INTRODUCTION

The study of shear viscosity of molecular fluid is of great interest in various research areas, both applied and fundamental. Several potential models have been proposed for molecular fluids of non-spherical molecules. The Gaussian overlap (GO) model of Berne and Pechukas is of current interest because it is simpler and provides analytically tractable expressions for studying non-spherical molecules via the Gaussian overlap with constant energy (GOCE) potential. Enskog expressions for transport properties (TP's) of dense hard sphere (HS) gases are available. Enskog theory was revised for real systems, and perturbation theory was used to determine the effective hard sphere diameter for the real molecular fluids.

Dey employed the perturbation theory to determine the effective hard sphere diameter and obtain expression for radial distribution function (RDF) of the hard sphere (HS) fluid. Shear viscosity of the molecular fluid are expressed in terms of the HS fluid of properly chosen hard sphere diameter. The shear viscosity \( \mu_s \) of a dense HS fluid are obtained by the Revised Enskog theory (RET). Theory is applied to calculate shear \( \mu_s \) of fluid \( \text{N}_2 \). The theory provides good results at low density limit.

Key words: Shear viscosity, radial distribution function, molecular fluid.

ABSTRACT

Using perturbation theory for the molecular fluid to determine the effective hard sphere diameter and obtain expression for radial distribution function (RDF) of the hard sphere (HS) fluid. Shear viscosity of the molecular fluid are expressed in terms of the HS fluid of properly chosen hard sphere diameter. The shear viscosity \( \mu_s \) of a dense HS fluid are obtained by the Revised Enskog theory (RET). Theory is applied to calculate shear \( \mu_s \) of fluid \( \text{N}_2 \). The theory provides good results at low density limit.

Basic theory

The transport properties (TP's) such as the shear viscosity \( \mu_s \) of a dense hard sphere (HS) gas as a function of the number density \( p \) and absolute temperature \( T \) can be obtained by the revised Enskog theory (RET). They are expressed as:

\[
\mu_s = \frac{1}{2} \eta \sigma^3 \left[ \frac{8}{3 \sqrt{3}} \langle d_e \rangle^3 \right]^{1/2} \left[ \frac{4}{5} \left( \frac{4}{3} \pi \eta g_{HS} (d_e) \right)^{1/3} \right]^{-1/2} \text{ps}^{-1} \text{atom}^{-1} \text{K}^{-1/2}.
\]

Where

\[
\eta = \frac{\pi p d_e^3}{6}
\]

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.
Shear Viscosity of Molecular Fluids

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

\[ u_{GOCE} (\omega_1, \omega_2) = 4 \xi \left[ (\omega_1 \omega_2) \psi_0^2 - \psi_0^2 \right] \tag{3} \]

Where

\[ \sigma (\omega_1, \omega_2) = \sigma_0 \left[ 1 - \chi (\cos^2 \theta_1 + \cos^2 \theta_2 - 2 \chi \cos \theta_1 \cos \theta_2) \right] \tag{4} \]

Here the anisotropy parameter \( \chi \) is defined as

\[ \chi = \frac{K^2 - 1}{K^2 + 1} \tag{5} \]

\( K \) being the length to width ratio of a molecule i.e. \( K = \frac{2a}{2b} \)

In order to proceed, we need to determine the value of the effective hard sphere diameter \( d_e \) for each value of \( p \) and \( T \) using some preservative scheme Singh et al.\(^5\) 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 of overlap (HGO) system, where \( d_o \) is a function of density and temperature. For the GOCE model, \( d^*_o = \frac{d_o}{\sigma_o} \) is expressed as\(^3\,7\).

\[ d^*_o = d^*_B \left[ 1 = \frac{\xi \delta}{\delta} \right] \tag{6} \]

Where

\[ d^*_B = \left[ 1.068 + 0.3837/T^* \right] \left[ 1 + 0.4293T^* \right] \tag{7} \]

\[ \delta = \left[ 210.31 + 404.6/T^* \right]^{-1} \tag{8} \]

\[ \xi = \frac{(2 - 7.5 \eta + 0.5 \eta^2 - 5.7865 \eta^4 - 1.51 \eta^5)}{2(1 - \eta/2)(1 - \eta)} \tag{9} \]

With

\[ \eta = \rho V_m = (\pi/6) \rho K d_0^3 \]

\( \eta \) 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 \( d_e = K^{1/3} d^*_o \).

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 2.50 K. They are reported in Table 1. It is found that \( d^*_e \) decreases with increase of density \( \eta \) and increase of \( T \).

Then the RDF \( g_{HS} (d_e) \) is given by\(^7\)

\[ g_{HS} (d_e) = (1 - \eta/2)/(1 - \eta) \] \text{(method 1)} \tag{10} \]

The RDF \( g_{HS} (d_e) \) can also be obtained from the compressibility factor \( Z_{HGO} \) of the HGO fluid\(^8\)

\[ Z_{HGO} = 1 + 4 \eta \alpha g_{HS} (d_e) \] \text{(method 2)} \tag{11} \]

Where

\[ Z_{HGO} = \frac{[1 + (3 \alpha - 2) \eta + (3 \alpha^2 - 3 \alpha + 2) \eta^2]}{1 - \eta^3} \tag{12} \]

And the shape factor \( \alpha \) is defined by\(^8\)

\[ \alpha = R S/3 \nu_m \tag{13} \]

Here \( R \) is the \((1/4\pi)\) multiple of the mean curvature integral, \( S \) the surface integral and \( \nu_m \) 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\(^3\,6\) for \( Z_{HS} \) as\(^9\)
Table 1: Values of $d^*$ for $N_2$ (K=1.30) using the GOCE model

| P (gm/cm$^3$) | T = 250K | T = 130K |
|----------------|----------|----------|
| 0.1            | 0.06775  | 1.09689  |
| 0.2            | 1.06730  | 1.09651  |
| 0.4            | 1.06675  | 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 $g_{HS}(d_o)$ for $N_2$ (K = 1.30) using the GOCE model

| P (gm/cm$^3$) | Method 1 | Method 2 | Method 3 |
|----------------|----------|----------|----------|
| 0.1            | 1.145    | 1.139    | 1.145    |
| 0.2            | 1.321    | 1.317    | 1.322    |
| 0.4            | 1.538    | 1.535    | 1.540    |
| 0.5            | 1.808    | 1.808    | 1.813    |
| 0.6            | 2.150    | 2.152    | 2.157    |
| 0.7            | 2.586    | 2.593    | 2.597    |
| 0.8            | 3.153    | 3.166    | 3.171    |

We calculate shear viscosity $\mu_s$ for fluid $N_2$ using the RDF $g_{HS}(d_o)$ obtained under different approximations. We compare the shear viscosity $\mu_s$ of fluid $N_2$ at T = 250K using the RDF $g_{HS}(d_o)$ under different methods with the experimental data in Fig. 1. Theoretical values agree well among themselves. However, when compared with experimental data, they are in agreement in low density regions only.

\[
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\]

Fig. 1: The shear viscosity $\mu_s$ of $N_2$ as a function of density $\rho$ at $T = 250K$
Concluding remarks

We have employed the RET to determine the shear viscosity $\mu_s$ for the fluid $N_2$, using the values of the RDF $g_{HH}(r)$ under different approximations. We get identical results. 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.

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