Dense Fluid Theory of Mixtures

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ABSTRACT
Previous studies have indicated that most of the existing theories of mixtures tend to fail for solutions containing species with large molecular size and intermolecular energy differences. In this work a dense fluid mixture theory, which is similar to the mixture theory of imperfect gases, is introduced. This theory is applicable for mixtures of molecules with large size and energy differences. The new theory is shown to be successful in predicting properties of Lennard-Jones fluid mixtures at, both, finite concentrations and infinite dilution.

I. INTRODUCTION
Statistical mechanics is of central importance in the fundamental study of mixtures and prediction of mixture properties. It provides equations that enable one, at least in principle, to calculate the thermodynamic and transport properties of mixtures from a knowledge of quantities on the molecular level. The energy and pressure equations allow the calculation of the internal energy and the compressibility factor from the molecular distribution functions and the intermolecular potentials of molecules in the mixture. The Kirkwood–Buff solution theory provides equations for the isothermal compressibility, partial molar volumes, and the derivatives of the chemical potential with respect to mole fractions $x_i$ in terms of the mixture radial distribution functions alone.

Exact equations for $n$-molecule distribution functions in terms of $(n+1)$-molecule functions are available. The Yvon–Born–Green and the Kirkwood integral equations are of this category of equations. In addition, a relation between the two-body and three-body distribution functions is derived by Salpeter which is given by an infinite series of irreducible clusters. The difficulty of working with the infinite number of terms forces one to make simplifying assumptions. The Kirkwood superposition approximation is one such closure assumption suggested in order to solve the integral equations for the distribution functions. The method of topological reduction was also utilized to derive integral equations for the distribution functions. In this approach a relation between the total and the direct correlation functions is assumed, in addition to the relation which defines the direct correlation function. The Percus–Yevick and the hypernetted chain integral equations are derived using this method. Except for the simplest models for pair interactions, such as hard sphere model, mixture calculations using the integral equations approach are extremely complicated and do not always produce the expected results.

The perturbation theory divides the potential function into a reference part and a perturbation part. The reference part represents a potential model for which the thermodynamic properties are known, such as the hard sphere model. The variational theory provides inequalities which may give least upper bound and highest lower bound to the Helmholtz free energy. In both, perturbation and variational theories, a reference system, for which thermodynamic properties and radial distribution functions are known, is needed. Mixture calculations based on these theories, although simpler than the integral equations approach, are still lengthy and usually no closed form expressions can be obtained.

The conformal solution theory presents yet another alternative to calculate mixture properties. The basic assumption in this theory is that all species interact by potential functions which have the same functional forms and they differ only in the values of the parameters of the model potential. Radial distribution functions of mixtures are approximated by that of a pure reference fluid, with the appropriate scaling of distance, temperature and density. Van der Waals mixture theory is a more widely used two-parameter conformal solution theory in this class. The van der Waals theory was extended to a three parameter potential, in which the stiffness of the potential function can be varied. A number of other conformal solution theories have been derived. The mean density approximation, the hard sphere expansion, and the density expansion are among those suggested.

The mixture theory of imperfect gases has the advantage of being applicable to all classes of mixtures, but it is limited to low densities. In the current work the imperfect gas theory is used to develop a mixture theory which is simple and applicable to asymmetric mixtures at all state conditions.

II. THEORY
In the theory of imperfect gases the compressibility of a pure gas can be represented by a viral expansion of the form

$$ P/kT = \rho + B(T)\rho^2 + C(T)\rho^3 + \cdots, $$

where $P$ is the pressure, $T$ is the temperature, and $k$ is Boltzmann constant. The quantities $B(T), C(T), \ldots$ are called the second, third,\ldots viral coefficients, respectively. The viral coefficients are functions of temperature only and their forms depend on the gas under consideration.

For multicomponent systems Eq (1) takes the following form:

$$ P/kT = \rho + B_m(T)\rho^2 + C_m(T)\rho^3 + \cdots, $$

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where the mixture virial coefficients $B_m$ and $C_m$ are given by

$$B_m = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j B_{ij}, \quad (3)$$

$$C_m = \sum_{i=1}^{c} \sum_{j=1}^{c} \sum_{k=1}^{c} x_i x_j x_k C_{ijk}. \quad (4)$$

In the above equations $c$ is the number of components in the mixture, and $x_i$ is the mole fraction of component $i$. It is worth mentioning here that the $i$th virial coefficient is related to irreducible clusters of $i$ molecules. Thus, in the virial expansion, the $N$-body problem is reduced to a series of one-body, two-body, three-body problems, and so on.

The derivation of the virial equation is based on the assumption that the pressure can be expanded in powers of the absolute activity. The resulting series has a radius of convergence beyond which the series no longer represents the fluid pressure. Since the virial expansion diverges when used for liquids the radius of convergence might have something to do with the gas-liquid phase transition. Nevertheless, this expansion is quite exact for mixtures of gases regardless of the relative differences in size, shape, and nature of the molecules forming the gas.

Theoretical treatment of liquid mixtures has required new methods that are directed more towards the many-body nature of liquids as discussed in the introduction. However, in order to develop an analytic theory of mixtures which can take advantage of the versatility of imperfect gas theory for asymmetric mixtures, the present theory is introduced. In this theory the pure dense fluid pressure is represented by the following expression:

$$P/kT = f(\rho, T; \{\alpha^{(l)}\}), \quad (5)$$

where $\{\alpha^{(l)}\}$ is a set which its elements represent either the intermolecular potential energy parameters, or the constants of a pure fluid equation of state. Extension of Eq. (5) to multicomponent mixtures can be achieved through different mixture theories. In the present theory it is assumed that Eq. (5) can be expanded as a power series in density as follows:

$$P/kT = \rho + \sum_{l=1}^{c} B(T; \{\alpha^{(l)}\}) \rho^l + \sum_{l=1}^{c} C(T; \{\alpha^{(l)}\}) \rho^l + \cdots, \quad (6)$$

where the virial coefficients $B, C, \ldots$ depend on some, or all, of the $l$ parameters $\{\alpha^{(l)}\}$. By utilizing the theory of mixtures of imperfect gases Eq. (6) can be extended to mixtures and the resulting mixture virial coefficients will then have the following forms:

$$B_m(T; \{\alpha_m^{(l)}\}) = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j B_{ij}(T; \{\alpha_{ij}^{(l)}\}), \quad (7)$$

$$C_m(T; \{\alpha_m^{(l)}\}) = \sum_{i=1}^{c} \sum_{j=1}^{c} \sum_{k=1}^{c} x_i x_j x_k C_{ijk}(T; \{\alpha_{ijk}^{(l)}\}), \quad (8)$$

and so on up to the $l/1$st virial coefficient.

In Eqs. (7) and (8), $\{\alpha_m^{(l)}\}$ is the set of parameters for the mixture under study. Provided that the unlike interaction virial coefficients can be obtained, the above set of $l$ equations can be solved for the $l$ unknowns $\{\alpha_m^{(l)}\}$. These parameters when replaced in Eq. (5) would provide a mixture theory which can be used for multicomponent mixture calculations. This mixture theory is specially useful when the results from the other mixture theories are difficult to obtain, or when there is no mixture theory available for the class of mixtures under consideration.

Equations (7) and (8) are derived from expanding the pressure in powers of density as shown in Eq. (6). If one expands the internal energy, rather than the pressure, then the following relations can be obtained

$$\frac{dB_m}{dT} = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \frac{dB_{ij}}{dT}, \quad (9)$$

$$\frac{dC_m}{dT} = \sum_{i=1}^{c} \sum_{j=1}^{c} \sum_{k=1}^{c} x_i x_j x_k \frac{dC_{ijk}}{dT}. \quad (10)$$

The mixture parameters obtained from Eqs. (9) and (10) should be replaced in the equation for the internal energy. Any other property can then be calculated from the appropriate thermodynamic relation. The constraint of replacing the mixture parameters only in the equation for the property which they are derived from is not necessary when the mixture parameters are temperature and density independent. Note that Eqs. (9) and (10) may be integrated with respect to temperature, and the constants of integration evaluated from the condition at $T = \infty$. This yields Eqs. (7) and (8), which still have to be replaced in the equation for the internal energy.

**III. EXAMPLES OF APPLICATIONS**

To illustrate the use of this theory, it is applied to a one-parameter, a two-parameter, and a three-parameter model dense fluids. Then it is used to predict properties of a model dense fluid (Lennard-Jones mixtures) for which computer simulation data are available.

**A. One-parameter model**

Hard sphere fluid is a suitable one-parameter model. The compressibility factor $Z$ of this fluid is represented well by the Carnahan-Starling equation

$$Z = P/kT = (1 + y + y^2 - y^3)/(1 - y)^3, \quad (11)$$

where $y = \pi \rho a^3/6$ and $a$ is the diameter of the hard sphere. For extension of a one-parameter model to mixtures only one equation (the second virial coefficient expression) is needed. In this case Eq. (11) gives the following expression for the second virial coefficient, which turns out to be the exact expression as derived from statistical mechanics,

$$B = \lim_{\rho \to 0} (Z - 1)/\rho = 2\pi a^3/3. \quad (12)$$

The mixture parameter $\sigma_m$, can now be obtained from Eq. (7):

$$\sigma_m^l = \sum x_i x_j \sigma_{ij}^l. \quad (13)$$

This expression is identical to the size mixing rule in the van der Waals mixture theory. Replacing Eq. (13) in Eq. (11) gives the hard sphere mixture equation.
B. Two-parameter model

The van der Waals equation is a two-parameter model which is given by

\[ \frac{\rho}{kT} = \rho/(1 - b\rho) - a\beta^2/kT, \]  

(14)

where \( a \) and \( b \) are two constants for a specific substance. Since this is a two-parameter equation two mixture expressions (based on the second and third virial coefficients) are needed. From Eq. (14) one gets the following expressions for the second and third virial coefficients of the van der Waals equation

\[ B = b - a/kT, \]  

(15)

\[ C = b^2. \]  

(16)

The mixture parameters are then

\[ b_m = \left[ \sum x_i x_j x_k C_{ijk} \right]^{1/2} \]  

(17)

\[ a_m = \sum x_i x_j (b_k k^T - a_{ij}), \]  

(18)

where \( C_{ijk} \)'s are calculated according to Eq. (16). The equations derived from the internal energy, Eqs. (9) and (10), give the following result:

\[ a_m = \sum x_i x_j a_{ij}. \]  

(19)

Although the van der Waals equation is a two-parameter model, only one of the parameters is needed in calculating the residual internal energy, which is given by

\[ U_r = \rho a \beta \]  

(20)

This is the reason behind obtaining only one relation, namely Eq. (19), when the internal energy is used to get the mixture parameters.

C. Three-parameter model

The variational-Yukawa equation is an example of a three-parameter fluid model. In this model the molecules interact by a one-Yukawa-potential function \( \phi \), which is given by

\[ \phi(r^*) = \begin{cases} \infty & r^* < 1 \\ -e^{-r^*/\sigma} \exp[-z(r^* - 1)] & r^* \geq 1 \end{cases} \]  

(21)

where \( r^* = r/\sigma, \sigma \) is the hard core diameter, \( e \) is the value of the potential at its minimum, and \( z \) is a third parameter which determines the steepness of the attractive tail. Jedrzejek and Mansoori13 derived a pure fluid equation of state for this potential based on the variational theory. Their equation is given by

\[ (A - A^*)/NkT = y(4 - 3y)/(1 - y)^2 - 12y^2G/T^*, \]  

(22)

where

\[ G = zL/[12y(L + Se^t)], \]  

\[ L = 12y[(1 + y/2)z + (1 + 2y)], \]  

\[ S = (1 - y)^2z^2 + 6y(1 - y)z^2 + 18y^2z - 12y(1 + 2y), \]  

and \( T^* = kT/e \). The second, third, and fourth virial coefficients, as obtained from Eq. (22), are

\[ B = b_0 \{1 - \beta(z)/T^*\}, \]  

(23)

\[ C = 5/8b_0 \{1 - \gamma(z)/T^*\}, \]  

(24)

\[ D = 9/32b_0 \{1 - \delta(z)/T^*\}, \]  

(25)

where

\[ b_0 = (2\pi\sigma^3)/3, \]  

\[ \beta(z) = 3(z + 1)/z^2, \]  

\[ \gamma(z) = 6\psi_1 - 24(1 + z)^2 e^{-z}]/5z^6, \]  

and

\[ \delta(z) = \psi_1 - \psi_3 - 6(1 + z)e^{-z}[z^3(z + 4) + \psi_1 + 4(z + 1)\psi_2 + 144(1 + z)^3 e^{-2z}]/z^6. \]  

The quantities \( \psi_1, \psi_2, \) and \( \psi_3 \) are polynomials in \( z \) which are given by

\[ \psi_1 = 5z^4 - 4z^3 - 12z^2 + 24z + 24, \]  

\[ \psi_2 = z^3 - 3z^2 + 6 \]  

and

\[ \psi_3 = z^3(z + 1)(z^3 - 6z^2 + 18z - 24). \]  

The mixture parameters are then obtained by solving the following set of equations:

\[ \sigma_m \{1 - \beta(z_m)\epsilon_m/kT\} = \sum x_i x_j (3/2\pi)B_{ij}, \]  

(26)

\[ \sigma_m \{1 - \gamma(z_m)\epsilon_m/kT\} = \sum x_i x_j x_k (3/2\pi)^2 C_{ijk}, \]  

(27)

\[ \sigma_m \{1 - \delta(z_m)\epsilon_m/kT\} = \sum x_i x_j x_k x_l (3/2\pi)^3 D_{ijkl}, \]  

(28)

where \( B_{ij}, C_{ijk}, \) and \( D_{ijkl} \) are obtained from Eqs. (23)–(25).

D. Lennard-Jones model

Next the current mixture theory is tested by comparing its prediction of mixture properties to exact values. Simulation data for mixtures of model fluids are very useful in testing mixture theories because for such mixtures one can eliminate the errors resulting from the inadequate representation of the potential functions and other sources. The Lennard-Jones potential, which is given by

\[ \phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \]  

(29)

is a widely studied model potential. Mixture simulation data for a wide range of size and energy ratios for this potential model are available. The data are used to test the current mixture theory and the result is also compared to the prediction of the van der Waals mixture theory.

To apply the proposed mixture theory one needs an equation which describes the behavior of the pure fluids. Ree16 and Nicolas et al.17 have proposed equations of state for Lennard-Jones fluid. In this work Nicolas et al.17 equation is used. Since the Lennard-Jones fluid is a two-parameter fluid, the second and third virial coefficients are needed. The expressions for the second and the third virial coefficients, as derived from Nicolas et al.17 equation, are
where the \( C_i \)'s are numerical constants of the equation. The mixture parameters \( \epsilon_m \) and \( \sigma_m \) are then defined by solving the following set of equations:

\[
C^* \left( \frac{kT}{\epsilon_m} \right) B^* \left( \frac{kT}{\epsilon_m} \right) = \sum \sum x_i x_j C_{ij} \left( \sum x_i x_j B_{ij} \right)^2,
\]

\[
\sigma_m^2 = \sum x_i x_j \sigma_{ij}^0 B^* \left( \frac{kT}{\epsilon_j} \right) / B^* \left( \frac{kT}{\epsilon_m} \right).
\]

It should be pointed out that the expressions for \( \epsilon_m \) and \( \sigma_m \) according to the present theory differ from the expressions based on the van der Waals mixture theory, which are given below:

\[
\epsilon_m \sigma_m^2 = \sum x_i x_j \epsilon_{ij} \sigma_{ij}^0,
\]

\[
\sigma_m^2 = \sum x_i x_j \sigma_{ij}^0.
\]

The use of Eqs. (32) and (33) in calculating \( \epsilon_m \) and \( \sigma_m \) requires a knowledge of the unlike interaction third virial coefficients \( C_{ij}, C_{ijk}, C_{ik}, \ldots, C_{ijk} \) (\( i \neq j \neq k \)). There exists no exact way of obtaining such unlike interaction coefficients from pure component coefficients when the potential function is not known. However, the following approximations exist in the literature.

1. The first approximation is based on \( C_{ijk} \) for hard sphere mixture, which is known exactly. When the \( \sigma_{ij} \)'s, in \( C_{ijk} \) for hard sphere, are replaced by \( \left\{ \frac{18C_{ij}/5\pi^2} {1.6} \right\} \) the following approximation is obtained:

\[
C_{ijk} = 1/15 \left[ \Lambda_{ij} + \Lambda_{ik} + \Lambda_{jk} + 18(\Lambda_{ij} \Lambda_{ik} \Lambda_{jk}) \right]^{1/3}
+ 16(\Lambda_{ij} \Lambda_{jk})^{1/3} + (\Lambda_{ij} \Lambda_{jk})^{1/3} + (\Lambda_{ij} \Lambda_{jk})^{1/3}
+ (\Lambda_{ik} \Lambda_{jk})^{1/3} + (\Lambda_{ij} \Lambda_{jk})^{1/3}
-
9\Lambda_{ij}^{2/3} \Lambda_{ik}^{2/3} + 9\Lambda_{ij}^{2/3} \Lambda_{jk}^{2/3} - 9\Lambda_{ij}^{2/3} \Lambda_{ik}^{2/3}.
\]

where \( \Lambda_{ij} = \left( \left( C_{ij}^{1/6} + C_{ij}^{1/6} \right) / 2 \right)^6 \).

2. The second approximation is based on the statistical mechanical expression for the third virial coefficient which, subject to several simplifying assumptions, reduces to:

\[
C_{ijk} = \left( C_{ij} C_{ik} C_{jk} \right)^{1/3},
\]

where \( C_{ij} \) is obtained from the third virial coefficient of the pure component \( i \) by replacing all the parameters \( \left\{ \alpha^{(l)} \right\} \) by those of the pair \( ij \). (\( \alpha_{ij}^{(l)} \)).

3. A number of scaling approximations have been tested by comparison with exact values of \( C_{ij} \) for square-well and Lennard-Jones potentials. As a result the following expression is recommended:

\[
C_{ijk} = \left( 2\pi N_A^3 / 3 \right)^2 \left[ \sigma_{ij} \sigma_{ik} \sigma_{jk} \right] \left[ C^* \left( kT / \epsilon_{ijk} \right) \right],
\]

where

\[
\epsilon_{ijk} \equiv (\epsilon_i \epsilon_j \epsilon_k),
\]

and \( C^* = C / \left( (2\pi N_A^3 / 3)^2 \sigma_i^6 \right) \) is the reduced pure fluid third virial coefficient.

In another effort to develop an expression for \( C_{ijk} \), Eq. (38) was modified empirically to become:

\[
C_{ijk} = \left( 2\pi N_A^3 / 3 \right)^2 \left[ (\sigma_{ij} + \sigma_{ik} + \sigma_{jk}) / 3 \right]^6 \times C^* \left( kT / \epsilon_{ijk} \right),
\]

where \( C^* \) and \( \epsilon_{ijk} \) have the same definitions as in Eqs. (38) and (39), respectively.

Equations (32) and (33) along with the different approximations for the unlike interaction third virial coefficients are used to calculate Henry's constant, pressure and internal energy of Lennard-Jones mixtures at various conditions.

Henry's constant of component \( i \) in a mixture \( H_i \) is defined by:

\[
\ln \left( H_i / kT \right) = \mu_i^w / kT = \left( \mu_i - \mu_{i}^w \right) / kT,
\]

where \( \mu_i^w \) is the residual chemical potential of component \( i \) in the mixture at its infinite dilution. From Eq. (41) it can be shown that when the compressibility factor of the fluid is given in the form \( Z = f \rho \sigma_a^3 / kT / \epsilon_m \) as in the case of Lennard-Jones model, then Henry's constant of component \( i \) in a multicomponent mixture is given by:

\[
\ln \left( \frac{H_i}{p \rho T} \right) = \frac{G^*}{NkT} + N \left[ \frac{\partial \epsilon_m}{\partial N_{i}} \right]_{N_{i}=0} \frac{U^*}{NkT}
+ \frac{N \left[ \partial \sigma_m^2 / \partial N_{i} \right]_{N_{i}=0} (Z^* - 1),
\]

where \( G^* \) and \( U^* \) are the residual Gibbs energy and internal energy, respectively. The superscript (\( \bullet \)) indicates a solute-free mixture (i.e., with \( x_i = 0 \)). For binary mixtures \( \epsilon^*, \sigma^*, G^* \bullet, U^* \bullet, \) and \( Z^* \bullet \) are properties of the pure solvent. Equation (42) is valid for all density independent choices of the parameters.

When Eq. (42) is combined with the proposed model for \( \sigma_m \) and \( \epsilon_m \), Eqs. (32) and (33), Henry's constant for component 1 of a binary mixture takes the following form:

\[
\ln \left( H_i / p \rho T \right)
= \mu_{i2} / kT + \left( U_{2} / NkT + T^* B'_{22} (Z_2 - 1) / B_{22} \right)
\times \text{B}_{22} \text{C}_{222} \left( 1 + 3C_{12}/C_{222} - 4B_{12} / B_{22} \right)
\times T^*(2B_{12} / C_{222} - C_{122} / C_{222})
+ 2[B_{12} / B_{22} - 1] (Z_2 - 1).
\]

In the above equation \( B' \) and \( C' \) are derivatives of \( B \) and \( C \) with respect to the reduced temperature \( T^* \), respectively. In a similar manner it can be shown that the van der Waals mixture theory gives the following expression for Henry's constant:

\[
\ln \left( H_i / p \rho T \right)
= \mu_{i2} / kT + 2(\sigma_{12} / \sigma_{22})^3 (\epsilon_{12} / \epsilon_{22} - 1) U_2 / NkT + 2 \times \left( (\sigma_{12} / \sigma_{22})^3 - 1 \right) (Z_2 - 1).
\]

The Henry's constant predictions by Eqs. (43) and (44) are shown in Figs. 1 and 2 along with the computer simulation.
data of Lennard-Jones mixture for different energy and size parameters ratios.

According to Fig. 1 the van der Waals theory predicts a linear dependence of Henry's constant on \( f = \frac{\varepsilon_{12}}{\varepsilon_{22}} \) while Eq. (43), with Eqs. (37)–(40) for \( C_{122} \), predicts the same behavior as the simulation data. The quantitative agreement of Eq. (43) with the simulation data is also good particularly when \( C_{122} \) is calculated from Eq. (37). The approximation for \( C_{122} \) as given by Eq. (36) is not as good as the other three approximations. The reason for this could be due to the fact that the approximation given by Eq. (36) is derived from the repulsive "hard-sphere" third virial coefficient in which there are no accounts for attractive energies. Figure 1 also indicates that the prediction by Eq. (43) is sensitive to the approximation used for \( C_{ij} \). Figure 2 shows the comparison for molecules with the \( \varepsilon_{12}/\varepsilon_{22} = 1 \) but different size ratios \( h = (\sigma_{12}/\sigma_{22})^3 \). In this figure the van der Waals theory predicts a linear dependence of Henry's constant on \( h \), while the prediction based on Eq. (43) with the use of the different approximations for \( C_{ij} \) is in better agreement with the simulation data. One may conclude from Figs. 1 and 2 that the dependence of \( C_{ij} \) on size as given by Eq. (38) is better than that given by Eq. (40). In addition, Eq. (36) seems to be limited to molecules with \( \varepsilon_{12}/\varepsilon_{22} \) close to unity. Due to this observation, and for the sake of clarity, only predictions with the use of Eqs. (37) and (38) for \( C_{ij} \) are reported in the remaining figures.

In addition to the infinite-dilution test one should test a mixture theory at finite concentrations and for different size and energy ratios of species of the mixture. Comparison of the compressibility factor and the internal energy of a number of equimolar mixtures with the computer simulation data is presented in Figs. 3–7. Figure 3 shows the com-
compressibility factor as a function of $\sigma_{11}/\sigma_{22}$. For $\epsilon_{11}/\epsilon_{22} = 1$, the van der Waals mixing rule predicts a constant value of the compressibility. On the other hand, the model proposed in this work, Eqs. (32) and (33), perform much better both qualitatively and quantitatively.

In addition, Fig. 3 shows that when $\sigma_m$ and $\epsilon_m$ of the new model are replaced in the pressure equation, the prediction is better than when they are replaced in the energy equation for $\epsilon_{11}/\epsilon_{22} = 1$ and $T = 200$ K. When such a comparison is made at a number of other conditions, it was found that while the compressibility prediction by the two methods is about the same, the internal energy prediction from the energy equation is much better than that from the pressure equation. To understand this behavior one should notice that in calculating the internal energy from the pressure equation, derivatives of the unlike interaction third virial coefficients are needed. Due to the approximate nature of those coefficients, their derivatives would have a larger error, especially near the maximum of $C_{ijik}$. It seems that this is the source of the large error in the internal energy values, when it is calcu-

![FIG. 4. Variation of the compressibility factor of equimolar Lennard-Jones mixture with $\epsilon_{11}/\epsilon_{22}$. The points represent the simulation data (Refs. 23 and 24). For other details see caption to Fig. 3.](image1)

![FIG. 5. Internal energy for equimolar Lennard-Jones mixture at 270 K and $\rho^* = 0.8$. The points represent the simulation data (Ref. 23). For other details see caption to Fig. 3.](image2)

![FIG. 6. Variation of the compressibility factor of equimolar Lennard-Jones mixture with temperature at $\rho^* = 0.8$. The points represent the simulation data (Ref. 23). For other details see caption to Fig. 3.](image3)

![FIG. 7. Variation of the internal energy of equimolar Lennard-Jones mixture with temperature at $\rho^* = 0.8$. The points represent the simulation data (Ref. 23). For other details see caption to Fig. 3.](image4)
lated from the pressure equation. In the remainder of the calculations reported here, all mixture properties are calculated from the energy equation.

Figure 3 also shows the compressibility factor at $\epsilon_{11}/\epsilon_{22} = 4.5$ for two different densities. At this large value of $\epsilon_{11}/\epsilon_{22}$ the van der Waals mixing rules predict a decrease in the compressibility factor with increasing $\sigma_{11}/\sigma_{22}$, which is opposite to what the simulation data shows. The new model predicts the correct behavior with good accuracy. Note that at $\sigma_{11}/\sigma_{22}$ close to unity the two models predict almost the same values, but as the ratio $\sigma_{11}/\sigma_{22}$ increases the van der Waals model start to deviate from the simulation data, while the new model continues to predict the compressibility with the same accuracy.

Figure 4 shows the compressibility as a function of $\epsilon_{11}/\epsilon_{22}$ for two values of $\sigma_{11}/\sigma_{22}$. The general trend of Fig. 3 is also observed here. A noticeable difference in this figure is the relatively large deviation of both models at $T = 270$ K. The pure fluid equation could be the source of the error in this case because $T^* = kT/\epsilon_{22}$ is outside the recommended temperature range $0.5 < T^* < 6$. Figure 5 shows the prediction of the residual internal energy as a function of $\epsilon_{11}/\epsilon_{22}$. The new model is again in better agreement with the simulation data. This is more pronounced at large $\epsilon_{11}/\epsilon_{22}$ values.

To study the effect of temperature on the accuracy of prediction by the two models, the compressibility and the residual internal energy are plotted versus temperature in Figs. 6 and 7 for $\sigma_{11}/\sigma_{22} = 1.3$ and $\epsilon_{11}/\epsilon_{22} = 3.0$. The proposed model is again in better agreement with the simulation data for compressibility. The van der Waals theory predicts negative compressibilities below 56 K. In predicting the internal energy the van der Waals theory performs slightly better for temperatures less than 160 K.

**V. CONCLUSIONS**

A new dense fluid theory, for mixtures consisting of species with large size and energy differences has been developed. This theory is based on the theory of dilute gas mixtures. The new theory is tested for mixtures of Lennard-Jones fluids and it is compared to the van der Waals mixture theory. It is found that at size and energy ratios close to unity the two theories perform equally well. As the size and energy differences between the species of the mixture increase the prediction of van der Waals theory deteriorates, while the prediction by the proposed dense fluid theory remains accurate.

Since this new theory is based on the imperfect gas mixture theory it is quite accurate for mixture predictions at low densities. It is demonstrated here that at high densities predictions by the new theory are also accurate. The performance of the new theory is also tested at different temperatures. The theory is found to predict mixture properties quite well for a wide range of temperatures.

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