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-CH_4 of Lennard-Jones fluid mixtures [1].

Basic theory : We consider a system of n_1, particles of mass m_1 and n_2 particles of mass m_2 in a volume V. They interact through a Lennard-Jones (LJ) (12-6) potential.

$$U_{ab}(r)=4\in_{ab}\left[\left(\frac{\sigma_{ab}}{r}\right)^{12}-\left(\frac{\sigma_{ab}}{r}\right)^{6}\right] \quad (1)$$

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

$$\sigma_{12}=(\sigma_{11}+\sigma_{22})/2 \quad (2)$$

and

$$\in_{12}=\in_{11}^{k}\in_{22}^{(1-k)} \quad (3)$$

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. $T^*=kT/\in_{11}$

Number density $\rho^*=N\sigma_{11}^{3}/v$

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].

$$J_v = N_v m_v (u_v - u)/V \quad (5)$$

$$u_v = \frac{1}{N_v m_v} \sum_i^{n_v} p_i \quad (6)$$

and

$$u = \sum_i^n p_i \Big/ N_1 m_1 + N_2 m_2 \quad (7)$$

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

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

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 $\sigma_{11}\left(m_1 \big/ \in_{11} \right)^{1/2}$, viscosity in $(m_1 \in_{11})^{1/2} / \sigma_{11}^2$ and thermal conductivity in $k\left(m_1 \big/ \in_{11} \right)^{-1/2} / \sigma_{11}^2$. 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 species through the other.

$$J_{Q'} = \frac{1}{2V} \sum_v \sum_{i=1}^{N_v} \left[\left(\frac{p_i}{m_v} - u\right) m_v \left(\frac{p_i}{m_v} - u\right)^2 + \sum_j \left(\frac{p_i}{m_v} - u\right) . \left(\Phi_{ij} I - Q_{ij} F_{ij}\right) \right] \quad (9)$$

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

$$C_{v0} = \frac{1}{3N_v} \sum_{i=1}^{N_v} \left(\frac{p_i(o)}{m_v} - u \right) . \left(\frac{p_i(t)}{m_v} - u \right) \quad (10)$$

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

$$\eta = \frac{V}{kT} \int_0^\infty < p_{\alpha\beta}^{(0)} p_{\alpha\beta}(t) > dt \quad (11)$$

where $P_{\alpha\beta}$ is the $\alpha\beta(\alpha \neq \beta)$ component of the pressure tensor, P, which is

$$P_{\alpha\beta} = \frac{1}{V}\left(\sum_{v}\sum_{i=1}^{N_v} m_v\left[\frac{p_{\alpha i}}{m_v} - u_v\right]\left[\frac{p_{\beta i}}{m_v} - u_\beta\right] - \sum_{i=1}^{N-1}\sum_{j>i}^{N}\left(r_{\alpha ij}\frac{r_{\beta ij}}{r_{ij}}\right)\frac{d\phi(r_{ij})}{d_r}\right) \quad (12)$$

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

$$K = \frac{v}{k_b T^2}\int_0^\infty < J_{Q\alpha}(0) J_{Q\alpha}(t) > dt \quad (13)$$

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

$$k = k_{q'Q'} + k_{Q'j} + k_{jj} \quad (14)$$

where

$$k_{q'Q'} = \frac{v}{k_B T^2}\int_0^\infty < J_{Q'\alpha}(0) J_{Q'\alpha}(t) > dt \quad (15)$$

$$k_{q'j} = \frac{2(a-b)v}{k_B T^2}\int_0^\infty < J_{Q'\alpha}(0) J_{'\alpha}(t) > dt \quad (16)$$

$$k_{jj} = \frac{(a-b)^2 v}{k_B T^2}\int_0^\infty < J_{'\alpha}(0) J_{'\alpha}(t) > dt \quad (17)$$

making use of $J_1 = -J_2$. This decomposition shows clearly how the terms $k_{Q'j}$ (16) and k_{jj} (17) will disappear as $\alpha \to \beta$. 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 η_{12}. In the single one - component fluid the shear viscosity as $\rho \to 0$ is

$$\eta_{11} = \frac{5}{16}\left(\frac{(m_1 k_B T/\pi)^{1/2}}{\sigma^2 \Omega^{(2,2)}(T_{11}^*)}\right) \quad (18)$$

If we define the quantity, η'_{12}

$$\eta'_{12} = \frac{5}{16}\left(\frac{[2\pi m_1 m_2 k_B T/(m_1+m_2)]^{1/2}}{\pi\sigma_{12}^2 \Omega^{(2,2)}(T_{11}^*)}\right) \quad (19)$$

Then,

$$\eta'_{12} = \frac{(X_n + Y_n)}{(1+Z_n)} \quad (20)$$

where

$$X_n = \frac{x_1^2}{\eta_{11}} + \frac{2x_1x_2}{\eta'_{12}} + \frac{x_2^2}{\eta_{22}} \quad (21)$$

If,

$A(T_{12}^{*})=\frac{\Omega^{(2,2)}(T_{12}^{*})}{\Omega^{(41)}(T_{12}^{*})}$, then

$$Y_n=\frac{3}{5}A(T_{12}^{*})\left(\frac{x_1^2 m_1}{\eta_{11}m_2}+\frac{2x_1x_2(m_1+m_2)^2(\eta_{12}^{1})^2}{4m_1m_2\eta_{12}^{'}\eta_{11}\eta_{22}}+\frac{x_2^2m_2}{\eta_{22}m_1}\right)$$

$$Z_n=\frac{3}{5}A(T_{12}^{*})\left\{\frac{x_1^2m_1}{m_2}+2x_1x_2\frac{\left[(m_1+m_2)^2\left(\frac{\eta_{12}^2}{\eta_{11}}+\frac{\eta_{12}^2}{\eta_2}\right)-1\right]}{4m_1m_2+\frac{x_2^2m_2}{m_1}}\right\} \quad (22)$$

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}.

$$k_{11}=\frac{75}{64}\left(\frac{(m_1k_B^3T/\pi)^{1/2}}{\sigma^2m_1\Omega^{(2/2)}(T_{11}^{*})}\right) \quad (23)$$

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

$$k_{12}^{1}=\frac{75}{64}\left(\frac{k_B^3T(m_1+m_2)/(2\pi m_1m_2)^{1/2}}{\sigma^2\Omega^{(2/2)}(T_{12}^{\ *})}\right) \quad (24)$$

Then,

$$k_{12}^{-1}=\frac{(X_k+Y_k)}{(1+z_k)} \quad (25)$$

where,

$$X_k=\frac{x_1^2}{k_{11}}+\frac{2x_1x_2}{k_{11}'}+\frac{x_2^2}{k_{22}} \quad (26)$$

If

$$B(T_{12}^{*})=\frac{5\Omega^{(1,2)}(T_{12}^{*})-4\Omega^{(1,3)}(T_{12}^{*})}{\Omega^{(1,1)}(T_{12}^{*})} \quad (27)$$

then

$$Y_k=\frac{x_1^2U^{(1)}}{k_{11}}+\frac{2x_1x_2U^{(Y)}}{k_{11}'}+\frac{x_2^2U^{(2)}}{k_{22}} \quad (28)$$

$$Z_k=x_1^2U^{(1)}+2x_1x_2U^{(Z)}+x_2^2U^{(2)} \quad (29)$$

$$U^{(1)}=\frac{4}{15}A(T_{12}^{*})-\frac{1}{2}\frac{\left[12B(T_{12}^{*})15+1\right]m_1}{m_2}+\frac{1}{2}\frac{(m_1-m_2)^2}{m_1m_2} \quad (30)$$

$$U^{(2)}=\frac{4}{15}A(T_{12}^{*})-\frac{1}{2}\frac{\left[12B(T_{12}^{*})/5+1\right]m_2}{m_1}+\frac{1}{2}\frac{(m_1-m_2)^2}{m_1m_2} \quad (31)$$

$$U^{(y)} = \frac{4}{15}A\left(T_{12}^{*}\right)\left[\left(\frac{(m_1+m_2)^2}{4m_1m_2}\right)\left(\frac{(k_{12}^{'})^2}{k_{11}k_{12}}\right) - \frac{1}{12}\left(\frac{12}{5}B\left(T_{12}^{*}\right)/5+1\right)\right]$$

$$-\frac{5}{32A\left(T_{12}^{*}\right)}\frac{\left(\frac{12}{5}B\left(T_{12}^{*}\right)-5\right)(m_1-m_2)^2}{m_1m_2} \qquad (32)$$

$$U^{(Z)} = \frac{4}{15}A\left(T_{12}^{*}\right)\left[\left(\frac{(m_1+m_2)^2}{4m_1m_2}\right)\left(\frac{k_{12}^{'}}{k_{11}}+\frac{k_{12}^{'}}{k_{12}}-1\right) - \frac{1}{12}\left(\frac{12}{5}B\left(T_{12}^{*}\right)+1\right)\right] \qquad (33)$$

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].

$$\Omega^{(l,s)}(T) = \frac{1}{\pi\sigma^2}\left[(s+1)!(k_BT)^{s+2}\right]^{-1}\int_0^x Q^{(i)}(E)\exp.\left(-\frac{E}{k_BT}\right)E^{s+1}dE \qquad (34)$$

an integral over l,

$$Q^{l}(E) = 2\pi\left(1-\frac{1}{2}\frac{(1+(-1))^l}{l+1}\right)^{-1}\int_0^x(1-\cos'\theta)\beta\delta\alpha. \qquad (35)$$

where, β = Impact parameter

X = Scattering angle

$E = \frac{1}{2}\mu v^2$ = kinetic energy

$\mu = \frac{m_1m_2}{m_1+m_2}$ = reduced mass

v = Initial relative velocity between the particles.

Table 1. Molecular fluid parameters for the LJ molecules.

Molecule	m_1/u	$\in_{11/k}/k$	$\sigma_{11/nm}$	m_1^*	$\in_{11}^*$	σ_{11}^*
Ar[a]	39.95	119.8	0.3405	1	1	1
Kr[a]	83.90	167.0	0.3633	2.0976	1.340	1.06696
CH_4^a	16.04	152.0	0.374	0.4015	1.26874	1.09838

Table 2. Shear viscosity η and *k* of equimolar binary mixture at $\rho \to 0$.

System	T	Theory	Expt.	Simulation
Ar – Kr	1.81	0.210		0.22
	2.49	0.270	0.278	0.27
	8.347	0.595		0.63

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

System	T	Theory	Expt.	Simulation
Ar – Kr	1.81	0.5295		0.63
	2.49	0.681		0.75
	8.347	1.492		1.92

CONCLUSIONS

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

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