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ESTIMATION OF THERMAL CONDUCTIVITY OF POLAR 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 thermal conductivity λ of the modified LJ (12-6) fluid with $\mu^* = \mu/(\varepsilon\sigma^3) = 2$ and $Q^* = Q/(\varepsilon\sigma^5) = 2$ for different range of damping factor K. The thermal conductivity decreases due to the polar moments. This deviation decreases with the increase of damping factor K.

Key words: Modified Lennard – Jones fluid, Thermal conductivity, Damping factor

INTRODUCTION

The study of thermal conductivity of fluid is of great interest because of their wide spread application in many technological process. Aim of the present work is to develop a theory for estimating the thermal conductivity 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 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].

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) 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 [3] have employed the EDHST for estimating the TP's of the molecular fluid.

In the present work, we extend this approach to study the thermal conductivity 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

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

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].

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

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

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

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

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

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

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

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] -

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

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

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

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

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

Where

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

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

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

Thus, the polar fluid in the presence of the 'modified' LJ (12-6) potential can be expressed as the LJ(12-6) potential. In the following sections, we apply this theory to estimate the thermal conductivity of the modified polar LJ (12-6) fluid.

Thermal conductivity of 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[5] to predict the thermal conductivity λ, which is expressed as -

$$\lambda = [g_{HS}(de)]^{-1} [1 + (6/5)(4\eta g_{HS}(de)) + 0.7575 (4\eta g_{HS}(de))^2]\, \lambda_0 \qquad \dots(9)$$

where

$$\lambda_0 = (75k/64\, \pi\, de^2)(\pi k\, T/m)^{1/2} \qquad \dots(10)$$

$\eta = (\pi\rho de^3/6)$ 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[6] and following the method of Verlet and Weis[7]. 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[8] -

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

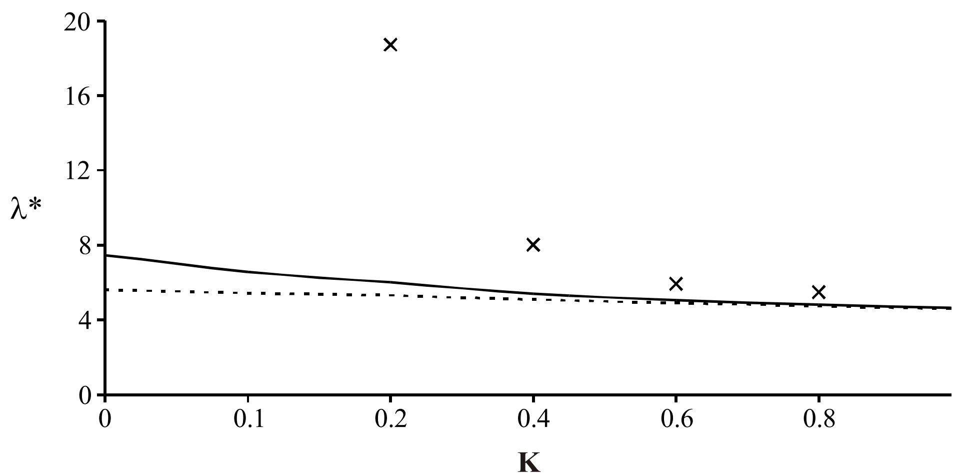

Fig. 1: Thermal conductivity λ^* for the modified LJ (12-6) model with embedded point dipole and linear quadrupole as a function of K for $\rho^* = 0.6$ at $T^* = 3.0$. Here — represents $\mu^* = 2.0$, $Q^* = 0.0$, - - - - $\mu^* = 0.0$, $Q^* = 2.0$ and xxx denotes the LJ (12-6) model

CONCLUSION

We calculate the shear viscosity ξ and thermal conductivity λ 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 $\xi^* = \xi\sigma^2 / (m\in)^{1/2}$ and $\lambda^* = \lambda\sigma^2/k\,(m\in)^{1/2}$ 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 Figs. 1 for $\rho^* = 0.6$ at $T^* = 3.0$. Thermal conductivity 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 $\in \rightarrow \in_T(K, T^*)$.

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REFERENCES

1. S. F. O'Shea, G. S. Dubey and J. G. Rasaiah, J. Chem. Phys., **1,** 10**7** (1997).
2. B. P. Karki, B. K Singh, T. K. Dey and S. K. Sinha, Indian J. Phys. **73B**, 615 (1999).
3. B. P. Karki and S. K. Sinha, Indian J. Phys., **75B**, 327 (2001).
4. C. G. Gray and K. E. Gubbins, Theory of Molecular Fluids, Vol. 1, Oxford, Clarendon (1984).
5. Tarun Kumar Dey, Indian J. Appl. Phys., **46**, 403 (2008).
6. S. K. Sinha, J. Ram and Y. Singh, Physica, **133A**, 247 (1985).
7. L. Verlet and J. J. Weis, Phys. Rev., A**5**, 939 (1972).
8. Y. Singh and S. K. Sinha, Phys. Rep., **79**, 213-325 (1981).

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