Phase equilibria and thermodynamic properties of molecular fluids from perturbation theory

I. Pure fluids

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(Received May, 26, 1993; accepted in final form August 16, 1993)

ABSTRACT


A thermodynamic perturbation theory for fluid mixtures composed of rigid, nonspherical molecules is presented. In this theory the important isotropic and anisotropic interactions arising from two-body electrostatic, induction, dispersion and repulsion forces and from three-body induction and dispersion forces are treated as perturbations of the reference system represented by the Lennard-Jones pair interactions. This form of the perturbation theory differs from its previous versions in that the properties of the reference Lennard-Jones system are computed using an accurate form of the perturbation theory. Numerous comparison of theoretical results with experimental data for vapor–liquid phase equilibria and thermodynamic properties of several pure fluids composed of spherical (argon, krypton, xenon), octopolar (methane), quadrupolar (ethylene, ethane, carbon dioxide) and dipolar (hydrogen bromide) molecules show the very good performance of the perturbation theory. Part II of this work reports results for vapor–liquid phase equilibria and thermodynamic excess properties of binary fluid mixtures.

Keywords: theory, molecular interactions, perturbation theory, vapor–liquid equilibria, pure fluid.

INTRODUCTION

Phase equilibria and thermodynamic properties play key roles in the understanding of how intermolecular forces cause nonidealities in fluids and fluid mixtures. Their precise knowledge is important to the design and efficient operation of many industrial processes such as enhanced oil
recovery, coal-rich gas processing, supercritical extraction, biotechnology and coal-based feedstock chemical processing, among others. For fluid mixtures consisting of rigid, nonspherical, polar molecules, which are moderately nonspherical in shape and do not exhibit chemical effects such as hydrogen bonding, thermodynamic perturbation theory based on the spherically symmetric reference system (SSRS) is a reliable, theoretical approach available for predicting nonideal solution behavior. The nonideal solution behavior in such mixtures is attributed to differences in the molecular size and shape, polarity, dispersion, and polarizability parameters appearing in the intermolecular potential energy functions. This approach has been exploited in several forms of the perturbation theory (for review see, for example, Mansoori and Haile, 1983; Singh and Shukla, 1983; Gray and Gubbins, 1984; Lucas, 1986; Lee, 1988).

One of the recent forms of such a thermodynamic perturbation theory for fluids consisting of linear, nonspherical molecules was reported by Shukla et al. (1983). The theory was based on the spherically symmetric reference system (Pople, 1954) and Pade’ approximant (Stell et al., 1974) in terms of third-order perturbation expansion. In this theory, the anisotropic terms, which typically include contributions from electrostatic, dispersion, induction and short-range interactions, were treated as perturbations of an isotropic reference system represented by an equation of state for argon. Using only two adjustable parameters, perturbation theory was successfully subjected to comprehensive tests against experimental results for phase equilibria and thermodynamic properties of a variety of pure molecular fluids. Employing the van der Waals one-fluid theory (VDW1) for computing properties of the reference mixture (based on the equation of state for argon) and adopting a particular set of combination rules (Kohler, 1957) for determining unlike potential parameters, the theory was shown to describe successfully experimental results for thermodynamic properties of numerous nonideal binary fluid mixtures consisting of spherical and moderately nonspherical molecules without fitting unlike parameters to mixture data (Shukla et al., 1984a,b). Nevertheless, it was found to be somewhat inadequate in its predictions of phase equilibria and thermodynamic excess properties, especially for those highly nonideal fluid mixtures in which parameters of the components differed significantly. This inadequacy of the perturbation theory might be caused by the approximation involved in computing properties of the reference mixture and also by the inadequate representation of unlike parameters rather than by any inherent deficiency in the basic approach.

In several recent publications we have demonstrated convincingly that the VDW1 theory generally fails for the large size and energy parameter ratios of the components (Shukla et al., 1986; Shukla and Haile, 1987, 1988), and
the combination rules used earlier (Kohler, 1957) were found to be inadequate in estimating unlike parameters for describing thermodynamic excess properties of simple fluid mixtures (Shukla, 1987, 1989). We have also shown that a new form of the perturbation theory, called MPT2 (Shukla, 1987, 1991a,b), represents a significant improvement over the common VDW1 theory in describing thermodynamic properties of highly nonideal, simple fluid mixtures. When combined with a particular set of combination rules, based on Kohler (1957), Smith (1972) and Kong (1974), MPT2 could predict reliably experimental results for phase equilibria and thermodynamic excess properties of even highly nonideal, simple fluid mixtures (Shukla, 1989, 1991b) solely from the properties of their pure components.

The purpose of this research work is to present an improved version of the perturbation theory of binary molecular fluid mixtures consisting of rigid, nonspherical molecules by incorporating two major corrections in the previous perturbation theory of molecular fluid mixtures (Shukla et al., 1983). First, instead of using VDW1 theory (which is based on the mixing rules), we use perturbation theory (which is independent of mixing rules) (Shukla, 1987, 1991a,b) to determine properties of the reference mixture accurately. Second, unlike potential parameters of the mixture are determined using a more reliable set of combination rules (Kohler, 1957; Smith, 1972; Kong, 1974). We apply this theory to describe phase equilibria and thermodynamic excess properties of real fluid mixtures solely from the properties of their pure components. As the reliable predictions of phase equilibria and thermodynamic properties of binary fluid mixtures depend largely on the accurate descriptions of those of the pure components involved in the mixtures, in this work (Part I) we attempt to describe accurately phase equilibria and thermodynamically properties of some pure fluids. In Part II, results are presented for phase equilibria and thermodynamic excess properties of a few, selected, binary fluid mixtures involving the molecular systems presented in this paper.

The presentation is organized as follows. The intermolecular interactions are outlined in the next section. Perturbation theory as applied to molecular fluid mixtures is presented in the following section. Then the method is described of how to determine properties of the reference system, followed by the method of estimating potential parameters. Theoretical results and their comparisons with experimental data for pure fluids and the conclusions of the paper follow in the final two sections.

INTERMOLECULAR INTERACTIONS

We consider a binary fluid mixture of \( N( = N_A + N_B) \) molecules of components A and B contained in a fixed volume \( V \), at a constant
The total potential energy of interaction of the system is approximated as the sum of pair and three-body interactions, which depend on both orientation and related center of mass coordinates of molecules but are independent of rotational momenta and internal vibrational states.

The pair potential energy between two molecules of species $\alpha$ and $\beta$ is written as the sum of an isotropic term $u_{\alpha\beta}^0$ and an anisotropic term $u_{\alpha\beta}^3$:

$$u_{\alpha\beta}(r_{12}, \omega_1, \omega_2) = u_{\alpha\beta}^0(r_{12}) + u_{\alpha\beta}^3(r_{12}, \omega_1, \omega_2)$$  \hspace{1cm} (1)

where $r_{12}$ is the distance between the center of molecule 1 of species $\alpha$ to that of molecule 2 of species $\beta$, and $\omega_i = \theta_i \phi_i \chi_i$ ($\theta, \phi$ for the linear molecule) is the orientation of the molecule $i$. We choose $u_{\alpha\beta}^0$ to be an unweighted average of the total pair interaction energy over all orientations (Pople, 1954; Gray and Gubbins, 1984):

$$u_{\alpha\beta}^0(r_{12}) = \langle u_{\alpha\beta}(r_{12}, \omega_1, \omega_2) \rangle_{\omega_1 \omega_2}$$  \hspace{1cm} (2)

where

$$\langle (\cdots) \rangle = \int \int (\cdots) \, d\omega_1 \, d\omega_2 \left/ \left( \int d\omega_1 \int d\omega_2 \right) \right.$$

In this work, the atomic part of the isotropic pair interaction is represented by

$$u_{\alpha\beta}^0(r_{12}) = u_{\alpha\beta}^{LJ}(r_{12}) + u_{\alpha\beta}^{(n-8)}(r_{12})$$  \hspace{1cm} (3)

with

$$u_{\alpha\beta}^{LJ}(r_{12}) = 4\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r_{12})^{12} - (\sigma_{\alpha\beta}/r_{12})^6]$$  \hspace{1cm} (4)

and

$$u_{\alpha\beta}^{(n-8)}(r_{12}) = \varepsilon_{\alpha\beta}C_1[(\sigma_{\alpha\beta}/r_{12})^n - C_2(\sigma_{\alpha\beta}/r_{12})^8]$$  \hspace{1cm} (5)

where $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are energy and size parameters in the Lennard-Jones (L-J) potential. In the present study, the parameters $n$, $C_1$ and $C_2$ are assumed to be the universal constants characteristic of the fluid argon as discussed below.

The full isotropic pair potential also includes a contribution due to induction (ind) forces:

$$u_{\alpha\beta}^{ind} = -\alpha_{\beta}(\mu_\alpha^2/r_{12}^6 + 1.5 Q_\alpha^2/r_{12}^8) - \alpha_{\beta}(\mu_\beta^2/r_{12}^6 + 1.5 Q_\beta^2/r_{12}^8)$$  \hspace{1cm} (6)

and contributions due to repulsive (rep) interactions (Downs et al., 1979; Shukla et al., 1983):

$$u_{\alpha\beta}^{rep}(r_{12}) = \sum_{ab} e_{ab} \rho_{ab}^{1/2} \varepsilon_{ab} \left\{ 88(\rho_a^2 + \rho_b^2)(\sigma_{\alpha\beta}/r_{12})^{14} + (4004/15)(3\rho_a^4 \\
+ 10\rho_a^2 \rho_b^2 + 3\rho_b^4)(\sigma_{\alpha\beta}/r_{12})^{16} + 4576(\rho_a^6 + 7\rho_a^4 \rho_b^2 \\
+ 7\rho_a^2 \rho_b^4 + \rho_b^6)(\sigma_{\alpha\beta}/r_{12})^{18} + 97240(5\rho_a^8 + 60\rho_a^6 \rho_b^2) \right\}$$
In the above equations, $\alpha$, $\mu$ and $Q$ are the isotropic polarizability, dipole moment and quadrupole moment of a molecule, respectively. $\rho_a$ and $\rho_b$ are the reduced eccentricities of the atoms of a molecule, and $e_{ab}$ and $s_{ab}$ are scaling parameters for energy and distance in the site-site expansion of the repulsive part of the Lennard-Jones pair potential (Shukla et al., 1983).

The anisotropic pair potential $u_{ab}^a$ includes contributions from permanent multipoles, anisotropic dispersion, repulsion and induction forces, and they are represented in terms of the spherical harmonic expansion (Shukla et al., 1983; Gray and Gubbins, 1984; Lucas, 1986). If the molecular orientations are referred to the intermolecular axes frame, that is, the $z$-axis is taken to lie along $r_{12}$, this expansion is

$$u_{ab}(r_{12}\omega_1\omega_2) = \sum_{l_1}^{\infty} \sum_{l_2}^{\infty} \sum_{m_1}^{\infty} \sum_{n_1}^{\infty} \sum_{l_1}^{l_2} \sum_{n_2}^{l_2} \left[ E_{ab}(l_1, l_2, l; n_1 n_2; r_{12}) \right. \\
\times C(l_1 l_2 l; m_1 m_1 0) \left( \frac{2l + 1}{4\pi} \right)^{1/2} D_{m_1 n_1}^{l_1}(\omega_1) * D_{m_2 n_2}^{l_2}(\omega_2) * \right]$$

(8)

Here, $m = -m$, $E_{ab}(l_1, l_2, l; n_1 n_2; r_{12})$ is a strength coefficient, $D_{mn}(\omega)$ is a generalized spherical harmonic and $C(l_1, l_2, l; m_1 m_1 0)$ is a Clebsch–Gordan coefficient as defined by Rose (1957). The sum is over $l$, $l_2$, and $l$ (each from 0 to $\infty$), $m_1$ and $n_1$, $n_2$ (each from $-l_1$ to $l_1$, $-l_2$ to $l_2$, respectively). The term $l_1 l_2 l = 0 0 0$ corresponds to the isotropic potential $u_{00}^a$, and the terms $l_1 l_2 l \neq 0 0 0$ represent the anisotropic potential $u_{ab}^a$. The strength coefficients $E_{ab}$ for the electrostatic, induction, dispersion and site-site repulsion contributions for linear molecules are given elsewhere (Shukla et al., 1983, 1984a,b; Lucas, 1986).

The full isotropic potential includes three-body nonadditive dispersion forces given by the well known Axilrod–Teller term:

$$u_{disp0bn}^{3\beta} = 2 \frac{(R_x + R_y + R_z)R_x R_y R_z}{(R_x + R_y)(R_x + R_z)(R_y + R_z)} \left( \cos \theta_x \cos \theta_y \cos \gamma + 1 \right)$$

(9)

$$r_{12}^3 r_{13}^3 r_{23}^3$$

where:

$$\frac{1}{R_x} = \frac{1}{4} \left( \frac{1}{\epsilon_{ab} \sigma_{ab}^{6} \alpha_y} + \frac{1}{\epsilon_{xy} \sigma_{xy}^{6} \alpha_y} - \frac{1}{\epsilon_{xy} \sigma_{xy}^{6} \alpha_x} \right)$$

(10)

with similar expressions for $R_y$ and $R_z$. Here, $\theta_i$ are the angles of the triangle formed by the three molecules.
We also consider the anisotropic three-body nonadditive, induction interactions which are given as (Shukla et al., 1984a):

\[ u^{\text{indbn}}_{2\beta\gamma} = u^{\text{indbn}}_{2\beta\gamma}^{(I)} + u^{\text{indbn}}_{2\beta\gamma}^{(II)} + u^{\text{indbn}}_{2\beta\gamma}^{(III)} \]  

with:

\[
u^{\text{indbn}}_{2\beta\gamma}^{(I)} = -\left[ \sum_{l_1=0}^{\infty} \sum_{l_2} \sum_{l'_1} E^{\text{indbn}}_{\beta\gamma x_l} (l''_1, l_1 l_2 l', l'_1 l'_2; r_{\beta\gamma} r_{\gamma l}) \right. \\
\times \sum_{m_1 m_2} C(l_1 l'_1 l''_1; m_1 m'_1 m_1 + m'_1) C(l_1 l_2 l; m_1 m_2 m) \\
\times C(l_1' l_2' l''; m'_1 m'_2 m') D^{l_1}_{m_1 m'_1} (\omega_2) * D^{l_1}_{m_2 m'_2} (\omega_2) * \\
\times D^{l'_1}_{m_3 m'_3} (\omega_2) * Y^m_{l_1} Y^{m'}_{l_2} Y^{m''}_{l_1} \left] \right.
\]

The terms \( u^{\text{indbn}}_{2\beta\gamma}^{(II)} \) and \( u^{\text{indbn}}_{2\beta\gamma}^{(III)} \) are obtained from eqn. (12) by replacing \( E^{\text{indbn}}_{\beta\gamma x_l} \) by \( E^{\text{indbn}}_{\beta\gamma x_l} \) and \( E^{\text{indbn}}_{x_l \beta\gamma} \) by \( E^{\text{indbn}}_{x_l \beta\gamma} \), respectively. The strength coefficients \( E^{\text{indbn}}_{\beta\gamma x_l} \) in mixtures are given elsewhere (Shukla et al., 1984a).

In the present work, only those terms which contribute significantly to the free energy are taken into consideration, and the three-body nonadditive short-range forces and the induction forces higher than the three-body forces are neglected. Since the inclusion of the full isotropic and anisotropic site–site contributions to the free energy did not yield adequate convergence (Lucas, 1986), we restrict ourselves in our calculations only to the isotropic repulsive terms which also converge only for the values of the eccentricity \( \rho < 0.1 \). For zero eccentricity of a molecule and with no long-range anisotropy, the potential function (eqn. 1) reduces to that for atomic fluids. In particular, the combination of eqns. (4), (5) and (9) represents a suitable potential function for argon (as described below). In the framework of MPT2, this potential function is simple to use in calculating thermodynamic properties of the fluid argon. As a consequence, the present form of the perturbation theory of molecular fluids can be compared directly with the perturbation theory based on the equation of state for argon as the reference system.

**THERMODYNAMIC PERTURBATION THEORY**

In this work, we expand properties of the real system about those of the spherically symmetric reference system, in which the molecules interact with a L-J(12-6) pair potential. The total intermolecular potential energy can be
written as:

\[ U = \sum_{i<j} \sum_{\alpha\beta} u_{i\beta}^{L-J}(r_{ij}) + \lambda_1 \left\{ \sum_{i<j} \sum_{\alpha\beta} \left[ u_{i\beta}^{n-8}(r_{ij}) + u_{i\beta}^{rep0}(r_{ij}) \right] + u_{i\beta}^{ind0}(r_{ij}) \right\} + \sum_{i<j<k} \sum_{\alpha\beta\gamma} u_{i\beta}^{disp0bn}(r_{ij}r_{ik}r_{jk}) \left[ \sum_{i<j} \sum_{\alpha\beta} u_{i\beta}(r_{ij}, \omega_i, \omega_j) \right] + \sum_{i<j<k} \sum_{\alpha\beta\gamma\delta} u_{i\beta}^{indbn}(r_{ij}r_{jk}r_{ik}, \omega_i, \omega_j, \omega_k) \right) \]

(13)

For \( \lambda_1 = \lambda_2 = 0 \), eqn. (13) reduces to the potential energy of the reference system; for \( \lambda_1 = \lambda_2 = 1 \), the full potential energy is recovered.

We now expand the configurational Helmholtz free energy of the full system \( A \) about that of the reference L-J system \( A^{L-J} \). The perturbation expansion in \( \lambda_1 \), the isotropic contribution to potential energy, is carried out to the first-order. The perturbation expansion in \( \lambda_2 \), the anisotropic contribution to full potential energy, is carried out to the third order. In the third-order term, only the multipole moment contributions are important enough to be considered. In order to ensure the convergence of the perturbation series, the full expansion of the free energy is given using the Pade’ approximant (Stell et al., 1974):

\[ A = A^{L-J} + A_1^{n-8} + A_1^{disp0bn} + A_1^{0} + A_2 \left( \frac{1}{1 - A_3/A_2} \right) \]

(14)

where

\[ A_1^0 = A_1^{rep0} + A_1^{ind0} \]  

(15)

\[ A_2 = \frac{1}{2} \left[ \frac{\partial^2 A}{\partial \lambda_2^2} \right] \]  

(16)

and

\[ A_3 = \frac{1}{6} \left[ \frac{\partial^3 A}{\partial \lambda_3^3} \right] \]  

(17)

The various terms which contribute to the Helmholtz free energy, as used in the present work, are collected in the Appendix. As can be seen in the Appendix, perturbation contributions to the free energy involve integrals, \( J_1^{(n)} \), over the pair distribution functions, \( g_{2\beta} \), and \( L_{2\beta}(l' l'' ; n n') \) and \( K_{2\beta}(l' l'' ; n n'^n) \) over the triplet distribution functions \( g_{3\beta} \), for the reference L-J fluid. They are defined as

\[ J_1^{(n)} = \int_0^r dr_1^* r_{12}^{-(n-2)} g_{2\beta}^{L-J}(r^*) \]  

(18)
\[ L_{g_{ij}}(l; nn') = \int_0^\infty dr_{12}^* r_{12}^{*(n-2)} \int_0^\infty dr_{13}^* r_{13}^{*(n'-2)} \times \int_{-1}^1 d(\cos \alpha_1) \]
\[ \times g_{ij}^{L-J}(r_{12}^*, r_{13}^*, r_{23}^*) P_1(\cos \alpha_1) \] (19)

\[ K_{n_{jr}}(ll''; nn'n'') = \int_0^\infty dr_{12}^* r_{12}^{*(n-2)} \int_0^\infty dr_{13}^* r_{13}^{*(n'-2)} \times \int_{-1}^1 d(\cos \alpha_1) \]
\[ \times r_{23}^{*n''} g_{ij}^{L-J}(r_{12}^*, r_{13}^*, r_{23}^*) \Psi_{ll'}(\alpha_1 \alpha_2 \alpha_3) \] (20)

where:

\[ \Psi_{ll'}(\alpha_1 \alpha_2 \alpha_3) = \sum_{mm'm''} C(ll''; mm'm'') Y_{m}(\omega_{12}) Y_{m'}(\omega_{13}) Y_{m''}(\omega_{23}) \] (21)

\[ P_1(\omega) \] is the Legendre function, and \( \alpha_1 \) is the angle between \( r_{12} \) and \( r_{13} \). \( Y_{lm} \) is a spherical harmonic with superscript * denoting the conjugate complex value.

We refer to eqn. (14) as PTHN, which accounts explicitly for the effects of intermolecular forces and uses an accurate form of the perturbation theory in determining properties of the L-J reference mixture (as described in Part II of this work). For the particular choices of the compositions, \((X_A = 0, X_B = 1)\) or \((X_A = 1, X_B = 0)\), the above equations for the Helmholtz free energy readily reduce to one of the pure components of the mixture.

We note that a combination of the first three terms in eqn. (14) describes adequately the phase equilibria and thermodynamic properties of the pure fluid argon and thus resembles the equation of state for argon, represented by

\[ A_{\text{argon}} = A^{L-J} + A_1^{n-8} + A_2^{\text{disp0bn}} \] (22)

When the right hand side of the eqn. (22) is replaced by the equation of state for argon (where the free energy and other thermodynamic properties are calculated using the equation of state for argon), eqn. (14) is equivalent to the perturbation theory based on the equation of state for argon as the reference system given by

\[ A = A_{\text{argon}} + A_1^0 + A_2 \left( \frac{1}{1 - A_3/A_2} \right) \] (23)

Results based on eqn. (23), called PTHO, will be also reported here (wherever necessary) for the comparisons with PTHN. Note the present form of the PTHO for the pure fluids differs from the perturbation theory based on the equation of state for argon as the reference (Shukla et al., 1983) in the way of incorporating the form of the site–site intermolecular interactions only.

Previous studies indicate that the effects of the three-body dispersion forces on thermodynamic properties are significant (Clancy and Gubbins, 1981;
Singh and Shukla, 1983). Calculations by Gray et al. (1985) suggest that for some fluids multibody induction forces may also have important effects on the thermodynamic properties. Since the contributions due to the latter forces appear to be unimportant for the fluids considered here, they are ignored in this work.

PROPERTIES OF THE REFERENCE SYSTEM

For pure fluids the integrals $J$, $K$ and $L$ (eqns. (18–20)) are evaluated using the pair distribution function of L-J pair potential (reference system). The three-body distribution function is replaced by the pair distribution function using the usual superposition approximation. These integrals are functions of both temperature and density and are evaluated by the empirical equations, as suggested by Nicolas et al. (1979) and Gubbins and Twu (1978). Since the properties of the pure L-J fluids calculated by using the multi-parameter analytical equation (Nicolas et al., 1979), and as obtained from the accurate version of the perturbation theory (described in detail by Shukla, 1991a) differ only slightly, they are evaluated using the equation of state (Nicolas et al., 1979). This equation of state is known to fit simulation results for thermodynamic properties of the L-J (12-6) fluid over a wide range of conditions. However, in the case of PTHO, the free energy $A_{argon}$ in eqn. (23) is evaluated using the equation of state for argon (Twu et al., 1980). However, the integrals in the latter case are determined using the same method as used in the PTHN.

Once the properties of the reference fluid are known, properties of the real fluid, such as pressure, internal energy, chemical potential and entropy are determined from eqn. (14) using the usual thermodynamic relations. Vapor–liquid phase equilibrium is calculated by solving the equations for pressures and chemical potentials of the vapor and liquid phases simultaneously based on the phase equilibrium conditions. Likewise, critical temperature and density are calculated by imposing the stability condition that the first and the second derivatives of the pressure with respect to density must vanish.

POTENTIAL PARAMETERS

Isotropic polarizability ($\alpha$) and anisotropic polarizability ($\kappa$) as well as multipole moments (dipole moment $\mu$, quadrupole moment $Q$ and octopole moment $\Omega$) of molecules are taken from independent sources (Gray and Gubbins, 1984). Their values are given in Table 1(a).

Eccentricities ($r_i$) of the molecules are determined from their bond lengths which are also available from experiments (Herzberg, 1966) and are given in
Table 1(b). As mentioned above, only the isotropic terms $l_1 l_2 l = 0 \ 0 \ 0$ in the first-order perturbation are considered to model the shape of the molecules. Sample results for the compressibility factor and internal energy of the L-J (12-6) plus the isotropic site-site term, eqn. (7), are presented in Figs. 1 and 2 at the temperature $T^* = kT/\epsilon = 1.289$ and density $\rho^* = \rho \sigma^3 = 0.85$, $k$ being the Boltzmann constant. In either case, the agreement between theory and simulation (Lucas, 1986) is satisfactory only below $\rho_b < 0.1$. (Note the simulation results are for the full site-site ($r^{-12} - r^{-6}$) fluid as described in Shukla et al., 1983). Therefore, in order to ensure the proper convergence of the spherical harmonic expansion of the site-site repulsion model, the interaction sites are placed universally at a distance which is 1/3 of the length of the actual bond of a molecule. In fact, for this choice the reduced eccentricity ($\rho_b$) of a molecule considered in this work remains always below 0.1.

**TABLE 1(a)**

Molecular parameters from independent sources

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<th>System</th>
<th>$\sigma$ (Å)</th>
<th>$\kappa$</th>
<th>$\mu$ (esu cm)</th>
<th>$Q$ (esu cm$^3$)</th>
<th>$\Omega$ (esu cm$^3$)</th>
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**TABLE 1(b)**

Parameters for the site-site potential function a

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<th>$r_b$ (Å)</th>
<th>$r_c$ (Å)</th>
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a Relative molecular masses used for atoms H, C, and O are 1.008, 12.011 and 15.994, respectively.
TABLE 1(c)
Fitted potential parameters

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<th>System</th>
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<tr>
<td></td>
<td>(231.400)</td>
<td>(3.963)</td>
</tr>
<tr>
<td>Methane</td>
<td>146.686</td>
<td>3.606</td>
</tr>
<tr>
<td></td>
<td>(150.100)</td>
<td>(3.751)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>226.988</td>
<td>3.907</td>
</tr>
<tr>
<td></td>
<td>(232.433)</td>
<td>(4.077)</td>
</tr>
<tr>
<td>Ethane</td>
<td>259.215</td>
<td>4.027</td>
</tr>
<tr>
<td></td>
<td>(263.774)</td>
<td>(4.208)</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>219.881</td>
<td>3.459</td>
</tr>
<tr>
<td></td>
<td>(248.63)</td>
<td>(3.570)</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>230.211</td>
<td>3.610</td>
</tr>
<tr>
<td></td>
<td>(237.089)</td>
<td>(3.779)</td>
</tr>
</tbody>
</table>

* Values in parentheses are from the theory based on the equation of state for argon as the reference system (PTHO).

Fig. 1. Compressibility factor ($Z = PV/NkT$) for L-J + $\sigma_{\text{rep}}^0$ fluid from theory and simulation, site–site ($r^{-12}) - r^{-6}$, as a function of the reduced eccentricity ($\rho_b$). Simulation results are from Lucas (1986).
Ethylene and ethane are treated as linear molecules having two super-atoms CH₂ and CH₃ groups, respectively, while carbon dioxide is treated as having three atoms in a line. Their site-site parameters are also reported in Table I(b). Hydrogen bromide is treated as having a spherical shape. Since ethylene is a nonaxial molecule, it has been modeled using the effective axial approximation. In fact, it has been shown recently by Gubbins et al. (1981) and Lobo et al. (1988) that for ethylene the full nonaxial approach that includes quadrupolar, dispersion and dispersion-quadrupolar interactions is equivalent to the effective axial treatment. Therefore, we apply here the effective axial approach, which is more efficient than the full nonaxial method, for computing properties of the fluid ethylene.

The value of $n$ is universally taken to be $n = 14$. For the fluid argon, potential parameters $\epsilon$, $\sigma$, $C_1$ and $C_2$ are determined by fitting simultaneously 56 data of its saturated liquid density and vapor pressure ranging from the temperature that lies between the triple point ($T_p = 83.8$ K) and very close to the critical point ($T_c = 150.86$ K), but excludes the critical point from the fit. For all other fluids, the values of $n$, $C_1$ and $C_2$ are assumed to be the same as for argon. Values of $\epsilon$ and $\sigma$ (only two parameters) are as those giving the best fit to their saturated liquid density and vapor pressure data from the triple point temperature to close to the critical point temperature, excluding indeed the temperatures about 4 K below the critical point. Potential parameters $\epsilon$ and $\sigma$ thus obtained for three atomic fluids argon, krypton, xenon, one octopolar fluid methane, three quadrupolar fluids ethylene, ethane, carbon dioxide and one dipolar fluid hydrogen bromide, are summarized in Table I(c).
RESULTS AND DISCUSSION

In this section, we apply the third-order perturbation theory (PTHN; eqn. (14)), in order to compute vapor–liquid phase equilibria and thermodynamic properties of eight selected fluid systems, namely, argon, krypton, xenon, methane, ethylene, ethane, carbon dioxide and hydrogen bromide. These will form the components of the mixtures considered in Part II of this paper.

As one of our goals is also to present an adequate potential function for argon, so that the PTHN can be directly compared with that of the similar form of the perturbation theory of molecular fluids based on the accurate equation of state for argon (i.e. PTHO), we first present extensive comparisons of theoretical and experimental results for phase equilibria and thermophysical properites of argon in the inhomogeneous as well as in the homogeneous, dense fluid regions. The experimental data for argon used in these comparisons are obtained from the equation of state (Twu et al., 1980), which accurately correlates the various sets of the measured data for argon. Figure 3 presents comparisons of vapor–liquid phase equilibria of the fluid argon. From the triple point to close to the critical point, theoretical predictions are seen to be in excellent agreement with experimental data. This is discussed below. Also shown in Fig. 3 are the effects of three-body nonadditive dispersion forces on the vapor–liquid phase equilibrium of argon (the difference between the full line and the broken line). Effects of the three-body nonadditive dispersion forces are substantial, especially at the liquid densities.

Table 2 contains the average absolute deviations (AAD) of the results for the various thermodynamic properties of the system argon along the
TABLE 2
Average absolute deviation (AAD) between theory and experiment for argon. Critical point is excluded from the comparison. Experimental data are obtained from the accurate equation of state for argon (Twu et al., 1980)

<table>
<thead>
<tr>
<th>Property</th>
<th>%AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated vapor pressure</td>
<td>0.6</td>
</tr>
<tr>
<td>Saturated liquid density</td>
<td>0.2</td>
</tr>
<tr>
<td>Saturated vapor density</td>
<td>2.0</td>
</tr>
<tr>
<td>Saturated liquid entropy</td>
<td>1.0</td>
</tr>
<tr>
<td>Saturated liquid internal energy</td>
<td>0.5</td>
</tr>
<tr>
<td>Bulk liquid density</td>
<td>0.5</td>
</tr>
<tr>
<td>Bulk liquid entropy</td>
<td>1.5</td>
</tr>
<tr>
<td>Bulk liquid internal energy</td>
<td>1.0</td>
</tr>
</tbody>
</table>

saturation line as well as in the homogeneous fluid range. The %AAD for 56 data points in the temperature range 83.8–147 K along the saturation line and for 200 data points (which cover the wide ranges of the temperature, 86.7–500 K, and pressure 10–6700 bar) in the homogeneous, dense fluid phase are well within the experimental uncertainties. These latter calculations are performed by considering temperature and pressure as independent variables. However, as the critical point is approached, theory is found to show deviation from experiment. For instance, theoretical values of the critical temperature, pressure and volume are found to be 154 K, 51 bar and 86 cm³/mol, while their values determined from the equation of state for argon (Twu et al., 1980) are determined to be 151 K, 49 bar and 75 cm³/mol, respectively.

These discrepancies between the present theory and experiment near the critical point of argon may be due in part to the first-order approximation in the perturbation theory at very low densities and also to the fact that the properties very close to the critical point and at the critical point itself have been excluded from the fit of the potential parameters. However, these differences between theory and experiment very close to the critical point are not an impediment for the applications of PTHN for our interests, for we will restrict the present work to describing properties of the subcritical fluid mixtures only.

We further test the adequancy of the potential for argon in the dense gas region. Figure 4 presents a comparison between theory and experiment for the second virial coefficient, while Fig. 5 shows a similar comparison for the viscosity. The values of the virial coefficient and viscosity are computed for the intermolecular potential model of eqns. (4) and (5) following the
methods described elsewhere (Ameling et al., 1985). In these calculations, the parameters used are those determined from the fit of the saturated liquid densities and vapor pressure, reported in Table 1(c). Theoretical results are seen to be in very good agreement with experimental data for both the second virial coefficient (Dymond and Smith, 1980) and the viscosity (Maitland and Smith, 1972). Although these comparisons in the gaseous region are not as good as the comparisons based on another accurate but more complicated form of the potential function for argon (Ameling et al., 1985), the present form of the potential function (i.e. the combination of eqns. (4), (5) and (9)) is nevertheless remarkably successful in describing accurately the
thermodynamic properties and phase equilibria of dense fluid argon and is simple enough to be applied in the perturbation theory calculations.

Figures 6 and 7 show the results of vapor–liquid phase equilibria for the more volatile simple fluids, krypton and xenon. These fluids differ from argon in their energy, size and polarizability parameters. As for the fluid argon, theoretical results agree well with experimental data, except very close to the critical point, where theory is again found to deviate from experiment. A similar comparison is presented in Fig. 8 for an octopolar fluid, methane. Because of the very weak octopole moment, methane is seen to behave in a very similar way to the atomic fluid argon.
In order to further examine the reliability of the PTHN in accounting adequately for nonideal behavior, we present in Figs. 9 and 10 results for the vapor–liquid coexistence curve for two quadrupolar fluids, namely, ethylene and ethane. The molecules of these fluids exhibit strong quadrupole moment and appreciable nonsphericity in their shapes. The eccentricities of ethylene and ethane molecules are determined assuming them to be linear in shape and having two superatoms CH$_2$ and CH$_3$, respectively. However, the actual eccentricities for these molecules may be higher due to the steric effects caused by hydrogen atoms. Even in these cases, the theory is seen to agree well with experiment.
We have also investigated in some detail the phase equilibria and thermodynamic properties of another quadrupolar fluid, carbon dioxide. The molecules of this fluid are strongly quadrupolar and are more nonspherical in shape than those of ethylene and ethane. Figure 11 presents results for vapor-liquid phase equilibria, while Figs. 12–14 show results for the vapor pressure, residual internal energy and residual entropy along the saturation line. In the range of the fitted parameters $\epsilon$ and $\sigma$ (excluding of course the critical point), the agreement between theory and experiment is remarkable. Also shown in Figs. 11–14 are the results obtained from the PTHO (eqn. (23)). In this approach, properties of the reference system, which is now
equivalent to eqn. (22), have been determined directly from the equation of
state for argon (Twu et al., 1980), keeping all other molecular parameters
the same as those used in PTHN. Moreover, the same method is adopted
for computing the structural properties of the reference system in both
theories except that the different values of $\epsilon$ and $\sigma$ are obtained from the
simultaneous fit of the saturated liquid density and the vapor pressure data,
as contained in Table 1(c). Both theories are seen to agree well with
experiment. Since the critical point is again excluded from the fit, the
deviation between PTHO and experiment close to the critical point is to be expected. Moreover, the dense fluid homogeneous properties of carbon dioxide as predicted by PTHN and PTHO are given in Table 3. As for the saturated properties, theoretical results for internal energy and entropy are well within the experimental uncertainties.

In order to check the convergence of the perturbation expansion and the explicit effects of the different branches of the intermolecular interactions on the thermodynamic properties, we also show the relative importance of the contributions of various types of pair and three-body interactions to the Helmholtz free energy. Table 4 presents the magnitudes of the various contributions to the interaction forces for the fluid carbon dioxide at a selected temperature close to its boiling point, $T = 250$ K and $V = 42.0174$ cm$^3$/mol. The contributions arising due to pair induction and repulsion interactions in the first-order perturbation are significant, the latter contribution amounts to the strong nonsphericity in the shape of the carbon dioxide molecule. In the second-order term, the contribution arising from electrostatic interactions (quadrupolar in this case) is most significant, whereas contributions from pair induction and dispersion interactions are small but significant. The contributions from the cross terms of pair electrostatic, induction and dispersion interactions are also important enough to be considered. The effects of three-body nonadditive induction and the total three-body additive forces arising from dispersion and induction interactions are of further significance and amount to an increase in the free energy of the system. The three-body nonadditive dispersion contribution to the second-order term of the free energy is found to be of negligible
### TABLE 3
Thermodynamic functions for carbon dioxide in the homogeneous liquid phase

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$V$ ($\text{cm}^3 \text{mol}^{-1}$)</th>
<th>$-U$ ($\text{J mol}^{-1}$)</th>
<th>$-S$ ($\text{J mol}^{-1} \text{K}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EXP</td>
<td>PTHN</td>
<td>EXP</td>
</tr>
<tr>
<td>220</td>
<td>10</td>
<td>37.69</td>
<td>37.56</td>
<td>13406</td>
</tr>
<tr>
<td>220</td>
<td>50</td>
<td>37.43</td>
<td>37.23</td>
<td>13503</td>
</tr>
<tr>
<td>220</td>
<td>100</td>
<td>37.12</td>
<td>36.86</td>
<td>13617</td>
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<tr>
<td>250</td>
<td>20</td>
<td>42.03</td>
<td>42.02</td>
<td>11554</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>41.54</td>
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<td>250</td>
<td>100</td>
<td>40.85</td>
<td>40.74</td>
<td>11892</td>
</tr>
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<td>200</td>
<td>39.79</td>
<td>39.55</td>
<td>12217</td>
</tr>
<tr>
<td>250</td>
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<td>39.76</td>
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<td>300</td>
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<td>42.74</td>
<td>42.29</td>
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<td>300</td>
<td>600</td>
<td>41.71</td>
<td>41.20</td>
<td>10747</td>
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%AAD  

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<thead>
<tr>
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<th>PTHN</th>
<th>EXP</th>
<th>PTHN</th>
</tr>
</thead>
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<tr>
<td>(0.7)</td>
<td>1.2</td>
<td>(1.5)</td>
<td>(5.3)</td>
<td></td>
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</tbody>
</table>

*Values in parentheses are %AAD from the perturbation theory based on the equation of state for argon as the reference system (PTHO). Experimental data (Exp.) are from Angus et al. (1973). r denotes the residual part of the free energy.

Significance, and hence is not reported here. In the third-order perturbation, only significant contributions arise from electrostatic interactions and they contribute substantially to the total free energy.

By comparing the various orders of contributions in the perturbation theory, it is clear that for the type of systems considered in this work the proper convergence has been achieved in the perturbation expansion. The net effect of the anisotropy in the pair as well as in the three-body interactions is found to decrease the total free energy of the system. These comparisons show that both the short- and the long-range forces are important in describing thermodynamic behavior of the fluid systems. Note the first term in Table 4 represents that part of the free energy of the atomic
TABLE 4

Individual contributions of various terms in the Helmholtz free energy expansion for carbon dioxide at \( T = 250 \, \text{K}, \, V = 42.0174 \, \text{cm}^3 \, \text{mol}^{-1} \) \(^a\)

<table>
<thead>
<tr>
<th>Term</th>
<th>( A'/NkT )</th>
<th>( A_1/NkT )</th>
<th>( A_2/NkT )</th>
<th>( A_3/NkT )</th>
<th>( A_4/NkT )</th>
<th>( A_5/NkT )</th>
<th>( A_6/NkT )</th>
<th>( A_7/NkT )</th>
<th>( A_8/NkT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A'/NkT ) (argon)</td>
<td>-1.8288</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_1/NkT ) (ind0)</td>
<td>-0.3206</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( A_1/NkT ) (rep0)</td>
<td>+0.8370</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>( A_1/NkT ) (elec)</td>
<td>-1.9111</td>
<td></td>
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<td></td>
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<tr>
<td>( A_2/NkT ) (ind, a)</td>
<td>-0.0051</td>
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<td></td>
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<tr>
<td>( A_2/NkT ) (disp, a)</td>
<td>-0.1425</td>
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<tr>
<td>( A_2/NkT ) (elec–ind)</td>
<td>+0.0373</td>
<td></td>
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<td>( A_2/NkT ) (elec–disp)</td>
<td>+0.3221</td>
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<tr>
<td>( A_3/NkT ) (ind–disp)</td>
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<tr>
<td>( A_3/NkT ) (indbn)</td>
<td>+0.0802</td>
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<td></td>
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<tr>
<td>( A_3/NkT ) (b)</td>
<td>+0.0856</td>
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<tr>
<td>( A_3/NkT ) (elec, a)</td>
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<tr>
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<tr>
<td>( A_4/NkT ) (total)</td>
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<tr>
<td>( A_5/NkT ) (total)</td>
<td>+0.5196</td>
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<td></td>
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<td>-2.5008</td>
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</tbody>
</table>

\( a \) \( a, \, ba \) and \( bn \) denote two-body, three-body additive and three-body nonadditive contributions to free energy. Values in parentheses are from the theory based on the equation of state for argon as the reference (PTHO).

Finally, Figs. 15 and 16 compare theoretical and experimental results for the vapor–liquid phase equilibria and the vapor pressure of a dipolar fluid, hydrogen bromide. Hydrogen bromide is composed of molecules of almost spherical shape but of substantial dipole and quadrupole moments. Again, PTHN (\( \equiv \) PTHO) performs very well. Also, in Table 5 we report the explicit contributions of the various terms to the Helmholtz free energy at \( T = 198.67 \, \text{K} \) and \( V = 35.5635 \, \text{cm}^3/\text{mol} \). As in the case of carbon dioxide, the electrostatic interactions have a large effect while other forces have relatively small but significant effects on the Helmholtz free energy. Since the inclusion of the repulsion terms did not yield any improvement upon the theory in describing thermodynamic properties of the fluid, in agreement with our previous results (Shukla et al., 1983, 1984a), the site–site terms are completely ignored here, and hydrogen bromide is treated as having a spherical shape.
CONCLUSIONS

We have presented a third-order thermodynamic perturbation theory of molecular fluid mixtures based on the spherically symmetric reference system represented by the Lennard-Jones pair interactions. Theory accounts explicitly for the isotropic and anisotropic intermolecular interactions and has been applied to predict vapor–liquid phase equilibria and thermodynamic properties of some selected pure fluids such as argon, krypton, xenon, methane, ethylene, ethane, carbon dioxide and hydrogen bromide. Comparisons of theoretical results with experimental data show a
TABLE 5
Individual contributions of various terms in free energy expansion for hydrogen bromide at $T = 198.67$ K, $V = 35.5635$ cm$^3$ mol$^{-1}$

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1/NkT$ (argon)</td>
<td>-3.4967</td>
</tr>
<tr>
<td>$A_1/NkT$ (ind0)</td>
<td>-0.6620</td>
</tr>
<tr>
<td>$A_2/NkT$ (elec, dipole–dipole)</td>
<td>-0.2606</td>
</tr>
<tr>
<td>$A_2/NkT$ (elec, dipole–quadrupole)</td>
<td>-1.0067</td>
</tr>
<tr>
<td>$A_3/NkT$ (elec, quadrupole–quadrupole)</td>
<td>-2.0339</td>
</tr>
<tr>
<td>$A_3/NkT$ (elec)</td>
<td>-3.3012</td>
</tr>
<tr>
<td>$A_2/NkT$ (ind, a)</td>
<td>0.0267</td>
</tr>
<tr>
<td>$A_2/NkT$ (disp, a)</td>
<td>0.0418</td>
</tr>
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<td>$A_2/NkT$ (elec–ind)</td>
<td>0.0383</td>
</tr>
<tr>
<td>$A_2/NkT$ (elec–disp)</td>
<td>0.0659</td>
</tr>
<tr>
<td>$A_2/NkT$ (ind–disp)</td>
<td>-0.0345</td>
</tr>
<tr>
<td>$A_2/NkT$ (indbn)</td>
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<td>$A_2/NkT$ (b)</td>
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<td>$A_3/NkT$ (elec, a)</td>
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<tr>
<td>$A_3/NkT$ (total)</td>
<td>1.8479</td>
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<tr>
<td>$A'/NkT$ (total)</td>
<td>-5.9126</td>
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</tbody>
</table>

very good performance of the theory. For the pure fluids considered in this paper, the present theory (PTHN; eqn. (14)) is almost equivalent to the third-order perturbation theory of molecular fluids based on the equation of state for argon (PTHO; eqn. (23)), for the proposed spherical part of the potential function resembles a true potential function for argon. In the subsequent publication (Part II) we show that the PTHN can predict reliably the phase equilibria and the thermodynamic excess properties of binary fluid mixtures composed of the components considered in this paper. Also, it will be demonstrated that the PTHN offers a significant improvement over the PTHO (in which the thermodynamic properties of the reference mixture are computed using the van der Waals one-fluid theory) in accounting for the nonideal solution behavior in fluid mixtures.

LIST OF SYMBOLS

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k \quad \text{Boltzmann constant}

K \quad \text{three-body nonadditive integral}

L \quad \text{three-body additive integral}

Q \quad \text{quadrupole moment}

r \quad \text{intermolecular separation distance}

r_a \quad \text{location of a site}

S^r \quad \text{residual entropy}

T \quad \text{absolute temperature}

U^r \quad \text{residual internal energy}

\textbf{Greek letters}

\alpha \quad \text{isotropic polarizability}

\epsilon \quad \text{potential well-depth}

\kappa \quad \text{anisotropic polarizability}

\mu \quad \text{dipole moment}

\rho \quad \text{number density}

\sigma \quad \text{molecular diameter}

\Omega \quad \text{octopole moment}

\omega \quad \text{Euler's angle}

\textbf{Abbreviations}

disp \quad \text{two-body dispersion interaction}

elec \quad \text{electrostatic interaction}

ind \quad \text{two-body induction interaction}

indbn \quad \text{three-body induction interaction}

L-J \quad \text{Lennard–Jones potential}

PTHN \quad \text{theory based on eqn. (14)}

PTHO \quad \text{theory based on eqn. (23)}

\textbf{REFERENCES}


APPENDIX: CONTRIBUTIONS TO THE HELMHOLTZ FREE ENERGY USED IN THIS WORK

First-order terms

\[
\frac{A_{1}^{14-8}}{NkT} = \frac{2\pi \rho}{kT} \sum_{\alpha\beta} X_{\alpha} X_{\beta} \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^{3} C_{1} [J_{x\beta}^{(14)} - C_{2} \cdot J_{x\beta}^{(8)}] \\
\frac{A_{1}^{\text{rep}}}{NkT} = \frac{2\pi \rho}{kT} \sum_{\alpha\beta} X_{\alpha} X_{\beta} \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^{3} \sum_{ab} e_{ab} s_{ab}^{12} \left(88(\rho_{a}^{2} + \rho_{b}^{2})J_{x\beta}^{(14)}ight) \\
+ \frac{4004}{15} (3 \cdot \rho_{a}^{4} + 10 \rho_{a}^{2} \rho_{b}^{2} + 3 \rho_{b}^{4})J_{x\beta}^{(16)} \\
+ 4576(\rho_{a}^{6} + 7 \rho_{a}^{4} \rho_{b}^{2} + 7 \rho_{a}^{2} \rho_{b}^{4} + \rho_{b}^{6})J_{x\beta}^{(18)} \\
+ 19448 \left(\rho_{a}^{8} + 12 \rho_{a}^{6} \rho_{b}^{2} + \frac{126}{5} \rho_{a}^{4} \rho_{b}^{4}\right)J_{x\beta}^{(20)} \\
+ 67184 \left(\rho_{a}^{10} + \frac{55}{3} \rho_{a}^{8} \rho_{b}^{2} + 66 \rho_{a}^{6} \rho_{b}^{4} + 66 \rho_{a}^{4} \rho_{b}^{6}\right) \\
+ \frac{55}{3} \rho_{a}^{2} \rho_{b}^{8} + \rho_{b}^{10}\right)J_{x\beta}^{(22)} + \cdots
\]

(A1)

with the site-site parameters

\[
e_{ab}s_{ab}^{12} = \left(\left(\frac{(e_{xx}s_{xx}^{12}/e_{x\beta}s_{x\beta}^{12})e_{aa}s_{aa}^{12}}{e_{bb}s_{bb}^{12}}\right)^{1/13}\right) + \left(\frac{(e_{xx}s_{xx}^{12}/e_{x\beta}s_{x\beta}^{12})e_{aa}s_{aa}^{12}}{e_{bb}s_{bb}^{12}}\right)^{1/13}/2\right)^{1/13}/2
\]

(A3)
and

$$\sum_{ab} e_{ab}s_{ab}^{12} = 1 \tag{A4}$$

For the relation between the site-site parameters of different atoms of a molecule, the following rules are assumed:

$$e_{aa}s_{aa}^{12} = (m_a/m_b)^2 e_{bb}s_{bb}^{12}$$

$$e_{ab}s_{ab}^{12} = \left[\left(e_{aa}s_{aa}^{12}\right)^{1/13} + \left(e_{bb}s_{bb}^{12}\right)^{1/13}\right]^{1/2} \tag{A.5}$$

where, $m_a$ and $m_b$ are the atomic masses, and

$$e_{ab} = e_{ab}/e_{a}\beta$$

$$s_{ab} = \sigma_{ab}/\sigma_{a}\beta$$

$$\rho_a = r_a/\sigma_{a}\beta$$

$$\rho_b = r_b/\sigma_{a}\beta$$

$$\frac{A_1^{\text{ind}}}{NkT} = -\frac{2\pi\rho}{kT} \sum_{ab} X_{a} X_{b} \gamma_a \left[2 \frac{\mu_a^4}{\sigma_{a}\beta} J_{ab}^{(6)} + 3 \frac{Q^2_\beta}{\sigma_{a}\beta} J_{ab}^{(8)}\right] \tag{A.6}$$

$$\frac{A_1^{\text{disp}}}{NkT} = \frac{8\pi^2\rho^2}{3kT} \frac{1}{\sqrt{\frac{5}{4\pi}}} \left[\frac{1}{14}\right] \sum_{\beta\gamma} X_{a} X_{b} X_{\gamma}$$

$$+ \frac{(R_a + R_{\beta} + R_{\gamma}) R_a R_{\beta} R_{\gamma}}{(R_a + R_{\beta})(R_a + R_{\gamma})(R_{\beta} + R_{\gamma})} \frac{K_{\alpha\beta\gamma} (222; 333)}{\sigma_{a}\beta \sigma_{a}\gamma \sigma_{\beta\gamma}} \tag{A.7}$$

**Second-order terms**

Second-order contribution to free energy contains the terms arising from the anisotropic, electrostatic, induction and dispersion interactions and their cross terms. The electrostatic term is considered to be a series of multipolar terms up to quadrupole moment for linear molecules and octopole moment for tetrahedral molecules. For a polar molecule, the leading term is dipole–dipole, for quadrupolar molecule the quadrupole–quadrupole and for tetrahedral molecule the octopole–octopole:

$$A_2 = A_2^{\text{elec}} + A_2^{\text{ind}} + A_2^{\text{disp}} + A_2^{\text{elec-disp}} + A_2^{\text{elec-ind}} + A_2^{\text{ind-disp}} + A_2^{\text{indbn}} \tag{A.8}$$

The whole terms of the second-order free energies can be written as

$$\frac{A_2^{\text{elec}}}{NkT} = -\frac{\pi\rho}{15(kT)^2} \sum_{\alpha\beta} X_{\alpha} X_{\beta} \left[10 \frac{\mu_a^2 \mu_\beta^2}{\sigma_{a}\beta} J_{ab}^{(6)} + 30 \frac{\mu_a^2 Q^2_\beta}{\sigma_{a}\beta} J_{ab}^{(8)}\right.$$

$$+ 42 \frac{Q^2_\beta Q^2_\beta}{\sigma_{a}\beta} J_{ab}^{(10)} + 96 \frac{\mu_a^2 \Omega^2_\beta}{\sigma_{a}\beta} J_{ab}^{(10)} + 432 \frac{Q^2_\beta \Omega^2_\beta}{\sigma_{a}\beta} J_{ab}^{(12)} + (57024/35) \frac{\Omega^2_\beta \Omega^2_\beta}{\sigma_{a}\beta} J_{ab}^{(14)} \left.\right] \tag{A.9}$$
\[ A_{2}^{\text{ind}} = A_{2a}^{\text{ind}} + A_{2b}^{\text{ind}} \] (A.10)

\[
\frac{A_{2a}^{\text{ind}}}{N k T} = - \frac{2 \pi \rho}{5(kT)^2} \sum_{a \beta} x_{\alpha} x_{\beta} \left\{ \alpha_{2}^{\mu_{\alpha}} \left( 1 + \frac{24}{5} \kappa_{\beta}^{2} \right) + \alpha_{\alpha} \alpha_{\beta} \mu_{\alpha}^{2} \mu_{\beta}^{2} \left( \kappa_{\alpha} + \kappa_{\beta} \right) + \frac{19}{5} \kappa_{\alpha} \kappa_{\beta} \right\} \frac{1}{\sigma_{\alpha \beta}^{9}} J_{\alpha \beta}^{(12)} + \left[ \frac{12}{7} \alpha_{\alpha}^{2} \mu_{\alpha}^{2} Q_{\alpha}^{2} \left( 17 + \frac{103}{5} \kappa_{\beta}^{2} \right) + 2 \alpha_{\alpha} \alpha_{\beta} \mu_{\alpha}^{2} Q_{\alpha}^{2} \left( \frac{6}{35} \kappa_{\beta} + \frac{9}{35} \kappa_{\alpha} \kappa_{\beta} \right) \right] \frac{1}{\sigma_{\alpha \beta}^{11}} J_{\alpha \beta}^{(14)}
\]

\[
+ \left[ \frac{9}{7} \alpha_{\alpha}^{2} Q_{\alpha}^{2} \left( 3 + \frac{47}{5} \kappa_{\beta}^{2} \right) + \frac{9}{35} \alpha_{\alpha} \alpha_{\beta} Q_{\alpha}^{2} Q_{\beta}^{2} \left( 8 \kappa_{\beta} + 8 \kappa_{\alpha} + \frac{61}{7} \kappa_{\alpha} \kappa_{\beta} \right) \right] \frac{1}{\sigma_{\alpha \beta}^{13}} J_{\alpha \beta}^{(16)} \right\} (A.11)
\]

and

\[
\frac{A_{2b}^{\text{ind}}}{N k T} = - \left( \frac{\pi \rho}{k T} \right)^2 \sum_{a \beta \gamma} x_{\alpha} x_{\beta} x_{\gamma} \sigma_{\beta \gamma}^{2} \left[ \frac{432}{25} \mu_{\alpha}^{2} Q_{\alpha}^{2} \alpha_{\beta} \alpha_{\gamma} \sigma_{\alpha \beta}^{2} \sigma_{\alpha \gamma}^{2} \right] L_{\alpha \beta \gamma}(1; 77)
\]

\[ + \left( \frac{4}{5} \mu_{\alpha}^{4} \alpha_{\beta} \alpha_{\gamma} + 2 \mu_{\alpha}^{2} \mu_{\beta}^{2} \alpha_{\alpha} \alpha_{\beta} \kappa_{\gamma} + \mu_{\alpha}^{2} \mu_{\gamma}^{2} \alpha_{\alpha}^{2} \kappa_{\gamma}^{2} \right) L_{\alpha \beta \gamma}(2; 66)
\]

\[ + \left( \frac{8}{175} \left( \mu_{\alpha}^{2} \alpha_{\beta} + \kappa_{\alpha} \alpha_{\beta} \mu_{\beta}^{2} \right) \left( 60 \kappa_{\gamma} Q_{\gamma}^{2} + 42 \kappa_{\alpha} \kappa_{\beta} Q_{\gamma}^{2} \right) \right) L_{\alpha \beta \gamma}(2; 68)
\]

\[ + \left( \frac{144}{1225} \right) \left( 100 \alpha_{\alpha}^{2} \alpha_{\beta} Q_{\alpha}^{2} + 140 \alpha_{\alpha} \alpha_{\beta} \kappa_{\gamma} Q_{\alpha}^{2} Q_{\beta}^{2} + 49 Q_{\alpha}^{2} Q_{\beta}^{2} \alpha_{\alpha}^{2} \kappa_{\gamma}^{2} \right) L_{\alpha \beta \gamma}(2; 88)
\]

\[ + \left( \frac{576}{175} \right) \frac{\alpha_{\alpha} \alpha_{\beta} \mu_{\alpha}^{2} Q_{\alpha}^{2} \sigma_{\alpha \beta}^{5} \sigma_{\alpha \gamma}^{5} L(3; 77) + \left( \frac{36}{49} \right) Q_{\alpha}^{2} \alpha_{\beta} \alpha_{\gamma} \sigma_{\alpha \beta}^{4} \sigma_{\alpha \gamma}^{4} L_{\alpha \beta \gamma}(4; 88) \right] (A.12)
\]

For linear molecules the dispersion contribution to \( A_{2}^{\text{disp}} \) is given as

\[ A_{2}^{\text{disp}} = A_{2a}^{\text{disp}} + A_{2b}^{\text{disp}} \] (A.13)

with

\[
\frac{A_{2a}^{\text{disp}}}{N k T} = - \frac{16 \pi \rho}{5(kT)^2} \sum_{a \beta} x_{\alpha} x_{\beta} \epsilon_{\alpha \beta} \sigma_{\alpha \beta}^{3} \left( \frac{\kappa_{\alpha}^{2}}{35} + \frac{133 \kappa_{\alpha}^{2} \kappa_{\beta}^{2}}{35} \right) J_{\alpha \beta}^{(12)} (A.14)
\]

\[
\frac{A_{2b}^{\text{disp}}}{N k T} = - \frac{64(\pi \rho)^2}{5(kT)^2} \sum_{a \beta \gamma} x_{\alpha} x_{\beta} x_{\gamma} \sigma_{\alpha \beta}^{2} \sigma_{\alpha \gamma}^{2} \epsilon_{\alpha \beta} \epsilon_{\alpha \gamma} \kappa_{\alpha}^{2} L_{\alpha \beta \gamma}(2; 66) (A.15)
\]
Note that we neglect higher order polarizability terms.

\[
\frac{A_{2}^{\text{elec-disp}}}{NkT} = \frac{288\pi\rho}{25(kT)^2} \sum_{\alpha\beta} X_\alpha X_\beta \sigma_{\alpha\beta}^{-2} \epsilon_{\alpha\beta}\kappa_{\alpha} \kappa_{\beta} Q_\alpha Q_\beta J_{\alpha\beta}^{(11)} \tag{A.16}
\]

\[
\frac{A_{2}^{\text{elec-ind}}}{NkT} = \frac{12\pi\rho}{35(kT)^2} \sum_{\alpha\beta} X_\alpha X_\beta \kappa_{\alpha} \alpha_{\alpha} Q_\alpha Q_\beta \left[ \frac{28\mu_{\alpha}^2}{\sigma_{\alpha\beta}^8} J_{\alpha\beta}^{(11)} + \frac{12Q_{\alpha}^2}{\sigma_{\alpha\beta}^{10}} J_{\alpha\beta}^{(13)} \right] \tag{A.17}
\]

\[
\frac{A_{2a}^{\text{ind-disp}}}{NkT} = -\frac{16\pi\rho}{35(kT)^2} \sum_{\alpha\beta} X_\alpha X_\beta \epsilon_{\alpha\beta}\kappa_{\alpha} \sigma_{\alpha\beta}^2 \sigma_{\beta\gamma}^2 \left[ \frac{7\mu_{\alpha}^2}{\sigma_{\alpha\beta}^3} J_{\alpha\beta}^{(12)} + \frac{12Q_{\alpha}^2}{\sigma_{\alpha\beta}^5} J_{\alpha\beta}^{(14)} \right] \tag{A.18}
\]

\[
\frac{A_{2b}^{\text{ind-disp}}}{NkT} = -\frac{32(\pi\rho)^2}{35(kT)^2} \sum_{\alpha\beta\gamma} X_\alpha X_\beta X_\gamma \epsilon_{\alpha\gamma}\epsilon_{\beta\gamma}\kappa_{\alpha} \sigma_{\alpha\beta}^2 \sigma_{\beta\gamma}^2
\]

\[
\times \left[ \frac{7\mu_{\alpha}^2}{\sigma_{\alpha\beta}^3} L_{\alpha\beta\gamma}(2; 66) + \frac{12Q_{\alpha}^2}{\sigma_{\alpha\beta}^5} L_{\alpha\beta\gamma}(2; 86) \right] \tag{A.19}
\]

Free energy contributions involving nonadditive three-body induction forces:

\[
\frac{A_{2}^{\text{indbn}}}{NkT} = \frac{\pi^{7/2}(kT)^2}{75} \sum_{\alpha\beta\gamma} X_\alpha X_\beta X_\gamma \left\{ \frac{64}{\sqrt{3\sqrt{18}}} \left( \alpha_{\alpha} \mu_{\beta}^2 \mu_{\gamma}^2 + \alpha_{\beta} \mu_{\alpha}^2 \mu_{\gamma}^2 + \alpha_{\gamma} \mu_{\alpha}^2 \mu_{\beta}^2 \right) \right. \\
\times \frac{K_{\alpha\beta\gamma}(222,333)}{\sigma_{\alpha\beta} \sigma_{\alpha\gamma} \sigma_{\beta\gamma}} + \frac{64}{105} \sqrt{3} \left[ \alpha_{\alpha} (Q_{\gamma}^2 \mu_{\alpha}^2 + Q_{\alpha}^2 \mu_{\gamma}^2) + \alpha_{\beta} (Q_{\alpha}^2 \mu_{\beta}^2 + Q_{\beta}^2 \mu_{\gamma}^2) \right. \\
+ \alpha_{\gamma} (Q_{\alpha}^2 \mu_{\alpha}^2 + Q_{\beta}^2 \mu_{\beta}^2) \left. \frac{K_{\alpha\beta\gamma}(233,344)}{\sigma_{\alpha\beta} \sigma_{\alpha\gamma} \sigma_{\beta\gamma}} \right) - \frac{32}{315} \sqrt{154} \\
\times \left[ \alpha_{\alpha} Q_{\alpha}^2 Q_{\beta}^2 + \alpha_{\beta} (Q_{\alpha}^2 Q_{\gamma}^2 + \alpha_{\gamma} Q_{\alpha}^2 Q_{\beta}^2) \right] \frac{K_{\alpha\beta\gamma}(334,445)}{\sigma_{\alpha\beta} \sigma_{\alpha\gamma} \sigma_{\beta\gamma}} \right\} \tag{A.20}
\]

**Third-order terms**

Only the multipolar contributions to \( A_3 \) are considered, while all other contributions are neglected beyond second order. For multipolar potentials the expressions for \( A_3 \) are

\[
A_3^{\text{elec}} = A_{3a}^{\text{elec}} + A_{3b}^{\text{elec}} \tag{A.21}
\]

where

\[
\frac{A_{3a}^{\text{elec}}}{NkT} = \frac{\pi\rho}{(kT)^3} \sum_{\alpha\beta\gamma} X_\alpha X_\beta \left[ \frac{24}{25} \mu_{\alpha}^2 \mu_{\beta}^3 Q_{\alpha} Q_{\beta} J_{\alpha\beta}^{(11)} + \frac{48}{75} \mu_{\alpha}^2 \mu_{\beta}^2 Q_{\alpha} Q_{\beta} J_{\alpha\beta}^{(11)} \right. \\
\left. + \frac{48}{35} \mu_{\alpha}^2 Q_{\alpha}^3 J_{\alpha\beta}^{(13)} + \frac{144}{245} Q_{\alpha}^3 Q_{\beta}^3 J_{\alpha\beta}^{(15)} \right] \tag{A.22}
\]
\[ A_{3b}^{\text{elec}} = \frac{\pi^{\frac{3}{2}} \rho^2}{(kT)^3} \sum_{a\beta} X_a X_\beta X_i \left[ \frac{32}{135} \sqrt{\frac{14}{5}} \frac{\mu_a^2 \mu_\beta^2 \mu_i^2}{\sigma_a \sigma_\beta \sigma_i} K_{a\beta i} \right] \]

\[ + \frac{192}{315} \sqrt{3} \frac{\mu_a^2 \mu_\beta^2 \Omega_i^2}{\sigma_a \sigma_\beta \sigma_i^2} K_{a\beta i} \]

\[ + \frac{256}{405} \frac{\mu_a^2 \mu_\beta^2 \Omega_i^2}{\sigma_a \sigma_\beta \sigma_i^2} K_{a\beta i} \]

\[ \times K_{a\beta i} \]

\[ \left. \left( \frac{128}{275} \sqrt{\frac{26}{\sigma_a \sigma_\beta \sigma_i^2}} \frac{\Omega_a^2 \Omega_\beta^2 \Omega_i^2}{\sigma_a \sigma_\beta \sigma_i^2} K_{a\beta i} \right) \right] \]

\[ \left. \left( \frac{221184}{11375} \sqrt{\frac{3553}{637}} \frac{\Omega_a^2 \Omega_\beta^2 \Omega_i^2}{\sigma_a \sigma_\beta \sigma_i^2} K_{a\beta i} \right) \right] \]

(A.23)

In the above equations, \( a, b, \) and \( b_n \) denote two-body, three-body additive and three-body nonadditive contributions to the Helmholtz free energy, respectively. In a binary mixture, \( \rho \) is the mixture number density, \( \rho = N( = N_A + N_B) / V \), \( X_A \) is the composition of the component A, \( X_A = N_A / (N_A + N_B) \). \( \alpha \) is the isotropic polarizability, \( \kappa \) is the anisotropy in the polarizability, \( \mu \) is the dipole moment, \( Q \) is the quadrupole moment and \( \Omega \) is the octopole moment of the molecule.