THEORETICAL SCHEME FOR TRANSPORT PROPERTIES OF LENNARD-JONES FLUID MIXTURES

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Abstract: Using Molecular dynamics to compute the transport properties of Lennard-Jones fluid mixtures using Green-Kubo formula. This formula is applied to estimate the transport properties (TP's) such as shear viscosity and thermal inductivity of Ar-Kr. The theory provides good result in low density regime where this experimental data and simulation is found very good.

Keywords: Lennard-Jones fluid mixture, Transport properties, Green-Kubo formula.

INTRODUCTION
In this present paper we concentrate on the transport properties of binary fluid mixtures at low density limit. One of the theoretical predictions based on Chapman-Enskog theory are available for comparison. In this present work we calculate the transport properties of Ar-Kr and Ar-CH₄ of Lennard-Jones fluid mixtures [1].

Basic theory: We consider a system of n₁, particles of mass m₁ and n₂ particles of mass m₂ in a volume V. They interact through a Lennard-Jones (LJ) (12-6) potential.

\[ U_{ab}(r) = 4 \varepsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r} \right)^{12} - \left( \frac{\sigma_{ab}}{r} \right)^{6} \right] \]  

(1)

where a and b are the species. The cross-interactions is expressed by the generalized mixing rules.

\[ \sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \]  

(2)

and

\[ \varepsilon_{12} = \varepsilon_{11} \varepsilon_{22}^{(1-k)} \]  

(3)

where k is a constant which is used to assess the sensitivity of physical properties to the strength of the cross-section. In terms of reduced units of LJ fluids.

Reduced temp. \[ T^* = \frac{kT}{\varepsilon_{11}} \]

Number density \[ \rho^* = \frac{N \sigma_{11}^3}{V} \]
**Transport Coefficients:** In absence of external forces and chemical reactions the transport coefficients for binary mixture of species $v = 1, 2$, can be derived from the microscopically defined fluxes of matter, $J_v$, and energy, $J_Q$. Using the notation of MacGown and Evans [2, 3, 4].

$$J_v = N_v m_v (u_v - u)/V$$  \hspace{1cm} (5)$$

$$u_v = \frac{1}{N_v m_v} \sum_j^m p_i$$  \hspace{1cm} (6)$$

and

$$u = \sum_i^m p_i / N_1 m_1 + N_2 m_2$$  \hspace{1cm} (7)$$

where $p_i$ is the particle momenta.

The heat flux employed in the transport coefficients thermal conductivity and soret (Dufour) coefficients, $J_Q$, is defined as follows

$$J_Q = J_Q' - \sum_v J_v \left[ \frac{h_v}{m_v} + \frac{1}{2} \left( \frac{J_v}{m_v \rho_v} \right)^2 \right]$$  \hspace{1cm} (8)$$

where $h_v$ is the specific partial enthalpy or species $v$. The term $h_v$ remains from the heat flux $J_Q'$.

Reduced time is in units or $\sigma_{11} (m_i / \epsilon_{11})^{1/2}$, viscosity in $(m_i \epsilon_{11})^{1/2} / \sigma_{11}^2$ and thermal conductivity in $k (m_i / \epsilon_{11})^{1/2} / \sigma_{11}^2$. The LJ (12 - 6) parameters are used in this work is represented in table 1[5].

Time correlation functions are interested numerically by Simpson's rule to obtain the transport coefficients. The enthalpy flux contributions as located with the interdiffusion of the one specie through the other.

$$J_Q = \frac{1}{2V} \sum_v \sum_{i=1}^{N_v} \left[ \left( \frac{p_i}{m_v} - u \right) m_v \left( \frac{p_i}{m_v} - u \right) + \sum_j^m \left( \frac{p_i}{m_v} - u \right) \left( \Phi_{ij} F_{ij} - Q_i q_j \right) \right]$$  \hspace{1cm} (9)$$

The momentum and position of particle $i$ and $q_i$, and $p_i$, respectively, $a_{ij}$ $F_{ij}$ is the dyad formed out of the two vectors. The species of $v$-dependent velocity ($v$) correlation function is

$$C_{v\alpha} = \frac{1}{3N_v} \sum_{i=1}^{N_v} \left( \frac{p_i (o)}{m_v} - u \right) \left( \frac{p_i (t)}{m_v} - u \right)$$  \hspace{1cm} (10)$$

The shear viscosity of the mixture is given by the following Green-Kubo relationship.

$$\eta = \frac{V}{kT} \int_0^\infty < p_{\alpha \beta}^{(o)} P_{\alpha \beta} (t) > dt$$  \hspace{1cm} (11)$$

where $P_{\alpha \beta}$ is the $\alpha \beta (\alpha \neq \beta)$ component of the pressure tensor, $P$, which is...
\[ P_{ij} = \frac{1}{V} \left( \sum_{v} \sum_{i=1}^{N_v} m_v \left[ \frac{p_{\alpha i}}{m_v} - u_i \right] \left[ \frac{p_{\beta j}}{m_v} - u_j \right] - \sum_{i=1}^{N-1} \sum_{j=1}^{N} \left( r_{ai} \frac{r_{bj}}{r_{ij}} \right) \frac{d\phi(r_{ij})}{d_r} \right) \]  

(12)

where \( r_{ai} \) is the \( \alpha \) cartesian component of \( r_{ij} \), Equation (12) is simplified in single component fluids

\[ K = \frac{v}{k_B T} \int_0^\infty <J_{Q\alpha}(0)J_{Q\alpha}(t)> dt \]  

(13)

where \( J_{Q\alpha} \) is the \( \alpha \) component of heat flux, \( J_Q \). We can calculate these components of \( k \) each determine by different time correlation function.

\[ k = k_{QQ} + k_{Qj} + k_{ij} \]  

(14)

where

\[ k_{QQ} = \frac{v}{k_B T} \int_0^\infty <J_{Q\alpha}(0)J_{Q\alpha}(t)> dt \]  

(15)

\[ k_{Qj} = \frac{2(a-b)v}{k_B T^2} \int_0^\infty <J_{Q\alpha}(0)J_{Q\alpha}(t)> dt \]  

(16)

\[ k_{ij} = \frac{(a-b)^2 v}{k_B T^2} \int_0^\infty <J_{\alpha\alpha}(0)J_{\alpha\alpha}(t)> dt \]  

(17)

making use of \( J_1 = -J_2 \). This decomposition shows clearly how the terms \( k_{Qj} \) (16) and \( k_{ij} \) (17) will disappear as \( \alpha \rightarrow \beta \), i.e. as a single component fluid is approached. Equation (17) only remains, being the m-species generalized expression for the single component fluid.

**SHEAR VISCOSITY**

The transport coefficients are presented in table 1 and compared with experimental data and kinetic theory (KT). The formula used are given as below:

The shear viscosity of the binary mixture is defined as \( \eta_{12} \). In the single one-component fluid the shear viscosity as \( \rho \rightarrow 0 \) is

\[ \eta_{11} = \frac{5}{16} \left( \frac{m_k k_B T}{\pi} \right)^{3/2} \]  

(18)

If we define the quantity, \( \eta'_{12} \)

\[ \eta'_{12} = \frac{5}{16} \left( \frac{2m m_2 k_B T / (m_1 + m_2)}{\pi \sigma_{12}^2 \Omega^{2,2}(T_{11})} \right)^{3/2} \]  

(19)

Then,

\[ \eta'_{12} = \frac{(X_n + Y_n)}{(1 + Z_n)} \]  

(20)

where

\[ X_n = \frac{x_1^2}{\eta_{11}} + \frac{2x_1 x_2}{\eta'_{12}} + \frac{x_2^2}{\eta_{22}} \]  

(21)

If,
\[ A(T_{12}^*) = \frac{\Omega^{(2,2)}(T_{12}^*)}{\Omega^{(4,1)}(T_{12}^*)}, \text{ then} \]

\[ Y_n = \frac{3}{5} A(T_{12}^*) \left( \frac{x_1^2 m_1}{\eta_1 m_2} + \frac{2 x_1 x_2 (m_1 + m_2)^2 (\eta_1^2 + \eta_2^2)}{4 m_1 m_2 \eta_1 \eta_2} + \frac{x_2^2 m_2}{\eta_2 m_1} \right) \]

\[ Z_n = \frac{3}{5} A(T_{12}^*) \left\{ \frac{x_1^2 m_1}{m_2} + \frac{2 x_1 x_2}{m_2} \left[ \frac{(m_1 + m_2)^2}{4 m_1 m_2} \left( \frac{\eta_1^2 + \eta_2^2}{\eta_1 \eta_2} \right) - 1 \right] \right\} \]

(22)

**THERMAL CONDUCTIVITY**

The one component fluid has thermal conductivity in the zero density in the zero density limit of the binary mixture is defined as \( k_{12} \).

\[ k_{11} = \frac{75}{64} \left( \frac{m_2 k_B T / \pi^{1/2}}{\sigma^2 \Omega^{(2,2)}(T_{12}^*)} \right)^2 \]

(23)

If we define the quantity, \( k_{12}^1 \).

\[ k_{12}^1 = \frac{75}{64} \left( \frac{k_B T (m_1 + m_2)/(2 m_1 m_2)^{1/2}}{\sigma^2 \Omega^{(2,2)}(T_{12}^*)} \right) \]

(24)

Then,

\[ k_{12}^{-1} = \frac{(X_k + Y_k)}{(1 + z_k)} \]

(25)

where,

\[ X_k = \frac{x_1^2}{k_{11}} + \frac{2 x_1 x_2}{k_{11}} + \frac{x_2^2}{k_{22}} \]

(26)

If

\[ B(T_{12}^*) = \frac{5 \Omega^{(1,2)}(T_{12}^*) - 4 \Omega^{(1,3)}(T_{12}^*)}{\Omega^{(1,3)}(T_{12}^*)} \]

(27)

then

\[ Y_k = \frac{x_1^2 U^{(1)}}{k_{11}} + \frac{2 x_1 x_2 U^{(2)}}{k_{11}} + \frac{x_2^2 U^{(2)}}{k_{22}} \]

(28)

\[ Z_k = x_1^2 U^{(3)} + 2 x_1 x_2 U^{(2)} + x_2^2 U^{(2)} \]

(29)

\[ U^{(1)} = \frac{4}{15} A(T_{12}^*) - \frac{1}{2} \left[ \frac{12 B(T_{12}^*)}{5 + 1} \right] m_1 + \frac{1}{2} \frac{(m_1 - m_2)^2}{m_1 m_2} \]

(30)

\[ U^{(2)} = \frac{4}{15} A(T_{12}^*) - \frac{1}{2} \left[ \frac{12 B(T_{12}^*)}{5 + 1} \right] m_2 + \frac{1}{2} \frac{(m_1 - m_2)^2}{m_1 m_2} \]

(31)
In the above expressions for the transport coefficients require a collision integral, which measures the temperature dependent collision cross-section [6, 8]. The collision integral consists of a series of three integrals, [6, 8, 9].

\[
\Omega^{(3)}(T) = \frac{1}{4\pi\sigma^2} \int (s+1)(k_B T)^{s+2} \int Q^0(E) \exp \left( - \frac{E}{k_B T} \right) E^{s+1} dE
\]

an integral over \( l, \)

\[
Q'(E) = 2\pi \left( 1 - \frac{1}{2} \left( 1 + (-1)^l \right) \right)^{-1} \int_0^\pi (1 - \cos \theta) \beta \delta \alpha.
\]

where, \( \beta = \) Impact parameter
\( X = \) Scattering angle
\( E = \frac{1}{2} \mu v^2 = \) kinetic energy
\( \mu = \frac{m_1 m_2}{m_1 + m_2} = \) reduced mass
\( v = \) Initial relative velocity between the particles.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \frac{m_1}{u} )</th>
<th>( \varepsilon_{11/\kappa} / k )</th>
<th>( \sigma_{11/\text{nm}} )</th>
<th>( m_i )</th>
<th>( \varepsilon_{11} )</th>
<th>( \sigma_{11} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(^a)</td>
<td>39.95</td>
<td>119.8</td>
<td>0.3405</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Kr(^a)</td>
<td>83.90</td>
<td>167.0</td>
<td>0.3633</td>
<td>2.0976</td>
<td>1.340</td>
<td>1.06696</td>
</tr>
<tr>
<td>( CH_4 )^a</td>
<td>16.04</td>
<td>152.0</td>
<td>0.374</td>
<td>0.4015</td>
<td>1.26874</td>
<td>1.09838</td>
</tr>
</tbody>
</table>
### Table 2. Shear viscosity $\eta$ and $k$ of equimolar binary mixture at $\rho \to 0$.

<table>
<thead>
<tr>
<th>System</th>
<th>T</th>
<th>Theory</th>
<th>Expt.</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar – Kr</td>
<td>1.81</td>
<td>0.210</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>2.49</td>
<td>0.270</td>
<td>0.278</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>8.347</td>
<td>0.595</td>
<td></td>
<td>0.63</td>
</tr>
</tbody>
</table>

### Table 3. Thermal conductivity $k$ of equimolar binary mixtures at $\rho \to 0$.

<table>
<thead>
<tr>
<th>System</th>
<th>T</th>
<th>Theory</th>
<th>Expt.</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
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<td>1.81</td>
<td>0.5295</td>
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<td>0.63</td>
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<tr>
<td></td>
<td>2.49</td>
<td>0.681</td>
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<td>0.75</td>
</tr>
<tr>
<td></td>
<td>8.347</td>
<td>1.492</td>
<td></td>
<td>1.92</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

The shear viscosity and thermal conductivity of Ar-Kr is estimated in table 2 and 3 where the simulation and theoretical results are found good. The experimental value for shear viscosity is agreed with estimated value.

### REFERENCES