



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 $\mu^* = \mu/(\epsilon\sigma^3) = 2$ 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 quadrupoles. This model is of great theoretical interest in studying the effect of the dispersive forces on the phase equilibria of polar fluid¹. 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 form². Recently, Singh and Sinha³ 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 diameter². 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 Sinha⁴ 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

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

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and ω_i represents the orientation coordinates $(\theta_i \phi_i)$ 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) potential¹.

$$u_0(r) = 4\epsilon [(\sigma/r)^{12} - K(\sigma/r)^6] \quad \dots(2)$$

where ϵ 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

$$u_a = u_{\mu\mu} + u_{\mu Q} + u_{QQ} \quad \dots(3)$$

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 by² -

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

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

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

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 as⁵ -

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

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 follow the method of Karki and Sinha⁴ and write the partition function in the form -

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

where $\Psi(r_{ij})$ is the orientation-independent 'preaveraged' potential. This effective pair potential can be expressed in the LJ(12-6) potential form³ -

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

Where

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

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

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

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 Sinha³ 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 results⁶ 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	-0.880	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

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

where

$$\xi_0 = (5/16 \pi de^2) (\pi mkT)^{1/2} \quad \dots(10)$$

$\eta = (\pi \rho de^3 / 6)$ 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 d_e is given as

$$d_e = d_B [1 + A\delta] \quad \dots(11)$$

where

$$d_B = \sigma_T [1.068 + 0.383 T_T^*] / [1 + 0.4293 T_T^*] \quad \dots(12)$$

$$\delta = [210.31 + 404.6 / T_T^*]^{-1} \quad \dots(13)$$

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

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

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

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

CONCLUSION

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

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 $\epsilon \rightarrow \epsilon_T(K, T^*)$. 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.

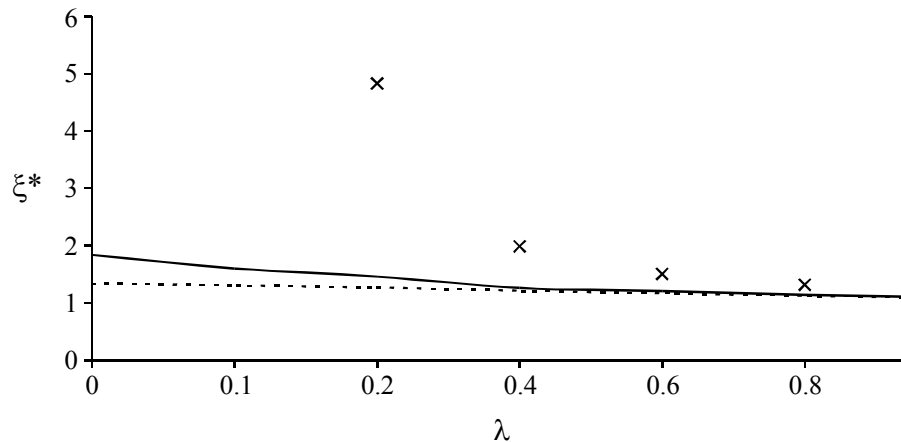


Fig. 1: Shear viscosity ξ^* for the modified LJ (12-6) model with embedded point dipole and linear quadrupole as a function of K for $\rho^* = 0.6$ at $T^* = 3.0$. Here — represents $\mu^* = 2.0$, $Q^* = 0.0$, - - - - $\mu^* = 0.0$, $Q^* = 2.0$ and xxx denotes the LJ (12-6) model

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