INTRODUCTION

The aim of this present paper is to develop a theory for estimating the thermodynamic properties of tetrahedral molecular fluids which are of great interest in recent years. This is related to a great number of natural phenomena as well as to a numerous industrial applications. One of the theoretical methods to deal with the problem is the 'preaveraged' potential. Using the 'preaveraged' potential method\(^1,2\) have derived the effective Lennard –Jones (ELJ) (12-6) potential to estimate the thermodynamic properties of simple molecular fluids such as \(\text{N}_2\) and \(\text{O}_2\).

In the present work, we apply this approach to compute the thermodynamic properties of fluids having tetrahedral symmetry like carbon tetrachloride (\(\text{CCl}_4\)). Such molecules have octopole and hexadecapole moments but not permanent moments of lower order, e.g., dipole and quadrupole.

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Thermodynamics of tetrahedral molecular fluids

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ABSTRACT

An effective pair potential for molecular fluid is expressed in the effective Lennard - Jones (ELJ) (12-6) potential form. We employ this theory to estimate the thermodynamic properties such as excess free energy \(A\), residual internal energy \(U\) at zero pressure and critical point location of Carbon tetrachloride (\(\text{CCl}_4\)). The agreement with experimental data is found to be fairly good.

Key words: Free energy, internal energy, critical point location

In section 2, we discuss the theoretical basis for obtaining the 'preaveraged' pair potential for a molecular fluid. This 'preaveraged' potential is expressed in the effective Lennard Jones (ELJ) (12-6) form. Section 3 is concerned with the evaluation of the thermodynamic properties and critical point location. Concluding remarks are given in section 4.

Basic theory

In the present study, we consider a molecular fluid of molecules whose molecules interact via pair potential, given by

\[
\begin{align*}
\mathbf{u}(r) &= \mathbf{u}_{\text{LJ}}(r) + \mathbf{u}_o(r) + \mathbf{u}_q(r) \\
&= \mathbf{u}_{\text{LJ}}(r) + \mathbf{u}_o(r) + \mathbf{u}_q(r) \quad \text{(1)}
\end{align*}
\]

where \(\mathbf{u}_{\text{LJ}}(r)\) is the central Lennard –Jones (LJ) (12-6) potential

\[
\mathbf{u}_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad \text{(2)}
\]

where \(\varepsilon\) and \(\sigma\) are the well - depth and
molecular diameter, respectively. The second term in Eq. (1) is the angle dependent part of pair interaction. For this we take 3

$$u_4(r, \omega_1, \omega_2) = u_{\text{perm}}(r, \omega_1, \omega_2) + u_{\text{in}}(r, \omega_1, \omega_2)$$...

where $u_{\text{perm}}$ is the interaction between permanent multiple moments of the molecules and $u_{\text{in}}$ is the interaction of the induced multipole moments in one molecules with the permanent multipole moments in other molecule. In the present case, we consider octopole and hexadecapole moments only and assume both dipole and quadrupole moments to be zero.

In order to obtain the effective pair potential, we start with the configurational integral in the case is defined as 4

$$Z_N = (4\pi)^N \int \cdots \int \exp \left[ -\beta \sum_{i<j} u_E(r_{ij}) \right] \prod_i \text{d} r_i \text{d} \omega_i$$...

where $r_{ij} = |r_i - r_j|$ is the center to center distance and $w_i$ represents the orientational co-ordinates $(\theta_i, \phi_i)$ of molecule $i$. Here $\beta = (kT)^{-1}$ (k being the Boltzmann constant $T$ absolute temperature). Using Eq.(1) in Eq.(4), the configurational integral can be expressed as in the following form 5.

$$Z_N = \int \cdots \int \exp \left[ -\beta \sum_{i<j} u_E(r_{ij}) \right] \prod_i \text{d} r_i \text{d} \omega_i$$...

where $u_E(r_{ij})$ is the orientational independent 'preaveraged' pair potential form which have expressed in the LJ (12-6) form as 6,7

$$u_E(r) = 4 \varepsilon \left( (\sigma_T / r)^{12} - (\sigma_T / r)^{6} \right)$$...

where

$$\sigma_T = \sigma / \sigma = F^{-1/6}$$...

and

$$\varepsilon = \varepsilon_T / \varepsilon = (A + B / T^*) F^2$$...

In these expressions, we have used the following reduced quantities

$$T^* = kT / \varepsilon$$,
$$\alpha^* = \alpha / \sigma^2$$, $$\Omega^* = \Omega / \varepsilon$$, and $$\phi^* = \phi / \varepsilon$$.

Here $\Omega$ and $\phi$ are the octopole and hexadecapole moments respectively, and $\alpha$ is the polarizability of

| System | $\sigma$ (A) | $\varepsilon$ (K) | $\alpha \times 10^{24}$ (cm$^3$) | $\Omega \times 10^{34}$ (esu cm$^2$) |
|--------|--------------|------------------|-----------------|-----------------|
| CCl$_4$ | 5.206         | 490.17           | 2.60            | -1.5            |

| Table 2: Excess free energy $A$, residual internal energy $U$ of CCl$_4$ at zero pressure |
|---------------------------------|
| $T$(K) | $-\beta A/N$ | $-\beta U/N$ |
| Theory | Bohn et al | Theory | Bohn et al |
|--------|------------|--------|----------|
| 298.15 | 6.470      | 6.910  | 10.294   | 10.531 |

| Table 3: Critical constants of molecular fluid CCl$_4$ |
|----------------|
| Present | Expt |
|--------|------|
| $T_c$ (K) | 587.7 | 556.3 |
| $V_c$ (cm$^3$.mol$^{-1}$) | 263.3 | 275.7 |
| $P_c$ (atm) | 51.4 | 45.0 |
the moments. Thus the effective pair potential can be expressed as the ELJ (12-6) potential form in terms of $\sigma_T$ and $\varepsilon_T$. Then the system can be treated as the LJ (12-6) system.

**Thermodynamic properties of molecular fluids**

We apply our theory to calculate the thermodynamic properties of molecular fluid like CCl$_4$, whose fluid parameters are given in Table 1. The values of central force parameters $\sigma$ and $\varepsilon$ are those reported in literature. Multipole moments and anisotropic polarizabilities are those given by Gray and Gubbins.

In our approach, we consider the reduced density $\rho^*=p\rho^*/\varepsilon$ and reduced temperature $T^*=kT^*/\varepsilon$ for the LJ (12-6) fluid and replace $p^*$ by $p^*_T=p^*_\sigma^*$ and $T^*$ by $T^*_T=T^*/\varepsilon$. Thus the free energy and pressures of the molecular fluid can be given by

$$A(\rho^*,T^*)=A_{LJ}(\rho^*_T,T^*_T), \quad \text{(13)}$$

$$P(\rho^*,T^*)=P_{LJ}(\rho^*_T,T^*_T), \quad \text{(14)}$$

Where $A_{LJ}(\rho^*_T,T^*_T)$ and $P_{LJ}(\rho^*_T,T^*_T)$ are, respectively, the free energy and pressure of the LJ (12-6) fluid at the reduced density $\rho^*_T$ and condensed temperature $T^*_T$.

In the present work, we are interested to calculate the thermodynamic properties such as excess free energy $A$, residual internal energy $U$ at zero pressure, using expressions given by

$$\beta A/N = -\frac{4.50151 - 2.23463 - 0.09664 (2x^2 - 1) + 0.01360 (4x^2 - 3) - 0.00255 [8x^2 (x^2 - 1) + 1]}{\varepsilon T} \quad \text{(15)}$$

$$\beta U/N = -\frac{5.47348 - 1.03040 x + 0.22325 (2x^2 - 1) - 0.06177 (4x^2 - 3) + 0.01857 [8x^2 (x^2 - 1) + 1]}{\varepsilon T} \quad \text{(16)}$$

where $x = 2.5/T^* - 3.25$

We employ this method to calculate the thermodynamic properties such as the excess free energy $A$, residual internal energy $U$ for CCl$_4$ at $T = 298.15$ K. They are compared with the results reported by Bohn et al.,\(^{10}\) in Table 2. The agreement is found to be good.

**Critical point location**

We apply our theory to study the critical temperature $T_c$, critical volume $V_c$, and critical pressure $P_c$ for CCl$_4$. For the LJ (12-6) fluid, they are given by

$$T^*_c = kT_c/\varepsilon = 1.26 \quad \text{(17a)}$$

$$V^*_c = V_c/\rho^* = 3.10 \quad \text{(17b)}$$

$$P^*_c = P_c/\sigma^3 = 0.117 \quad \text{(17c)}$$

In order to replace the critical constants for CCl$_4$, we replace $\varepsilon \rightarrow \varepsilon_T$ and $\sigma \rightarrow \sigma_T$ in Eq.(17). Thus

$$T^*_c = 1.26 \varepsilon \quad \text{(18a)}$$

$$V^*_c = 3.1 \sigma \quad \text{(18b)}$$

$$P^*_c = 0.117 \varepsilon / \sigma^3 \quad \text{(18c)}$$

Eq. (17a) may be solved by the iterative process. Knowing $T^*_c$, one may obtain $V^*_c$ and $P^*_c$. We apply Eq.(18) to calculate $T^*_c$, $V^*_c$, and $P^*_c$ for CCl$_4$. They are compared with the experimental data\(^{8,9}\) in Table 3. The agreement is found to be good.

**Concluding remarks**

The effective pair potential (EPP) is expressed in the LJ (12-6) potential form simply replacing $\varepsilon \rightarrow \varepsilon_T$ and $\sigma \rightarrow \sigma_T$. Then the system can be treated as the LJ (12-6) system. This approach is employed to calculate the thermodynamic properties of some molecular fluids, where the agreement is found to be good.

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