

## Phase equilibria of polar Lennard-Jones fluids

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**Abstract** - Liquid - vapour equilibria of polar Lennard-Jones fluids is studied taking into account of dipole and quadrupole moments. We employ an effective Lennard-Jones (ELJ) (12-6) potential to calculate critical point location for a range of values of both  $\mu^{*2} = \mu^2 / (\epsilon \sigma^3)$  and  $Q^{*2} = Q^2 / (\epsilon \sigma^5)$ . Our results are in good agreement with the Monte-Carlo simulation data.

**Keywords** - Polar Lennard-Jones fluids, critical point location, thermodynamic behaviour

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### 1. Introduction

The purpose of the present work is to study the phase equilibria of polar fluid consisting of Lennard - Jones (LJ) (12-6) spheres with embedded point dipoles and linear quadrupoles. Recently, Karki *et al* [1] have derived effective LJ (12-6) potential for estimating the thermodynamic properties of molecular fluids.

In the present work, we improve the effective LJ (12-6) potential and apply it to study the phase equilibria of the polar Lennard - Jones fluids.

### 2. Potential model

We consider a fluid whose molecules interact *via* pair potential of the form

$$u(r, \omega_1, \omega_2) = u_0(r) + u_a(r, \omega_1, \omega_2), \quad (1)$$

where  $r = |r_1 - r_2|$  is the centre - to - centre distance and  $\omega_i$  represents the orientational coordinates  $(\theta_i, \phi_i)$  of molecules  $i$ . Here,  $u_0(r)$  is the Lennard - Jones (LJ) (12-6) potential

$$u_0(r) = 4 \epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2)$$

where  $\epsilon$  and  $\sigma$  are, respectively, the well-depth and molecular diameter, and  $u_a(r)$  is the angle - dependent part, which is taken

$$u_a = u_{\mu\mu} + u_{\mu q} + u_{qq}, \quad (3)$$

where,  $u_{\mu\mu}$ ,  $u_{\mu q}$  and  $u_{qq}$  are contributions due to dipole - dipole, dipole - quadrupole and quadrupole - quadrupole interactions, respectively.

### 3. Effective pair potential

Karki *et al* [1] have expressed the orientation - independent 'preaveraged' pair potential in the compact form

$$\psi(r) = 4 \epsilon \left\{ \left[ A_{12} \left( \frac{\sigma}{r} \right)^{12} - \left[ A_6 \left( \frac{\sigma}{r} \right)^6 + A_8 \left( \frac{\sigma}{r} \right)^8 + A_{10} \left( \frac{\sigma}{r} \right)^{10} \right] \right] + \left[ A_{11} \left( \frac{\sigma}{r} \right)^{11} + A_{13} \left( \frac{\sigma}{r} \right)^{13} + A_{15} \left( \frac{\sigma}{r} \right)^{15} \right] \right\}. \quad (4)$$

In terms of the reduced quantities  $T^* = kT / \epsilon$ ,  $\mu^{*2} = \mu^2 / (\epsilon \sigma^3)$  and  $Q^{*2} = Q^2 / (\epsilon \sigma^5)$  the explicit expressions of the coefficients  $A_m$  are given as :

$$A_6 = 1 + (1/12 T^*) (\mu^{*2})^2, \quad (5a)$$

$$A_8 = (1/4 T^*) \mu^{*2} Q^{*2}, \quad (5b)$$

$$A_{10} = (7/20 T^*) (Q^{*2})^2, \quad (5c)$$

$$A_{12} = 1 + (7/1800 T^{*3}) (\mu^{*2})^4, \quad (5d)$$

$$A_{11} = (1/5 T^{*2}) (\mu^{*2})^2 Q^{*2}, \quad (6a)$$

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$$A_{13} = (6/35 T^{*2}) \mu^{*2} (Q^{*2})^2, \quad (6b)$$

$$A_{15} = (18/245 T^{*2}) (Q^{*2})^3. \quad (6c)$$

Karki *et al* [1] have neglected the terms appearing in the second bracket of the right hand side of eq. (4). In the present study we consider these terms to obtain the effective pair potential.

We approximate  $\sigma/r = \sigma/r_{\min} \approx 2^{-1/6}$  [2] and using the coefficients  $A_m$ , we define the terms

$$A = (1/12)(\mu^{*2})^2 + (1/4(2)^{1/3})(\mu^{*2} Q^{*2}) + (7/20(2)^{2/3})(Q^{*2})^2, \quad (7)$$

$$B = (2^{1/6}/5)(\mu^{*2})^2 Q^{*2} + (6/35(2)^{1/6})\mu^{*2} (Q^{*2})^2 + (18/245(2)^{1/2})(Q^{*2})^3, \quad (8)$$

$$C = (7/800)(\mu^{*2})^4. \quad (9)$$

Then eq. (4) can be expressed in the LJ (12-6) form

$$\psi(r) = 4\epsilon_T \left[ (\sigma_T/r)^{12} - (\sigma_T/r)^6 \right], \quad (10)$$

where

$$\hat{\sigma} \equiv \sigma_T / \sigma = F^{-1/6}, \quad (11)$$

$$\hat{\epsilon} \equiv \epsilon_T / \epsilon = (1 + (B/T^{*2}) + (C/T^{*3})) F^2 \quad (12)$$

and

$$F = (1 + A/T^*) / (1 + (B/T^{*2}) + (C/T^{*3})). \quad (13)$$

Then the polar fluid can be treated as the LJ (12-6) fluid.

#### 4. Critical constants

In order to test the theory we apply it to estimate the critical temperature  $T_C^*$ , critical volume  $V_C^*$ . For the LJ (12-6) fluid, they are given by

$$T_C^* \equiv kT_C / \epsilon = 1.26 \quad (14a)$$

$$V_C^* \equiv V_C / N\sigma^3 = 3.1 \quad (14b)$$

In order to estimate the critical constants for polar fluids, we replace  $\epsilon \rightarrow \epsilon_T$  and  $\sigma \rightarrow \sigma_T$  in eq. (14). Thus, we get

$$T_C^* = 1.26 \hat{\epsilon}, \quad (15a)$$

$$V_C^* = 3.1 \hat{\sigma}^3. \quad (15b)$$

Eq. (15a) may be solved by the iterative process. Knowing  $T_C^*$ , we obtain the reduced critical density  $\rho_C^* = 1/V_C^*$  for the polar fluid.

The values of the critical temperature  $T_C^*$  and critical density  $\rho_C^*$  are compared with the Monte Carlo (MC) data [3] in Table 1 for various values of  $\mu^{*2}$  and  $Q^{*2}$ . The resulting  $T_C^*$  is a bit higher than MC values except at  $\mu^{*2} = 2.0$  and  $Q^{*2} = 2.0$ , where the situation is reversed. However, the resulting  $\rho_C^*$  is higher than the MC values throughout the range of  $\mu^{*2}$  and  $Q^{*2}$  considered here. On the whole, the agreement is good.

**Table 1.** Values of the critical temperature  $T_C^*$  and critical density  $\rho_C^*$  for various dipole moment  $\mu^{*2}$  and quadrupole moment  $Q^{*2}$ .

$\mu^{*2}$	$Q^{*2}$	$T_C^*$		$\rho_C^*$	
		Present	MC	Present	MC
1.00	1.00	1.82	1.79 ± 0.02	0.34	0.34 ± 0.01
1.00	2.00	2.45	2.42 ± 0.02	0.36	0.33 ± 0.01
2.00	1.00	2.06	2.00 ± 0.02	0.34	0.32 ± 0.01
2.00	2.00	2.62	2.65 ± 0.03	0.35	0.33 ± 0.01

#### 5. Concluding remarks

The effective pair potential for the polar LJ (12-6) fluids is expressed in the LJ (12-6) form by simply replacing  $\epsilon \rightarrow \epsilon_T(T^*)$  and  $\sigma \rightarrow \sigma_T(T^*)$ . The values of  $\epsilon_T$  and  $\sigma_T$ , which decrease with increase of  $T^*$ , depend on  $\mu^{*2}$  and  $Q^{*2}$ . The effective LJ (12-6) potential is employed to estimate the critical temperature  $T_C^*$  and critical density  $\rho_C^*$  over a wide range of  $\mu^{*2}$  and  $Q^{*2}$ . The agreement with the MC [3] data is good. This theory can be employed to calculate other thermodynamic properties. This is not attempted here.

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