Theory for transport properties of non-spherical molecules of molecular fluids

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The transport properties of molecular fluids of non-spherical molecules via the Gaussian overlap potential with constant energy have been studied using perturbation method with a non-spherical reference system. Using Verlet-weis method, the effective diameter and radial distribution function have been derived. The theory is applied to calculate the transport properties such as shear viscosity and thermal conductivity of benzene. In all these cases, the agreement is found to be fairly good.

Keywords: Molecular fluid, Transport properties, Non-spherical molecules

1 Introduction
To study the transport properties (TP’s) of molecular fluids a considerable amount of work has been done during last decades. But, the transport properties of molecular fluids composed of non-spherical molecules are least understood. 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. The GO models considers an interaction between molecules whose repulsive parts are basically ellipsoids of revolutions. The hard Gaussian overlap (HGO) model is a useful reference system for molecular fluids of non-spherical molecules.

In the present work, we employ the effective diameter hard sphere theory (EDHST) for estimating the TP’s of some molecular fluids of non-spherical molecules.

2 Basic Theory
We assume that the structure of a dense molecular fluid is very similar to that of a hard convex body (HCB) fluid and attractive forces play a minor role in the dense fluid behaviour. The HCB fluid can be expressed in terms of hard sphere (HS) fluid of properly chosen effective hard sphere diameter \(d\). The HS fluid can be handled with the revised Enskog theory (RET) of van Beijern and Ernst to predict the TP’s such as shear viscosity \(\xi\) and thermal conductivity \(K\). They are expressed as:

\[
\xi = [\hat{g}_{hs}(d)]^{-1} \left[ 1 + (4/5)\{4\eta \hat{g}_{hs}(d)\} + 0.7615 \{4\eta \hat{g}_{hs}(d)^2\} \right] \xi_0
\]

\[
K = [\hat{g}_{hs}(d)]^{-1} \left[ 1 + (6/5)\{4\eta \hat{g}_{hs}(d)\} + 0.7575 \{4\eta \hat{g}_{hs}(d)^2\} \right] K_0
\]

where

\[
\xi_0 = (5/16\pi d^3)(\pi m k T)^{1/2}
\]

\[
K_0 = (75k/64\pi d^3)(\pi k T/m)^{1/2}
\]

\(\eta = (\pi \rho d^3/6)\) is the packing fraction (PF) and \(\hat{g}_{hs}(d)\) is the equilibrium radial distribution function (RDF) of HS fluid at the contact.

3 Reference System
The transport properties (TP’s) of non-spherical reference system can be obtained by a blip function expansion about a suitably chosen hard Gaussian Overlap (HGO) system. The HGO potential is defined as:

\[
\psi_{HGO}(r_{\omega_1\omega_2}) = \xi, \quad r < d(\omega_1\omega_2) = 0, \quad r > d(\omega_1\omega_2),
\]

where \(d(\omega_1\omega_2)\) is the distance of closest approach between two hard core molecules, \(r = |r_1 - r_2|\) is the center to center distance and \(\omega_i\) represents the orientation of molecule \(i\). We may take the expression of \(d(\omega_1\omega_2)\) given by Berne and Pechukas in terms of Euler angles:

\[
d(\omega_1\omega_2) = d_0 \left[ 1 - 3(\cos^2 \theta_1 + \cos^2 \theta_2 + 2\Xi \cos \theta_1 \cos \theta_2 \cos \theta_{12}) \right]^{-1/2}
\]

... (6)
where $\Xi = (\chi^2 - 1) / (\chi^2 + 1)$ ...

is an anisotropy parameter, $\chi$ being the shape parameter of a molecule i.e., $\chi = 2x/2y$ and $d_0 = 2y$. This model is valid for oblate ($\chi < 1$) as well as prolate ($\chi > 1$) shape of arbitrary symmetry. For $\chi = 1$, Eq. (5) reduces to the hard sphere potential for spherical molecules.

We have $V_{HGO} = \pi \sigma^3_0 \chi/6$. The effective hard sphere diameter $d$ is expressed as $d = \chi^{1/3} d_0$ and the RDF $\hat{g}_{hs}(d)$ of the HS fluid is given by:

$$\hat{g}_{hs}(d) = (1-\eta/2) / (1-\eta)^3$$ ...

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

is the PF of the HGO molecule of volume $V_m$ and density $\rho$.

The RDF $\hat{g}_{hs}(d)$ can be calculated using Eq. (8) and expressed as a function of density $\rho^* = \rho \sigma^3_0$. In this calculation, we consider $m = 1$, $kT = l$ and unit of length $l$, where $\chi = \chi d_0^2$ in Eqs (1 and 2). We apply the RET with expression of $\hat{g}_{hs}(d)$ to calculate the shear viscosity $\xi$ and thermal conductivity $K$ of HGO fluid presented in Tables 1 and 2 at different values of shape parameter $\chi$.

4 Perturbation Expansion

We consider a fluid of non-spherical molecules interacting via the Gaussian overlap with the constant energy (GOCE) model defined as:

$$\psi_{GOCE}(r_0, \omega_0) = 4 \varepsilon(\omega_0, \omega_2)[(\sigma(\omega_0, \omega_2)/r)^{12} - (\sigma(\omega_0, \omega_2)/r)^{6}]$$ ...

where

$$\varepsilon(\omega_0, \omega_2) = \varepsilon_0[1 - \Xi^2 \cos^2 \theta_{12}]^{1/2}$$ ...

$$\sigma(\omega_0, \omega_2)/\sigma_0 = d(\omega_0, \omega_2/d_0)$$ ...

For $\chi = 1$, Eq. (10) reduces to Lennard-Jones (LJ) potential for spherical molecules (Eqs 6-12).

We employ our theory to obtain the TP’s of the GOCE fluid, we divide the GOCE potential $\psi_{GOCE}$ into a reference part $\psi_0$ and perturbation part $\psi_P$ such that:

$$\psi_{GOCE}(r_0, \omega_0) = \psi_0(r_0, \omega_0) + \psi_P(r_0, \omega_0)$$ ...

Table 1 — RDF $\hat{g}_{hs}(d)$, shear viscosity $\xi$ and thermal conductivity $K$ for the HGO fluid

<table>
<thead>
<tr>
<th>$\chi$</th>
<th>$\rho^*$</th>
<th>$\hat{g}_{hs}(d)$</th>
<th>$\xi$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
<td>0.3</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3</td>
<td>3.263</td>
<td>1.224</td>
<td>4.961</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>2.444</td>
<td>0.700</td>
<td>2.928</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>1.889</td>
<td>0.419</td>
<td>1.802</td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
<td>1.1</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>4.532</td>
<td>2.212</td>
<td>8.725</td>
</tr>
<tr>
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<td>1.889</td>
<td>0.419</td>
<td>1.802</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 — Shear viscosity $\xi$ and thermal conductivity $K$ for HGO molecular fluids at $\rho^* = 0.6$ and RDF $\hat{g}_{hs}(d) = 4.532$

<table>
<thead>
<tr>
<th>$\chi$</th>
<th>Shear viscosity $\xi$</th>
<th>Thermal conductivity $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HGO MD</td>
<td>HGO MD</td>
</tr>
<tr>
<td>0.3</td>
<td>2.212 1.20</td>
<td>8.725 10.3</td>
</tr>
<tr>
<td>0.6</td>
<td>2.212 2.44</td>
<td>8.725 7.59</td>
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<tr>
<td>1.0</td>
<td>2.212 2.76</td>
<td>8.725 9.048</td>
</tr>
<tr>
<td>1.1</td>
<td>2.212 2.85</td>
<td>8.725 8.5</td>
</tr>
<tr>
<td>1.5</td>
<td>2.212 1.69</td>
<td>8.725 7.20</td>
</tr>
<tr>
<td>2.0</td>
<td>2.212 2.26</td>
<td>8.725 7.90</td>
</tr>
</tbody>
</table>

where

$$\psi_0(r_0, \omega_0) = \psi_{GOCE}(r_0, \omega_0) + \varepsilon_0, r < r_{min}(\omega_0, \omega_2),$$

$$= \psi_{GOCE}(r_0, \omega_0), r > r_{min}(\omega_0, \omega_2)$$ ...

where $r_{min}(\omega_0, \omega_2) = 2^{1/6} \varepsilon(\omega_0, \omega_2)$.

For the GOCE model, Singh et al. have given the expression for $d_0^* = d_0/\sigma_0$, as:

$$d_0^* \approx d_B^* [1 + (\sigma_{11}/2\sigma_{00})\delta]$$ ...

where

$$d_B^* = \int_0^l (1 - \exp[-\beta \psi_0(r^*)])dr^*$$ ...

and

$$\delta = \int_0^l (r^* / d_B^* - 1)^2 (d/dr^*)[\exp[-\beta \psi_0(r^*)]]dr^*$$ ...

where

$$\psi_0(r_0, \omega_0) = \psi_{GOCE}(r_0, \omega_0) + \epsilon_0, r < r_{min}(\omega_0, \omega_2),$$

$$= \psi_{GOCE}(r_0, \omega_0), r > r_{min}(\omega_0, \omega_2)$$ ...

where $r_{min}(\omega_0, \omega_2) = 2^{1/6} \epsilon(\omega_0, \omega_2)$.
σ₀₀=(1−η/2)/(1−η)³ ...(16a)

σ₁₁=[2−7.5η+0.5η²−5.78η³−1.51η⁴]/(1−η)⁴ ...(16b)

5 Application of Theory

We apply this theory to estimate the TP’s of molecular fluids of prolate (χ >1) and oblate (χ < 1) shaped molecules. We consider benzene (C₆H₆) using GOCE model potentials whose force parameters are available in literature in Refs (8,9). Then, we evaluate the shear viscosity $\xi^*$ and thermal conductivity $K^*$ at different values of shape parameter $\chi$ and density $\rho$ and compare with molecular dynamic (MD) in Tables 2 and 3. From Table 4, we find that the calculated values of shear viscosity $\xi$ and thermal conductivity $K$ are compared with the experimental data⁷,¹¹. The agreement is found to be slightly good at high temperature and decreases when temperature decreases.

6 Conclusions

We have developed a theory to calculate the TP’s of molecular fluids of non-spherical molecules interacting via GOCE potential model. In this model, we have used the simple approach to calculate the effective hard sphere diameter ($d$). Table 1 presents that RDF $g_\text{ns}(d)$ are in good agreement at low density $\rho$ or low value of shape parameter $\chi$. The deviation increases with an increase of $\rho$ or $\chi$. We have estimated the shear viscosity $\xi^*$ and thermal conductivity $K$ at different values of shape parameter $\chi$ and density $\rho$ and compare with molecular dynamic (MD) in Tables 2 and 3. From Table 4, we find that the calculated values of shear viscosity $\xi$ and thermal conductivity $K$ are compared with the experimental data⁷,¹¹. The agreement is found to be slightly good at high temperature and decreases when temperature decreases.

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