33-parame-
ter modified Benedict–Webb–Rubin (MBWR) equation [7]. Very recently, the equation has been
combined with the renormalization group theory [8] to describe comprehensively the behavior of the
pure LJ fluid both away from and nearby the critical point.

The extension of the EOS to mixtures [2] is also established by means of our analytical solution of
the OZ equation for mixtures [9] and is free from any mixing-rule. In contrast, for an empirical or
semi-empirical EOS such as the MBWR equation, such an extension is feasible only after a proper
mixing rule is introduced, which inevitably brings some extra uncertainties even if the original
equation is exact. Presently, the most mentioned mixing rule is from the van der Waals one-fluid
(VDW1) theory, which has been shown [2,10,11] unreliable for excess property and poor for pressure
and chemical potential. Our calculations [2] indicate that the newly proposed EOS performs equally
well for these different properties. It is felt that a theoretically based equation insures thermodynamic
consistency with much more confidence.

The purpose of this work is to further investigate the applicability of our new EOS for phase
equilibria calculations. In recent years, many computer simulations of phase equilibria of LJ mixtures
appeared in the literature. Vapor–liquid equilibrium (VLE) has been simulated by Harismiadis et al.
[12] via the Monte-Carlo method, by Vrabec et al. [13] via the molecular–dynamic (MD) method, and
by Georgoulaki et al. [14] at some extreme potential parameter ratios. Liquid–liquid equilibria (LLE)
simulation was made by Guo et al. [15] for binary systems, and by Tsang et al. [16] for ternary
systems. Vapor–vapor equilibria (VVE) data were also reported in the literature [14]. These
simulation results have covered a wide range of phase split situations of real fluids and are very
valuable to test the performance of a theoretical EOS. In contrast to computer simulations, theoretical
studies of phase equilibria are relatively limited. Of which, the VDW1 mixing rule is most often
applied to phase equilibria calculations [12,13,16,17] by combining with the MBWR equation [7] or
the equation of Kolafa and Nezbeda [18]. A combination of VDW1 with a cubic EOS has also been
investigated [14,19] but the combination seems to be less successful. An attempt to improve VDW1
was made recently by a density-dependent mixing rule [20]. In mixing-rule-free approaches, WCA-type
perturbation theories [21,22] have been applied to studying LJ mixtures. Nevertheless, the nature of a
WCA-type theory determines that the theory is more adequate for high densities, and its applicability
for phase equilibria calculations, especially at high temperatures, is unsatisfactory as described by
Vrabec et al. [13]. Recently, Fotouh and Shukla [11] made a low-density correction to a WCA-type
theory and some improvements were made for properties of LJ mixtures. More recently, their theory
was employed [17] to study extensively phase equilibria of LJ mixtures and to yield better results than
VDW1, after extensive computations.

Our EOS is an alternative to the WCA-type theories to study LJ mixtures without mixing rule. A
summary of this EOS can be found in Section 2. Also in Section 2, we give some details about
calculation methods for phase equilibria. The results of our work are shown extensively in Section 3.
Conclusions about the performance of our EOS for predicting phase equilibria and thermodynamic
properties are summarized in Section 4.
2. Theory and calculation methods

For an \( N \)-component mixture with density \( \rho \) and individual densities \( \rho_i \) \((i = 1, \ldots, N)\), or individual mole fractions \( x_i \) \((i = 1, \ldots, N)\), the EOS we have developed \cite{2} can be represented by:

\[
a = a_{\text{id}} + a_{\text{rep}} + a_1 + a_2
\]

where \( a \) is the reduced total Helmholtz free energy. Four terms on the right-hand side of Eq. (1) are illustrated as follows. The first term, an ideal mixture contribution, is:

\[
a_{\text{id}} = \sum_i x_i \ln(\rho_i \Lambda_i^3) - 1
\]

where \( \Lambda_i \) is the de Broglie wavelength of component \( i \), which is irrelevant to the present work. The repulsive-force term, \( a_{\text{rep}} \), may be determined by an EOS for additive hard-sphere mixtures such as that of Mansoori–Carnahan–Starling–Leland \cite{23}, plus a correction term to the additive assumption. Two-attractive force terms are given by:

\[
a_1 = 2\pi \rho \sum_i \sum_j x_i x_j \int_{\sigma_{ij}}^{\infty} g_{0,ij}(r) \delta u_{ij}(r) r^2 dr
\]

\[
a_2 = \pi \rho \sum_i \sum_j x_i x_j \int_{\sigma_{ij}}^{\infty} g_{1,ij}(r) \delta u_{ij}(r) r^2 dr
\]

where \( g_{0,ij} \) and \( g_{1,ij} \) are the reference system and the first-order RDF, respectively; \( \sigma_{ij} \) is the size parameter of the LJ potential; \( \delta u_{ij}(r) \) is the attractive part of the LJ potential. The split between the repulsive and the attractive forces can be found in Ref. \cite{2}. The most significant thing here is that, by our analytical OZ solution and subsequent mapping for the LJ potential, one can obtain the two RDFs in Eqs. (3) and (4), and \( a_1 \) and \( a_2 \) analytically. More details about them as well as \( a_{\text{rep}} \) have been well-documented \cite{2} and are not reproduced in this work.

There are two types of parameters for LJ molecules, the size parameters \( \sigma_{ij} \) and the energy parameters \( \varepsilon_{ij} \). Unlike potential parameters \( \sigma_{ij} \) and \( \varepsilon_{ij} \) \((i \neq j)\) are often expressed by like potential parameters as follows:

\[
\sigma_{ij} = l_{ij}(\sigma_{ii} + \sigma_{jj})/2
\]

\[
\varepsilon_{ij} = b_{ij}\varepsilon_{ii}\varepsilon_{jj}.
\]

Eq. (5) is the so-called Lorentz combination rule if \( l_{ij} = 1 \); and Eq. (6), the Berthelot combination rule if \( b_{ij} = 1 \). Once \( l_{ij} = b_{ij} = 1 \), the mixture is called the Lorentz–Berthelot (LB) mixture, which is treated as default if none of \( l_{ij} \) and \( b_{ij} \) is specified. In the VDW1 theory, a LJ mixture with \( \sigma_{ij} \) and \( \varepsilon_{ij} \) is simulated by a pseudo-pure LJ fluid with \( \sigma \) and \( \varepsilon \), which are determined by the following mixing rules:

\[
\sigma^3 = \sum_{i,j} x_i x_j \sigma_{ij}^3
\]

\[
\varepsilon \sigma^3 = \sum_{i,j} x_i x_j \varepsilon_{ij} \sigma_{ij}^3
\]
where \( x_i \) is the mole fraction of component \( i \). In this work, the above mixing rules are incorporated into the latest MBWR equation [7] to investigate the performance of VDW1.

In order to ensure correct results to be obtained in the numerical work, two methods are utilized in our phase equilibria calculations. One is the Newton–Raphson (NR) method for solving the standard phase equilibrium conditions, i.e.,

\[
P^\alpha = P^\beta
\]

\[
\mu_i^\alpha = \mu_i^\beta, \quad i = 1, \ldots, N
\]

where \( \alpha \) and \( \beta \) stand for two different phases (either V or L) respectively. Pressure \( P \) and chemical potential \( \mu_i \) can be obtained by:

\[
\frac{P}{\rho kT} = \rho \frac{\delta a}{\delta \rho}
\]

\[
\frac{\mu_i}{kT} = a + \rho \frac{\delta a}{\delta \rho_i}
\]

at temperature \( T \). The advantages and disadvantages of the NR method are well known. It is fast and gives correct results in most cases. However, the method is not applicable inside the critical region of mixtures, and is highly subjected to the initial guess of solution at other states. The most serious problem in this method is that its answer may be unphysical, especially when VLE and LLE intersect. One example will be demonstrated subsequently for vapor–liquid–liquid equilibria (VLLE) calculations.

The other method used in this work is the so-called equal area (EA) method [24,25], a descendant of Gibbs minimization techniques. The central point of these techniques is to minimize globally the total Gibbs free energy \( G \) of a mixture, or the Gibbs free energy of mixing \( \Delta G_{\text{mix}} \), defined by:

\[
\Delta G_{\text{mix}} = G - \sum_i x_i G_i
\]

where \( G_i \) is the Gibbs free energy of pure component \( i \) at the same \( T \) and \( P \) of that mixture. The EA method is free from any initial guess of solution and always converges to the physical answer, even when VLLE and the critical region are encountered. Technical details can be found in Refs. [24,25]. Downsides of this method are that the involved computation is rather tedious and both Gibbs free energy and its derivative with respect to molar composition have to be calculated over the whole range of molar composition. Also, in programming, one has to take care of the profiles of Gibbs free energy carefully in order to secure correct branches.

Since both methods have advantages and disadvantages, we end up with a combination of the NR method and the EA method in phase equilibria predictions. We use the EA method to analyze the nature of phase equilibria (VLE, LLE, VLLE or VVE) and to generate the first set of phase equilibria compositions. Then the NR method is employed to calculate the rest of phase envelope. Whenever the NR method fails or its results are suspicious, our program switches back to the EA method to analyze the phase equilibria statue. The strategy is a compromise between computation speed and physical reliability of the solution.
3. Results and discussion

It should be clarified in advance that throughout this paper, the reduced quantities $P^* = P\sigma_{11}^3/\epsilon_{11}$, $T^* = kT/\epsilon_{11}$, $\rho^* = \rho(\chi_1^4\sigma_{11}^4 + 2x_1x_2\sigma_{12}^4 + x_2^2\sigma_{22}^4)$ are used in Figs. 1, 2 and 4, and $\rho^* = \rho\sigma_{11}^3$ in the others.

3.1. VLE

Fig. 1 gives pressure-composition and pressure-density relations for a LJ mixture with parameters $\sigma_{22}/\sigma_{11} = 1$ and $\epsilon_{22}/\epsilon_{11} = 0.75$ at the two temperatures $T^* (= kT/\epsilon_{11}) = 0.75$ and $T^* = 1.00$. For this mixture, unlike potential parameters are by default determined by the LB combination rule, as mentioned earlier. In these two figures and also all other figures throughout this paper, results from computer simulation, VDW1 and our EOS are depicted. It is evident that for this moderate asymmetric mixture, both our EOS and VDW1 can describe phase equilibria. For the vapor branches, VDW1 is slightly better, but is much less satisfactory than ours for the liquid branches at both temperatures. This mixture has also been studied by the perturbation theories of Vrabec et al. [13], Bohn et al. [21] and Fotouh and Shukla [17], which are hereafter referred to as PT1 and PT2, respectively. Visual comparisons with those reported in Refs. [13] and [17] reflect that our EOS performs better than PT1 and slightly better than PT2 at $T^* = 0.75$. At $T^* = 1.00$, PT1 has some problems of describing the phase envelope because its restriction to high densities, and the performance of PT2 is unclear. Nevertheless, our equation gives nearly the same performance as at $T^* = 0.75$ because it is applicable to both low and high densities.

In Fig. 2, the envelopes for a highly asymmetric LJ mixture with $\sigma_{22}/\sigma_{11} = 0.5$ and $\epsilon_{22}/\epsilon_{11} = 0.66$ are also shown at $T^* = 0.75$ and $T^* = 1.00$. In this case, the two components have very different sizes, which present a severer examination of theory. As one can see, the newly proposed EOS yields almost perfect result for both composition and density curves. VDW1 is found to be good for
composition and vapor density calculations, but its results for liquid densities are systematically higher than the simulation data. The predicted liquid density curves are wider than the correct ones. We have observed [26] the same deficiency for the VDW1 theory for other mixtures with $\sigma_{22}/\sigma_{11} < 1.0$. These findings suggest that a conformal solution theory is questionable for liquid density calculations of mixtures even combined with a very accurate equation for pure fluids. When compared with PT1, the present EOS has a similar performance for composition predictions and a better performance for density calculations, where PT1 is in turn better than VDW1. Phase envelopes for a more highly asymmetric mixture with $\sigma_{22}/\sigma_{11} = 0.5$ and $\epsilon_{22}/\epsilon_{11} = 0.33$ at $T^* = 0.75$ are demonstrated in Fig. 3. One can see that for vapor branches our EOS performs nearly as good as VDW1 and for liquid branches the two theories show some differences. Again, as observed above, VDW1
overestimates liquid densities as well as compositions at high pressures. For this highly non-ideal mixture, our EOS shows once again good accuracy and the accuracy is apparently more impressive than that of PT2 [17].

Fig. 4 exhibits the phase envelopes of a LJ mixture with $\sigma_{22}/\sigma_{11} = 1.5$ and $\varepsilon_{22}/\varepsilon_{11} = 0.66$. For this mixture and more generally a type of mixtures with $\sigma_{22}/\sigma_{11} > 1.0$, composition differences between vapor and liquid are very narrow [12,13]. The performance of the present EOS seems to be less satisfactory. However, a subtle investigation of the MD data [13] and the MC data reported by Harismiadis et al. [12] for the same system suggested that there are substantial disagreements between them. Simulations for this type of mixtures are very difficult and there are high uncertainties, as described in their original papers [12,13]. We find that our prediction coincides better with those of Harismiadis et al. [12], especially at the liquid branch of $T^* = 1.00$ where largest differences occur between our results and the MD data. The MC data of Harismiadis et al. [12] are not depicted here because tabulated values are not available. If neglecting simulation uncertainties, our theory looks better than VDW1 and PT1. Final conclusions about the performance of these theories for these mixtures can be deduced only after more stable simulations become available.

3.2. LLE

Unlike VLE, a mixture exhibiting LLE must deviate from the LB combination rule to ensure the occurrence of the phase equilibria. Such an occurrence has been demonstrated in Section 3.1. Here,
we make some LLE calculations against computer simulation data reported by Guo et al. [15]. The LLE of a LJ mixture at $P^* = 0.125$ with potential parameters $\sigma_{22}/\sigma_{11} = 0.95$, $\varepsilon_{22}/\varepsilon_{11} = 0.75$, $l_{12} = 1.0$ and $b_{12} = 0.70$ is shown in Fig. 6. It is obvious that both our EOS and VDW1 are capable of describing the LLE, and relatively our description is somewhat better, especially at higher temperatures. Also, our EOS seems to yield very similar results to those of PT2. Another LLE calculation for a LJ mixture with $\sigma_{22}/\sigma_{11} = 0.95$, $\varepsilon_{22}/\varepsilon_{11} = 0.85$, $l_{12} = 1.0$ and $b_{12} = 0.80$ is shown in Fig. 7. Since potential parameter differences between the two components are reduced, the phase envelope is shrunk when compared with that shown in Fig. 6. It appears that this shrinking is considerably less
accounted for by VDW1 than by our EOS, as shown in the figure. VDW1 gives a much wider phase envelope and a much higher critical point. The present EOS clearly performs much better, although the performance is less satisfactory at low temperatures.

The outcome of phase equilibria envelopes (Fig. 8) for the LJ mixture with \( \sigma_{22}/\sigma_{11} = 0.80, \ e_{22}/e_{11} = 0.85, \ l_{12} = 0.95 \) and \( \nu_{12} = 0.70 \) is somewhat surprising. In order to enhance visual clearance, calculations from our EOS and VDW1 are depicted in two separate graphs. In both the original simulation [15] and the calculation made by Fotouh and Shukla [17], this LLE system is assumed to exhibit an upper critical solution temperature (UCST). So is in our original calculation.
Fig. 9. $\Delta G_{\text{mix}}$ of the LJ mixture in Fig. 8 at three sets of temperatures. The solid lines are calculated from our EOS and the dashed tangent lines are used to determine phase equilibria compositions.
[26] by the NR method. However, an application of the EA method described in Section 2 to the mixture yields a different result. When temperature rises to a certain value, VLLE and later VLE overtakes LLE and the UCST point is no longer physical. Instead, we have a VLLE point and the point is found to be at $T^* = 0.9750$ for our EOS, and to be at $T^* = 0.9741$ for VDW1. The occurrence of VLLE and VLE can be understood better by the $\Delta G_{\text{mix}}$ profiles shown in Fig. 9, where a pair of equilibria compositions are located by a tangent line. At lower temperatures, the liquid branch of $\Delta G_{\text{mix}}$ has lower energy and thus dominates phase behavior. As temperature rises, the vapor branch of $\Delta G_{\text{mix}}$ overtakes a portion of the liquid branch and finally touches the LLE tangent line, where VLLE emerges. As temperature continues to rise, LLE disappears and two sets of tangent lines, or two VLE, can be found to ensure the minimum of the Gibbs free energy for the whole system. It needs to be mentioned that the vapor branches of $\Delta G_{\text{mix}}$ for this mixture are all terminated somewhere because its vapor densities exist no longer. Such a sudden termination has been also observed for the Peng–Robinson equation [25]. It is very likely that when the NR method is applied one can continue to get answers until the UCST point is reached, which misleads the phase equilibria behavior of this system. Here, one can see the limitation of the NR method and the usefulness of Gibbs minimization techniques like the EA method adopted here. From previous studies about phase critical transitions [27,28], it appears that the UCST phenomena usually exist at higher pressures, which is terminated by VLLE at the so-called upper critical end point with decreasing pressure. Below the pressure of the upper critical end point, one is expected to observe a kind of VLLE or VLE behavior as shown in Fig. 8. As far as the LLE at $T^* < 0.975$ is concerned, the present EOS seems to be less accurate than VDW1 and PT2 when compared with simulation values. However, the simulation itself appears to be unstable and to have some uncertainties. These uncertainties may be brought in by the occurrence of the three-phase split described above. At this stage, it would be helpful to have more accurate simulation data for comparison and it is more desirable to have some simulation answers about the occurrence of VLLE found in this work.

Fig. 10. VVE of a LJ mixture with $\sigma_{22}/\sigma_{11} = 1.0$, $\epsilon_{22}/\epsilon_{11} = 1.0$, $l_{12} = 1.2$ and $b_{12} = 1.00$. The open circles are computer simulation data [14]. The solid and dashed lines are results from our EOS and VDW1, respectively.
3.3. VVE

VVE is seldom encountered in chemical engineering and industry and the equilibria happens only at some extreme conditions. Fig. 10 displays such an equilibria for a LJ mixture at $T^* = 3.00$ with $\sigma_{22}/\sigma_{11} = 1.00$, $e_{22}/e_{11} = 1.00$, $l_{12} = 1.20$ and $b_{12} = 1.00$. It is obvious that although both our EOS and VDW1 are capable of yielding VVE, their quantitative performance is disappointing. So is PT2 in which phase separation can not be located below a certain pressure value [17]. Inability of these theories for describing VVE is probably caused by strong repulsive forces among LJ molecules, where both temperatures and pressures are extremely high and interactions between two unlike molecules are rather non-additive. For this system, we feel that it is more adequate to use a reference system with non-additive hard-sphere diameters in our perturbation treatment [2]. However, such a reference system is not well developed and there are a number of issues to be resolved a priori.

4. Conclusions

The applicability of the newly proposed EOS for phase equilibria calculation is addressed in this work. We have made calculations for VLE, LLE, VLLE and VVE and compared our results with those of computer simulation, VDW1 and two other perturbation theories. These calculations and comparisons indicate that our EOS gives extensively better results than the VDW1 theory, and is comparable to or better than the two perturbation theories in tested VLE and LLE systems. In LLE calculations, we find that one LJ mixture should exhibit VLLE three-phase split and bypass the UCST point, which was not realized in previous studies. For VVE, all the mentioned theories including the present one can yield the phase split, but their quantitative performance is unsatisfactory.

In conjunction with our previous calculation [2], the present EOS has been used to predict some typical thermodynamic properties of LJ mixtures including pressure, excess free energy, chemical potential, VLE, LLE, VLLE and VVE. Overall, its performance is very satisfactory after comparing with several traditional theories. Together with its theoretical strength and analytical simplicity, the EOS is a valuable tool to study the behavior of LJ and even more realistic fluids.

5. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Helmholtz free energy</td>
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<tr>
<td>$a$</td>
<td>Reduced Helmholtz free energy</td>
</tr>
<tr>
<td>$b$</td>
<td>Parameter of the Berthelot combination rule</td>
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<tr>
<td>EA</td>
<td>Equal area method</td>
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<tr>
<td>EOS</td>
<td>Equation of state</td>
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<tr>
<td>$G$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$l$</td>
<td>Parameter of the Lorentz combination rule</td>
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<tr>
<td>LB</td>
<td>Lorentz–Berthelot</td>
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<tr>
<td>LJ</td>
<td>Lennard–Jones</td>
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<tr>
<td>LLE</td>
<td>Liquid–liquid equilibrium</td>
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<tr>
<td>MBWR</td>
<td>Modified Benedict–Webb–Rubin</td>
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MC Monte Carlo
MD Molecular dynamic
NR Newton–Raphson
OZ Ornstein–Zernike
$P$ Pressure
$P^*$ Reduced pressure
PT1 Perturbation theory of Vrabec et al. [13] and Bohn et al. [21]
PT2 Perturbation theory of Fotouh and Shukla [17]
RDF Radial distribution function
$T$ Temperature
$T^*$ Reduced temperature
UCST Upper critical solution temperature
VLE Vapor–liquid equilibrium
VLLE Vapor–liquid–liquid equilibrium
VDW1 van der Waals one-fluid
VVE Vapor–vapor equilibrium
WCA Weeks–Chandler–Anderson
$x$ Mole fraction

Greek letters
$\Delta$ Property change after mixing
$\varepsilon$ Energy parameter of the LJ potential
$\rho$ Density of fluids
$\rho^*$ Reduced density of fluids
$\sigma$ Size parameter of the LJ potential
$\mu$ Chemical potential

Subscripts
$i, j$ Species index

Superscripts
$\alpha, \beta$ Phase index

References