Int. J. Chem. Sci.: 7(4), 2009, 2513-2518

THEORETICAL SCHEME FOR THERMAL CONDUCTIVITY OF NON-SPHERICAL MOLECULAR FLUIDS

SATYENDRA PRASAD SINGH[a], MADAN KUMAR CHOUDHARY[b], MUKESH KUMAR SINHA and TARUN KUMAR DEY[*]

[*]Department of Physics, L. S. College, BRABU, MUZAFFARPUR – 842001 (Bihar) INDIA
[a]Department of Physics, R. V. S College of Engineering and Technology, Jharkhand, JAMSHEDPUR – 831012 (Jharkhand) INDIA
[b]Department of Physics, C. G. I. College, MUZAFFARPUR – 842001 (Bihar) INDIA

ABSTRACT

Thermal conductivity of molecular fluids of non-spherical molecules interacting via the Gaussian overlap with constant energy (GOCE) potential are studied using a perturbation theory. The thermal conductivity λ of the molecular fluid are expressed in terms of the hard sphere (HS) fluid of properly chosen hard sphere diameter. The thermal conductivity λ of a dense HS fluid are obtained by the Revised Enskog theory (RET). Theory is applied to estimate λ of fluid N_2. The agreement is good at low density limit.

Key words: Non- spherical molecules, Perturbation theory, Thermal conductivity.

INTRODUCTION

The present paper is concerned with the evaluation of thermal conductivity of molecular fluids composed of non-spherical molecules; such molecules interact via the Gaussian overlap with constant energy (GOCE) potential[1]. The complexity of all transport mechanism has made it difficult to obtain analytic results for realistic interaction potentials. Enskog expression's for the thermal conductivity of dense hard sphere (HS) gases are available[2]. Enskog theory was revised for real system and the perturbation theory[1] was used to determine the effective hard sphere diameters for the real molecular fluids.

Dey[3] employed the perturbation theory of Singh et al.[1] to determine the effective hard sphere diameter, which is a function of density ρ and temperature T, and radial distribution function (RDF) $g_{HS}(d_e)$ of the HS fluid. They used the revised Enskog theory

[*]Author for correspondence; E-mail: tkdeyphy@gmail.com

(RET) of van Beijeren and Ernst[4] to study the thermal conductivity of the molecular fluids of non-spherical molecules in terms of the HS fluid.

In the present work, we estimate the RDF $g_{HS}(d_e)$ under different approximations and extend this approach to study the thermal conductivity of the molecular fluids.

Theoretical scheme

The thermal conductivity λ of a dense hard sphere (HS) gas as a function of the number density ρ and absolute temperature T can be obtained by the revised Enskog theory (RET)[2]. They are expressed as -

$$\lambda = [g_{HS}(d_e)]^{-1}[1+(6/5)(4\eta g_{HS}(d_e)) + 0.7575(4\eta g_{HS}(d_e)^2]\lambda_0 \quad \ldots(1)$$

where

$$\lambda_0 = (75k/64\pi d_e^2)(\pi kT/m)^{1/2} \quad \ldots(2)$$

$\eta = (\pi\rho d_e^3/6)$ is the packing fraction, d_e is the hard sphere diameter and $g_{HS}(d_e)$ is the contact value of the equilibrium radial distribution function (RDF) of the HS fluid. Here m is the mass of sphere, k the Boltzmann constant and T the absolute temperature.

Thermalconductivity of non- spherical molecules

The idea is to apply the theory, a first approximation for molecular fluid of non-spherical molecules with axial symmetry, such molecules interact via the GOCE potential[1]

$$u_{GOCE}(r\omega_1\omega_2) = 4\in_0[\sigma(\omega_1\omega_2)/r)^{12} - (\sigma(\omega_1\omega_2)/r)^6] \quad \ldots(3)$$

where

$$\sigma(\omega_1\omega_2) = \sigma_2[1-\chi(\cos^2\theta_1 + \cos^2\theta_2 - 2\chi\cos\theta_1\cos\theta_{12})(1-\chi\cos^2\theta_{12})^{-1}]^{-1/2} \quad \ldots(4)$$

Here the anisotropy parameter χ is defined as

$$\chi = (K^2-1)/(K^2+1) \quad \ldots(5)$$

K being the length to width ration of a molecule i.e. K = 2a/2b.

In order to proceed, we need to determine the value of the effective hard sphere diameter d_e for each value of ρ and T using some perturbative scheme. Singh et al.[1] have divided the GOCE potential into reference and perturbation parts and the properties of the reference system are obtained in terms of the hard Gaussian overlap (HGO) system, where d_o is a function of density and temperature. For the GOCE model, $d_0^* = d_0 / \sigma_0$ is expressed as[1,5] -

$$d_0^* = d_B^* [1 + \xi \delta] \quad \dots(6)$$

where

$$d_B^* = [1.068 + 0.3837/T^*]/[1 + 0.4293T^*] \quad \dots(7)$$

$$\delta = [210.31 + 404.6 / T^*]^{-1} \quad \dots(8)$$

and

$$\xi = \frac{(2 - 7.5\eta + 0.5\eta^2 - 5.7865\eta^3 - 1.51\eta^4)}{2(1 - \eta/2)(1 - \eta)} \quad \dots(9)$$

with

$$\eta = \rho V_m = (\pi/6)\rho K d_0^3 .$$

η is the packing fraction of the HGO fluid of the reduced density $\rho^* = \rho \sigma_0^3$. We assume that the hard sphere of volume $V_m = (\pi/6) d_0^3$ is equal to that of the HGO molecule. Hence, the effective hard sphere diameter d_e is given by $d_e = K^{1/3} d_0$.

We have calculated the effective hard sphere diameter $d_e^* = d_e / \sigma_0$ for N_2 with K = 1.30 at T = 130 K and 250 K. These are reported in Table 1. It is found that d_e^* decreases with increase of density ρ and increase of T.

Then the RDF $g_{HS} = (d_e)$ is given by[5] -

$$g_{HS}(d_e) = (1 - \eta/2)/(1 - \eta) \qquad \text{(method 1)} \quad \dots(10)$$

The RDF $g_{HS}(d_e)$ can also be obtained from the compressibility factor Z_{HGO} of the

HGO fluid[3,6]

$$Z_{HGO} = 1 + 4\,\eta\,\alpha\, g_{HS}(d_e) \qquad \text{(method 2)} \qquad \ldots(11)$$

where

$$Z_{HGO} = [1 + (3\alpha - 2)\,\eta + (3\alpha^2 - 3\alpha + 2)\eta^2 - \alpha^2\,\eta^2]/(1-\eta)^3 \qquad \ldots(12)$$

and the shape factor α is defined by[6] -

$$\alpha = R\,S/3\,v_m \qquad \ldots(13)$$

Here R is the $(1/4\pi)$ multiple of the mean curvature integral, S the surface integral and v_m is the volume of the HGO molecule.

The RDF $g_{HS}(d_e)$ can be obtained from the expression of Z_{HS}. For high density regimes, we use the Pade $^{[4,3]}$ for Z_{HS} as[7] -

$$Z_{HS}^{[4,3]} = \frac{(1 + 1.024385\,\eta + 1.104537\,\eta^2 - 0.4611472\,\eta^3 - 0.74303382\,\eta^4)}{(1 - 2.975615\,\eta + 3.007000\,\eta^2 - 1.097758\,\eta^3)} \qquad \ldots(14)$$

(method 3)

The RDF $g_{HS}(d_e)$ for N_2 (K = 1.30) can be calculated using Eq. (10), (11) and (14). These are shown in Table 2 at T = 250 K and 130 K. They are in close agreement.

The thermal conductivity λ for fluid N_2 has been calculated using the RDF $g_{HS}(d_e)$ obtained under different approximations. Theoretical values agree well among themselves. However, when compared with experimental data, they are in agreement in low density regions only.

The values of thermal conductivity λ of fluid N_2 are compared in Fig. 2 at T = 130 K with the experimental data[4]. The agreement is good at low density only.

Concluding remarks

The RET has been employed to determine the thermal conductivity λ for the fluid N_2, using the values of the RDF $g_{HS}(d_e)$ under different approximations. Identical results were obtained. When compared with the experimental data, the agreement is good only at low density. By improving the expression, better results are expected at liquid density. However, it is not attempted in this case.

Table 1: Values of d_e^* for N_2 (K = 1.30) using the GOCE model

ρ (gm/cm^3)	d_e^*	
	T = 250 K	T = 130 K
0.1	1.06775	1.09689
0.2	1.06730	1.09651
0.3	1.06675	1.09651
0.4	1.06606	1.09545
0.5	1.06519	1.09467
0.6	1.06404	1.09365
0.7	1.06265	1.09229
0.8	1.06082	1.09050

Table 2: Values of RDF g_{HS} (d_e) for N_2 (K = 1.30) using the GOCE model

ρ (gm/cm^3)	g_{HS} (d_e) at T = 250 K			g_{HS} (d_e) at T = 130 K		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
0.1	1.145	1.139	1.145	1.160	1.155	1.160
0.2	1.321	1.317	1.322	1.359	1.355	1.360
0.3	1.538	1.535	1.540	1.601	1.599	1.604
0.4	1.808	1.808	1.813	1.931	1.932	1.936
0.5	2.150	2.152	2.157	2.350	2.354	2.358
0.6	2.586	2.593	2.597	2.866	2.876	2.880
0.7	3.153	3.166	3.171	3.656	3.675	3.683
0.8	3.893	3.918	3.929	4.692	4.724	4.752

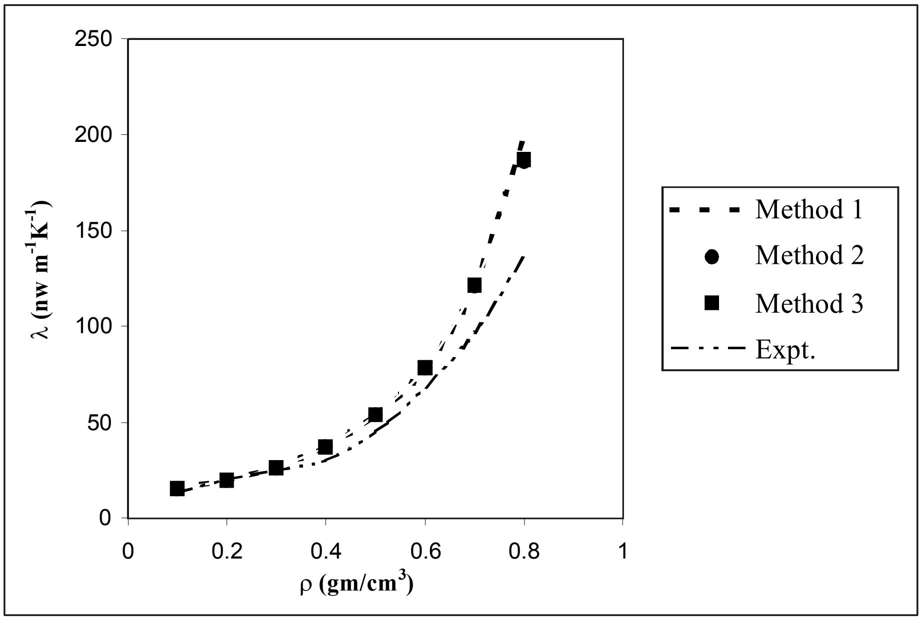

Fig. 2: The thermal conductivity λ of N_2 as a function of density ρ at T = 130 K

ACKNOWLEDGEMENT

One of us (TKD) acknowledges the financial support from the University Grants Commission, Regional Center, Kolkata .

REFERENCES

1. U. P. Singh, U. Mohanty and S. K Sinha, Mol. Phys., **68**, 1047 (1989).
2. J. R Dorfman and H. Van Beijeren, The Kinetic Theory of Gases, in Statistical Mechanics Part B, B. J. Berne, Ed. Plenum, New York (1977).
3. Tarun Kumar Dey, Indian J. Pure and Appl. Phys., **42**, 403 (2008).
4. R. Castillo and J. Orozco, Mol. Phys. **79**, 343 (1993).
5. L. Verlet and J. J. Weis, Phys. Rev., **A5**, 939 (1972).
6. T. Boublik.and I. Nezbeda, Coll. Czech. Chem. Commun., **51**, 2301 (1986).
7. M. Robles and L. I. Uruchurtu, J. Chem. Phys., **124**, 094112 (2006).

Accepted : 06.08.2009