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SHEAR VISCOSITY OF POLAR LENNARD– JONES FLUIDS

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ABSTRACT

An effective pair potential for the modified Lennard-Jones (LJ) (12-6) model with embedded point dipole and linear quadrupole is expressed in the LJ (12-6) form. This theory is employed to estimate the shear viscosity ξ of the modified LJ (12-6) fluid with $\mu^* = \mu/(\varepsilon\sigma^3) = 2$ for different range of damping factor K. These TP's decrease due to the polar moments. This deviation decreases with the increase of damping factor K.

Key words: Modified Lennard – Jones fluid, Shear viscosity, Damping factor

INTRODUCTION

The purpose of the present work is to develop a theory for estimating the shear viscosity of polar fluid consisting of modified Lennard-Jones (LJ) (12-6) spheres with embedded point dipole and linear qadrupoles. This model is of great theoretical interest in studying the effect of the dispersive forces on the phase equilibria of polar fluid [1]. In one of the theoretical method to deal with the problem of real or model fluids, the reference system is often represented by the LJ (12-6) potential and the effective pair potential is expressed in the LJ (12-6) potential form [2]. Recently, Singh and Sinha [3] have derived the effective LJ (12-6) potential, when the reference potential is the modified LJ (12-6) potential and studied the effect of the dispersive forces on the phase equilibria of the polar system.

The transport properties (TPs) of the effective LJ (12-6) fluid may be estimated through the evolution of the TP's of the hard sphere (HS) fluid with the properly chosen hard sphere diameter[2]. The effective diameter hard sphere theory (EDHST) [4] is an important

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method for studying the TPs of dense real fluids in terms of the HS fluid. Karki and Sinha [4] have employed the EDHST for estimating the TP's of the molecular fluid.

In the present work, we extend this approach to study the shear viscosity of the effective LJ (12-6) fluid, when the reference potential is the modified LJ (12-6) potential.

Basic theory

We consider a molecular fluid (of linear axially symmetric molecules), whose molecules interact via pair potential of the form

$$u(r\omega_1\omega_2) = u_o(r) + u_a(r\omega_1\omega_2) \qquad \ldots(1)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and ω_i represents the orientation coordinates (θ_i ϕ_i) of molecule i. Here $u_0(r)$ is the spherically symmetric central potential and u_a is the angle dependent electrostatic potential. For the central potential, we take the modified LJ(12-6) potential [1].

$$u_0(r) = 4\in [(\sigma/r)^{12} - K(\sigma/r)^6] \qquad \ldots(2)$$

where $\in$ and σ are, respectively, the well depth and molecular diameter and K the modified parameter (varying between 0 and 1). For angle-dependent part, we take

$$u_a = u_{\mu\mu} + u_{\mu Q} + u_{QQ} \qquad \ldots(3)$$

where $u_{\mu\mu}$, $u_{\mu Q}$ and u_{QQ} are contributions due to dipole-dipole, dipole-quadrupole and quadrupole-quadrupoles, respectively. They are given by[2] -

$$u_{\mu\mu} = (\mu^2/r^3)\,[\sin\theta_1 \sin\theta_2 \cos\phi - 2\cos\theta_1 \cos\theta_2] \qquad \ldots(4a)$$

$$u_{\mu Q} = (3\mu Q/2r^4)\,[\cos\theta_1 (3\cos^2\theta_2 - 1) - 2\sin\theta_1 \sin\theta_2 \cos\theta_2 \cos\phi] \qquad \ldots(4b)$$

$$u_{QQ} = (3Q^2/4r^5)\,[1 - 5(\cos^2\theta_1 + \cos^2\theta_2) - 15\cos^2\theta_1 \cos^2\theta_2 + 2(\sin\theta_1 \sin\theta_2 \cos\phi - 4\cos\theta_1 \cos\theta_2)^2] \qquad \ldots(4c)$$

where θ_1, θ_2 and $\phi = |\phi_1 - \phi_2|$ are the Euler angles, μ and Q are, respectively, the dipole moment and quadrupole moment of the molecule.

The partition function Q_N in this case is defined as [5] -

$$Q_N = (N!\,\Lambda^{3N} q^{-N})^{-1} \int \ldots \int \exp[-\beta \sum_{i<j} u(x_i, x_j) \prod_{i=1}^{N} dx_i \qquad \ldots(5)$$

where Λ is the thermal wavelength and q the rotational partition function of a single molecule and the vector $x_i = (\mathbf{r}_i\omega_i)$ represents both the position of the centre of mass and orientation of molecule i. Here $dx_i = (4\pi)^{-1}d\mathbf{r}_i d\omega_i$ and $\beta = (kT)^{-1}$ (k being the Boltzmann constant and T absolute temperature). Using Eq. (1) in Eq. (5), we follows the method of Karki and Sinha [4] and write the partition function in the form -

$$Q_N = (N!\, \Lambda^{3N} q^{-N})^{-1} \int \dots \int \exp [- \beta \sum_{i<j} \Psi(r_{ij})] \prod_{i=1}^{N} d\mathbf{r}_i \quad \dots(6)$$

where $\Psi(r_{ij})$ is the orientation-independent 'preaveraged' potential. This effective pair potential can be expressed in the LJ(12-6) potential form [3] -

$$\Psi(r) = 4\in_T [(\sigma_T/r)^{12} - (\sigma_T/r)^6] \quad \dots(7)$$

Where

$$\hat{\sigma} (K, T^*) = \sigma_T (K, T^*) / \sigma = F^{-1/6} \quad \dots(8a)$$

$$\hat{\in} (K, T^*) = \in_T (K, T^*) / \in = [1 + (b/T^{*2}) + (c/T^{*3})] F^2 \quad \dots(8b)$$

$$\text{and } F = [K + (a/T^*)]/ [1 + (b/T^{*2}) + (c/T^{*3})] \quad \dots(8c)$$

Thus, the polar fluid in the presence of the 'modified' LJ (12-6) potential can be expressed as the LJ(12-6) potential. Recently, Singh and Sinha[3] have employed this theory to study the phase equilibria of polar LJ (12-6) fluid.

In the following sections, we apply this theory to estimate the shear viscosity of the modified polar LJ (12-6) fluid.

As the exact results for the reduced second and third virial coefficients are available only for the dipolar LJ (12-6) fluid with K = 1.0, we calculate $B^*(T^*)$ and $C^*(T^*)$ for the dipolar LJ(12-6) fluid with K = 1.0 as a function of μ^{*2} for different values of T^*. They are compared with the exact results [6] in Table 1. The agreement is found to be good particularly for high value of T^* ($T^* \geq 2.0$). We calculate $B^*(T^*)$ and $C^*(T^*)$ of the polar LJ(12-6) fluid for different values of K at $T^* = 3.0$. These are reported in Table 2. We find that in both the cases (i) $\mu^{*2} = 2.0$, $Q^{*2} = 0$ and (ii) $\mu^{*2} = 0.0$, $Q^{*2} = 2.0$, B^* increases as K decreases. The values of C^* depend on K.

Table 1: The reduced second and third virial coefficients for the polar LJ (12-6) fluid with K = 1 as a function of μ^{*2}. Here $Q^{*2} = 0.0$

T*	μ^{*2}	B*		C*	
		Present	Exact	Present	Exact
1.00	0.848	-3.013	-3.010	0.746	0.740
	1.414	-3.935	-3.941	-	-
2.00	0.848	-0.717	0.717	0.525	0.549
	1.414	-0.880	-.0880	0.782	0.796
3.00	0.848	-0.153	-0.153	0.386	0.392
	1.414	-0.220	-0.220	-0.468	0.476

Table 2: The reduced second and third virial coefficients for the polar LJ (12-6) fluid with $\mu^{*2} = 2.0$, $Q^{*2} = 0.0$ and $\mu^{*2} = 0.0$, $Q^{*2} = 2.0$ at T* = 3.0 for different values of K

K	B*		C*	
	$\mu^{*2} = 2.0$ $Q^{*2} = 0.0$	$\mu^{*2} = 0.0$ $Q^{*2} = 2.0$	$\mu^{*2} = 2.0$ $Q^{*2} = 0.0$	$\mu^{*2} = 0.0$ $Q^{*2} = 2.0$
1.0	-1.0175	-2.5861	0.3906	-0.0954
0.8	-0.9867	-1.9399	0.4349	0.3540
0.6	-0.1657	-1.3910	0.3566	0.4535
0.4	0.1655	-0.9186	0.3949	0.4387
0.2	0.5063	-0.3012	0.4810	0.4118
0.1	0.6464	-0.3126	0.5411	0.4072
0.0	0.7666	-0.1325	0.6143	0.3795

Shear viscosity of dense polar fluid

We assume that the structure of a dense fluid is very similar to that of a hard sphere (HS) fluid and attractive forces play a minor role in the dense fluid behaviour. The polar fluid can be expressed in terms of HS fluid with properly chosen effective hard sphere diameter d_e. The HS fluid can be handled with the revised Enskog theory (RET) of van Beijeren and Ernst [7] to predict the TP's such as the shear viscosity ξ. These are expressed as

$$\xi = [g_{HS}(de)]^{-1}[1+(4/5)(4\eta g_{HS}(de)) + 0.7615\,(4\eta g_{HS}(de))^2]\,\xi_0 \qquad \ldots(9)$$

where

$$\xi_0 = (5/16\,\pi\, de^2)\,(\pi mkT)^{1/2} \qquad \ldots(10)$$

$\eta = (\pi\rho de^3/6)$ is the packing fraction and $g_{HS}(d_e)$ is the equilibrium radial distribution function (RDF) of the HS fluid at the contact. Here ρ is the number density and m is the mass of a particle.

In order to obtain the effective hard sphere diameter d_e, we divide the effective LJ(12-6) potential $\Psi(r)$ according to the Weeks-Chandler-Andersen (WCA) scheme [8] and following the method of Verlet and Weis [9]. Thus, the expression for de is given as

$$d_e = d_B\,[\,1 + A\delta\,] \qquad \ldots(11)$$

where

$$d_B = \sigma_T[1.068 + 0.383\,T^*_T] / [1 + 0.4293\,T^*_T] \qquad \ldots(12)$$

$$\delta = [210.31 + 404.6 / T^*_T]^{-1} \qquad \ldots(13)$$

$$A = [1 - 4.25\,\eta_\omega + 1.363\,\eta_\omega^2 - 0.8757\,\eta_\omega^3] / (1 - \eta_\omega)^2 \qquad \ldots(14)$$

with $\eta_\omega = \eta - \eta^2 / 16$

Knowing the packing fraction η, the RDF $g_{HS}(de)$ of the HS fluid is given by [10]

$$g_{HS}(de) = (1 - \eta / 2) / (1 - \eta)^3 \qquad \ldots(15)$$

CONCLUSION

We calculate the shear viscosity ξ for the modified LJ (12-6) fluid with embedded point dipole (μ^{*2} =2) and linear quadrupole (Q^{*2} = 2) for different values of damping factor K). The values of $\xi^* = \xi\sigma^2 / (m\in)^{1/2}$ for the modified LJ(12-6) fluid with (i) μ^* = 2.00, Q^* =

0.0 and (ii) $\mu^* = 0.0$, $Q^* = 2.0$ are compared with the modified LJ(12-6) fluid in Fig. 1 for $\rho^* = 0.6$ at $T^* = 3.0$. Shear viscosity decreases due to the polar moments. The deviation decreases with the increase of K.

The effective pair potential for the modified LJ(12-6) fluid with the embedded point dipole and linear quadrupole is expressed in the LJ(12-6) potential form simply by replacing $\sigma \rightarrow \sigma_T(K,T^*)$ and $\in \rightarrow \in_T(K,T^*)$. This potential is employed to study the virial coefficients and shear viscosity for $\mu^* = 2$ and $Q^* = 2$ for different values of K of the dispersive force.

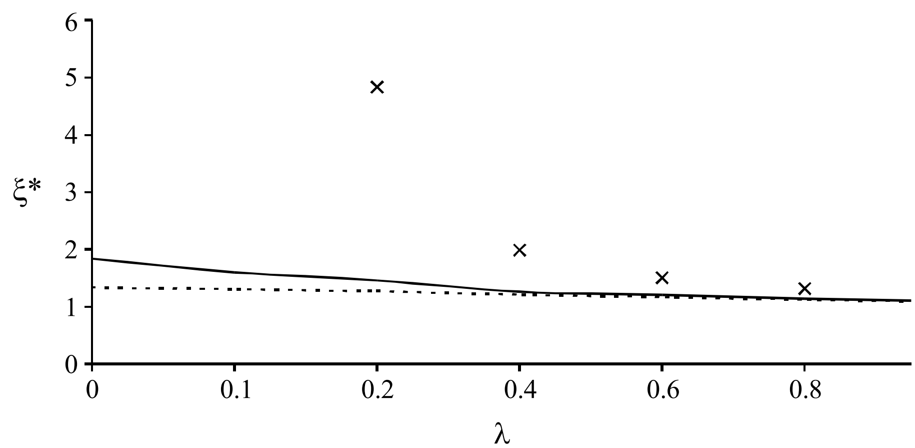

Fig. 1: Shear viscosity ξ^* for the modified LJ (12-6) model with embedded point dipole and linear quadrupole as a function of K for $\rho^* = 0.6$ at $T^* = 3.0$. Here — represents $\mu^* = 2.0$, $Q^* = 0.0$, - - - - - $\mu^* = 0.0$, $Q^* = 2.0$ and xxx denotes the LJ (12-6) model

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