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COMPUTATION FOR SURFACE TENSION OF MOLECULAR FLUIDS

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ABSTRACT

The effective pair potential for molecular fluid of molecules possessing tetrahedral symmetry is expressed in the effective Lennard-Jones (ELJ) (12 - 6) potential form in terms of effective diameter σ_T and well depth $\in_T$. We employ the effective diameter hard sphere theory (EDHST) for the ELJ (12-6) fluid in terms of the hard sphere fluid of properly chosen hard sphere diameter. We employ this theory to estimate surface tension γ of CCl_4. In all these cases, the agreement is fairly good.

Key words: Surface tension, Hard sphere, Molecular fluid

INTRODUCTION

The surface tension in the liquid-vapour interface systems remain an important area of current research because of their wide spread applications in many technological process such as cooling, lubrication, adhesion, wetting and drying. Many attempts have been made to measure the experimental surface tension of pure fluids using empirical or semiempirical approaches[1]; theoretical methods[2] based on Lennard-Jones (12-6) potential for its simplicity in having two adjustable parameters.

The aim of the present work is to compute surface tension of molecular fluids for CCl_4. One of the theoretical methods to deal with the problem is the effective diameter hard sphere (EDHST) theory[3-5] for estimating the surface tension γ of CCl_4.

Basic theory

In the present study, we consider a molecular fluid of molecules, whose molecules

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interact via pair potential, given by

$$u\ (r\ \omega_1\omega_2) = u_{LJ}\ (r) + u_a\ (r\omega_1\omega_2) \qquad \ldots(1)$$

where, u_{LJ} (r) is the central Lennard –Jones (LJ) (12-6) potential.

$$u_{LJ}\ (r) = 4\in [(\sigma/r)^{12} - (\sigma/r)^6] \qquad \ldots(2)$$

where, $\in$ and σ 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] -

$$u_a(r\omega_1\omega_2) = u_{perm}\ (r\omega_1\omega_2) + u_{in}\ (r\omega_1\omega_2) \qquad \ldots(3)$$

Where u_{perm} is the interaction between permanent multiple moments of the molecules and u_{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 the configurational integral in the case is defined as[3] -

$$Z_N = (4\pi)^{-N} \int \ldots \int \exp\,[-\,\beta \sum_{\iota<j} u\ (r_{ij}\ \omega_i\ \omega_j\ )] \prod_{\iota<1}^{N} dr_i\ d\omega_i, \qquad \ldots(4)$$

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

$$Z_N = \int \ldots \int \exp\,[-\beta \sum_{\iota<j} u_E\ (r_{ij})] \prod_{\iota<1}^{N} dr_i \qquad \ldots(5)$$

Where, u_E (r_{ij}) is the orientational-independent 'preaveraged' pair potential form[5], we have expressed u_E in the LJ (12-6) form as -

$$u_E(r) = 4\,\varepsilon_T\,[(\sigma_T/r)^{12} - ((\sigma_T/r)^6], \qquad \ldots(6)$$

where,

$$\hat{\sigma} \equiv \sigma_T/\sigma = F^{-1/6} \qquad \ldots(7)$$

$$\hat{\in} \equiv \varepsilon_T / \varepsilon = (A + B/T^*) F^2 \quad \text{...(8)}$$

and $F = C/(A + B/T^*)$, ...(9)

A, B and C are expressed as -

$$A = 1 - (60/7)\, \alpha^* \phi^{*2} \quad \text{...(10)}$$

$$B = -(528/175)\, [9(2^{-1/3})\, \Omega^{*4} + 65\, (2^{-2/3})\, \Omega^{*2} \phi^{*2} + (6500/21)\, \phi^{*4}] \quad \text{...(11)}$$

$$C = 1 + 12/5\, (2^{2/3})\, \alpha^* \Omega^{*2} \quad \text{...(12)}$$

In these expressions, we have used the following reduced quantities –

$T^* = kT/\varepsilon$,

$\alpha^* = \alpha/\sigma^3$, $\Omega^{*2} = \Omega^2/\varepsilon\, \sigma^7$ and $\phi^{*2} = \phi^2/\varepsilon\, \sigma^9$.

Here Ω and ϕ are the octopole and hexadecapole moments, respectively, and α is the polarizability of the moments. Thus, the effective pair potential can be expressed as the E L J (12-6) potential form in terms of σ_T and ε_T. Then the system can be treated as the L J (12-6) system.

Surface tension

We apply our theory to calculate the surface tension (ST) along the liquid-gas phase boundary. The ST of the LJ (12-6) fluid is described by [6] -

$$\gamma^* = \gamma\sigma^3/\in = 2.666[1 - T^*/T_c^*]^{1.27} \quad \text{...(13)}$$

Where $T_c^* = 1.26$. In case of molecular fluid, we replace $\in \rightarrow \in_T$ and $\sigma \rightarrow \sigma_T$ in Eq. (13). Then the ST of the molecular fluid is expressed as -

$$\hat{\gamma}^* = \gamma\sigma^3/\in\, = 2.666(\hat{\in}/\hat{\sigma}^2)[1 - T_T^*/T_C^*]^{1.27} \quad \text{...(14)}$$

Where $T_T^* = kT/\in_T = T^*/\hat{\in}$. In this approach, the amplitude is modified but the exponent remains a constant with a value of 1.27.

We employ Eq. (14) to predict the ST γ for CCl_4. These results are compared with the experimental data [7-9] in Table 1. The agreement is fairly good.

Table 1: The surface tension γ (in dyne/cm) of CCl_4

T C	Theor.	Expt.
15	28.31	27.65
35	25.93	25.21
55	23.60	22.76
75	21.32	20.31
95	19.08	17.86

Concluding remarks

We have derived the effective L J (12-6) potential simply replacing $\sigma \rightarrow \sigma_T$ (T*) and $\varepsilon \rightarrow \varepsilon_T$ (T*). Then the system can be treated as the L J (12-6) system. This approach is employed to estimate surface tension γ of CCl_4. In all these cases, the agreement is fairly good.

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