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Research Note

Non-Equilibrium Molecular Dynamics Simulation of Thermal Diffusion Effect

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In this paper, a Non-Equilibrium Molecular Dynamics (NEMD) method is used to calculate the thermal diffusion factor, α_T, for a binary mixture interacting via the Lennard-Jones potential. The α_T is obtained for Ar-Kr and Ar-Xe mixtures from the temperature and concentration gradients in the simulation box containing 108 particles. The reduced temperature range for this simulation is $1.0 \leq T^* \leq 3.0$.

INTRODUCTION

Thermal diffusion is caused by the relative motion of the components of a mixture due to the presence of a temperature gradient. By virtue of this motion, concentration gradient appears in the mixture and an ordinary diffusion is produced to eliminate this gradient. Steady-state is finally reached, in which the separating effect arising from thermal diffusion is balanced by the remixing effect of ordinary diffusion. Partial separation is then observed with heavy components mostly in the colder region and the light components in the hotter region. This phenomenon is known as the thermal diffusion or Soret effect, which was first discovered in liquids by Ludwig and later by Soret [1]. The Soret effect can be quantified by thermal diffusion factor α_T, which is defined as the relative concentration gradient divided by the relative temperature gradient [2-4]. Thermal diffusion factor is a convenient measure of the separation of components 1 and 2 caused by the temperature gradient. The degree of separation typically increases with increasing temperature. When the system behaves in this manner, α_T has a positive value, in which the heavier particles tend to be in the colder region and lighter particles in the hotter region. In a few systems, light species enrich in the cold region and then α_T decreases in magnitude with increasing temperature ($\alpha_T < 0$) [5].

Thermal diffusion is a relatively weak coupling phenomenon [6,7]. There are however, situations in which thermal diffusion is a dominant transport process, e.g., in isotope separation. Kinetic theory predicts that the thermal diffusion factor depends on the fluid density, temperature and mass ratio of components and also is very sensitive to the form of the intermolecular potential function and their measurements are thus a precise test for intermolecular potential [2,8].

In this paper, a Non-Equilibrium Molecular Dynamics (NEMD) algorithm has been used for direct calculation of the thermal diffusion factor. The Ar-Kr and Ar-Xe mixtures with mass ratios ~ 2 and ~ 3 were chosen for the simulations, hence the effect of mass ratio on thermal diffusion factor can be observed.

HEAT AND MASS FLUX IN A BINARY MIXTURE

The irreversible thermodynamics gives the entropy production per unit volume and unit time for a two-component mixture subject to temperature and composition gradients as:

$$\sigma = -\mathbf{J_q}.\frac{\nabla T}{T^2} - \mathbf{J_1}.\nabla\left[\frac{\mu_1 - \mu_2}{T}\right], \qquad (1)$$

where $\mathbf{J_q}$ and $\mathbf{J_l}$ are the heat and mass flux, T and ∇T are the temperature and temperature gradient, respectively and μ_k is the specific chemical potential of species k.

In a binary mixture when $\sum_i \mathbf{J}_i = 0$ and $\sum_i x_i = 1$, the following expression can be written:

$$\sigma = -\mathbf{J_q}.\frac{\nabla T}{T^2} - \frac{1}{T}\left[\frac{\partial(\mu_1 - \mu_2)}{\partial x_1}\right]\mathbf{J_1}.\nabla x_1, \qquad (2)$$

where x_i is the mole fraction of species i. In the linear region, when the fluxes and forces are small,

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the independent fluxes are a linear combination of the forces, i.e,

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - L_{q1}\frac{\nabla(\mu_1 - \mu_2)}{T}, \tag{3a}$$

$$\mathbf{J}_1 = -L_{1q}\frac{\nabla T}{T^2} - L_{11}\frac{\nabla(\mu_1 - \mu_2)}{T}, \tag{3b}$$

where L_{ij} are Onsager's phenomenological coefficients. For thermal diffusion effect, after some manipulation of Equations 3 at the stationary state, when the mass flux of each species is zero, the thermal diffusion factor, α_T, of a binary mixture is defined as [4]:

$$\alpha_T = -\frac{T}{x_1 x_2}\left(\frac{\nabla x_1}{\nabla T}\right)_{J_1=0} \tag{4}$$

Equation 4 is the straight way to calculate α_T by computer simulation as well as experimental method.

Up to now, there were two categories of molecular dynamic simulation methods, namely Non-Equilibrium Molecular Dynamics (NEMD) and Equilibrium Molecular Dynamics (EMD), which have been used to determine the transport coefficients [9-11]. An alternative way, which is considerably different, was introduced for calculation of thermal diffusion coefficient by Kincaid et al. [12] and then was improved by Hafskjold et al. [13,14]. The Kincaid approach has been used in this paper which is described in the next section.

COMPUTER SIMULATION ALGORITHM

The stochastic boundary conditions are used to establish a non-equilibrium steady-state in which the mass fluxes are zero, but temperature and composition gradients in the X-direction are non-zero. NEMD is applied to calculate α_T. A direct computation of ∇T and ∇x_i at steady-state, using Equation 4, leads to an estimation of α_T. ∇x_1 is determined by computing a linear least-square fit of the linear part of x_1, in which two or three points of each side are eliminated and the derivative of it is evaluated. A similar procedure has been used to determine ∇T. A system of 108 particles, enclosed in a cubic cell of each side L and fluid reduced density of $N^* = N\sigma^3/L^3 = 0.40$ are assumed, where N is density number.

Two systems, Ar-Kr and Ar-Xe, were modeled as Lennard-Jones fluids so that the intermolecular potential energy is given by:

$$\phi(r) = 4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}, \tag{5}$$

where ε and σ are the energy minimum and zero point of Lennard-Jones interaction, respectively. The potential is cut at r_c that is in our case $r_c = 2\sigma$.

There is a mixture of N_1 particles of heavier species (Kr or Xe) and N_2 particles of lighter species (Ar). The equation of motion of these particles in this algorithm is as follows:

$$m_i d^2\mathbf{r}_i/dt = \mathbf{F}_i, \tag{6}$$

where m_i is the mass of a particle of species i and $\mathbf{F}_i$ representing the total force on particle i. This equation of motion is solved starting from an initial set of positions and velocities. Periodic boundary conditions are used in the Y and Z directions, but not in the X direction. To have zero mass flux in the steady-state, the fuzzy-wall [10,12] boundary conditions are used.

The fuzzy-wall boundary conditions prevent particles from passing through the primary cell faces perpendicular to the X-axis. By changing the kinetic energy of reflected particle from fuzzy-wall, the temperature gradient is achieved in the cell as will be described in the next paragraph. The boundaries at $r_x = 0$ and $r_x = L$ have the local temperature T_L (low-temperature) and T_H (high-temperature), respectively. Any particle of species i that is reflected off the fuzzy-wall at $r_x = 0$ is given new velocity component v_x, v_y and v_z. The components v_y and v_z are generated randomly from Maxwell-Boltzmann velocity distribution at the temperature T_L, but $v_x(> 0)$ is randomly sampled from the Maxwell-Boltzmann flux distribution at the temperature T_L, whose probability density function can be written as:

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left[\frac{-mv_x^2}{2k_B T}\right], \tag{7}$$

where k_B is the Boltzmann constant. At $r_x = L$ the same procedure is used, but T_L is replaced by T_H and $v_x < 0$. The lack of periodic boundary condition in the X-direction caused a failure in energy conservation, but after long time intervals both kinetic and potential energies show stationary values. Once the stationary state has been reached, temperature T and mole fractions of species 1 and 2 (x_1 and x_2) can be computed. In X-direction, Equation 4 can be written as:

$$\alpha_T = -\frac{T}{x_1 x_2}\left[\frac{(dx_1/dr_x)}{(dT/dr_x)}\right]_{J_1=0} \tag{8}$$

In this work the quantities are defined as the reduced form in Molecular Dynamic (MD) units, which have been marked with a small triangle (△) and Lennard-Jones (LJ) units, which have been marked with an asterisk (*). For example [13]:

$$\rho^{\triangle} = \rho^*\left[\frac{L}{\sigma}\right]^3 = \rho^* L^{*3}, \tag{9a}$$

$$T^{\triangle} = \frac{k_B T}{\varepsilon} = T^*. \tag{9b}$$

Table 1. Reduced quantities used in this work.

Quantity	Lennard-Jones Units	Molecular Dynamics Units
Density	$\rho^* = (N/V)\sigma^3$	$\rho^\triangle = \rho^*(L_x^*)^3$
Temperature	$T^* = k_B T/\varepsilon$	$T^\triangle = T^*$
Mass	$m^* = m/m_1$	$m^\triangle = m^*$
Time	$t^* = \frac{t}{\sigma}(\frac{\varepsilon}{m_1})^{1/2}$	$t^\triangle = t^*/L_x^*$
Length	$r^* = r/\sigma$	$r^\triangle = r^*/L_x^*$
Velocity	$v^* = v(m_1/\varepsilon)^{1/2}$	$v^\triangle = v^*$
Mass flux	$J_k^* = J_k \frac{\sigma^3}{m_1}(\frac{m_1}{\varepsilon})^{1/2}$	$J_k^\triangle = J_k^*$

The various reduced quantities are listed in Table 1. In the present work the equations of motion are solved in each time step and the phase space trajectory of the system is then determined. Runs with about 200,000 time steps were used in both cases, where each time step was 0.005 $(m_1\sigma^3/\varepsilon)^{1/2}$ and σ, ε are the Lennard-Jones potential parameters. The MD cell was divided into $n = 7$ layers of equal width, perpendicular to the X-axis and the derived properties, i.e., composition and temperature of each layer, were recorded. The average physical quantities obtained for each sample, included at $N = 100$ time step, were saved. Lastly, using central limit theorem, the mean value of all samples was calculated. The first K samples that depend on each run for reduction at transient effect, were discarded. Each run has been carried out for 10^5 up to 3×10^5 time steps on a simulation box containing $N = 180$, $N/2$ of each component. The fluctuation in α_T is reduced with continuation of time steps (Figure 1) which is a good criterion for steady-state. At the beginning of simulation if the temperature drift was observed, the velocities were scaled in each time step to conserve the total momentum and to maintain the temperature. In each layer the temperature gradient is given by:

$$\frac{3}{2}Nk_BT = \frac{1}{2}\sum_{i\in\text{layer}}^{N_L} m_i(\mathbf{v_1} - \mathbf{v_2})^2, \tag{10}$$

where N_L is the number of particles in each layer. The mass flux of component k is:

$$\mathbf{J_k} = \frac{1}{V}\sum_i m_i(\mathbf{v_i} - \mathbf{v}), \tag{11}$$

where the summation is over all particles of species k in control volume.

RESULTS AND DISCUSSION

The equimolar Ar-Kr and Ar-Xe mixtures with total reduced density of $\rho^\bullet = 0.40$ modeled by LJ potential function were studied. The temperatures of boundaries are maintained at $T_L^\triangle = 1.0$ and $T_H^\triangle = 0.30$. In each layer, the mole fraction and temperature gradients are calculated and α_T can then be estimated from Equation 4. The average value for α_T over all layers was calculated.

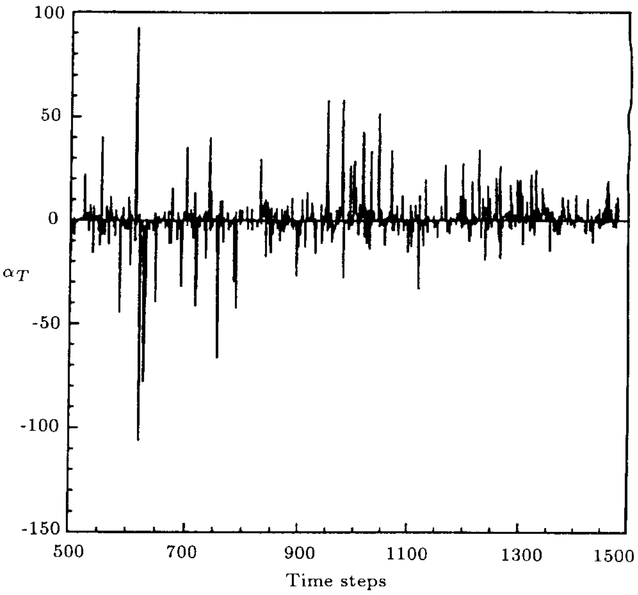

Figure 1. The fluctuation in α_T as a function of time step. On X-axis each unit equals to 100 time steps.

Table 2 gives a comparison of the thermal diffusion factor obtained from this work and from literature data. Our result for Ar/Kr system agrees with HEX algorithm computed by Hafskjold et al. [13] within the statistical uncertainty, but there is no thermal diffusion data for Ar/Xe mixture from the simulation techniques. Unfortunately, there are no experimental data for thermal diffusion factor of Ar/Kr and Ar/Xe at moderate and high densities (selected reduced density of this work, $\rho^\bullet = 0.40$, equals to density 1.16 g/cm^3 for Ar/Kr and 1.627 g/cm^3 for Ar/Xe). For obtaining thermal diffusion factor of dense gases, one can use the Enskog kinetic theory which

Table 2. Calculated thermal diffusion factor compared with literature values. Data are with $\rho^* = 0.4$, $T_L^* = 1.0$ and $T_H^* = 0.3$ for both mixtures and potential parameters for Ar-Kr mixture are $\sigma(\AA) = 3.285$, $\varepsilon/k_B(K) = 192$ and, for Ar-Xe mixture are $\sigma(\AA) = 3.662$, $\varepsilon/k_B(K) = 223$.

Mixture	α_T from **This Work**	α_T from **[13]**	α_T from **Enskog Theory**
Ar-Kr	1.24 ± 0.08	1.5 ± 0.1	1.02
Ar-Xe	1.40 ± 0.12	-	1.17

needs the equation of state data [15]. In Table 2 the values of α_T obtained from the Enskog correlate high-pressure thermal diffusion data are also shown for comparison purposes. The discrepancy between the found values of Ar/Kr and Ar/Xe systems from the present calculation and the thermal diffusion factor obtained from Enskog method may be due to the rigid sphere assumption of the Enskog theory. The simulation was not performed on different system sizes other than 108 particles, since α_T is not significantly dependent on system size for $N \geq 256$ [12]. However, NEMD has little size dependence above 100 molecules [9,11].

Figures 2 and 3 show the variation of temperature and mole fraction of Ar-Xe mixture along the simulation cell. It can be seen that temperature and mole fraction graphs show a little curvature in the middle of the curves, where the light component (Ar) has a tendency to the warmer region and heavy component (Kr or Xe) to the colder region, which agree with α_T sign (> 0) for these mixtures.

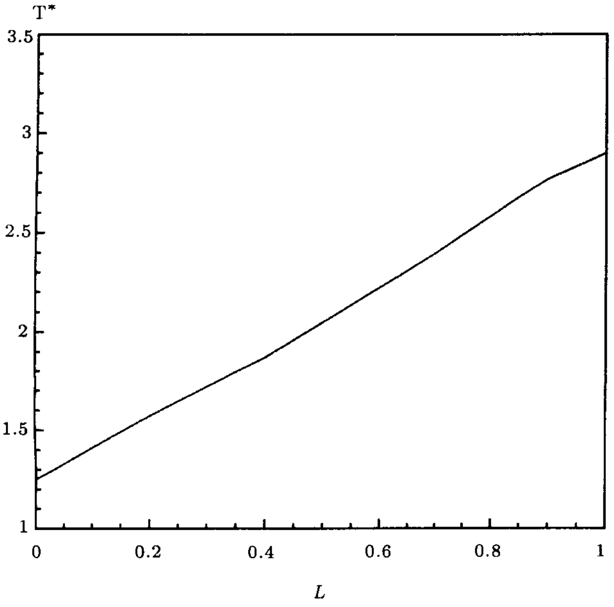

Figure 2. The variation of reduced temperature $T^* = k_B$ T/e along the simulation cell for Ar-Xe mixture.

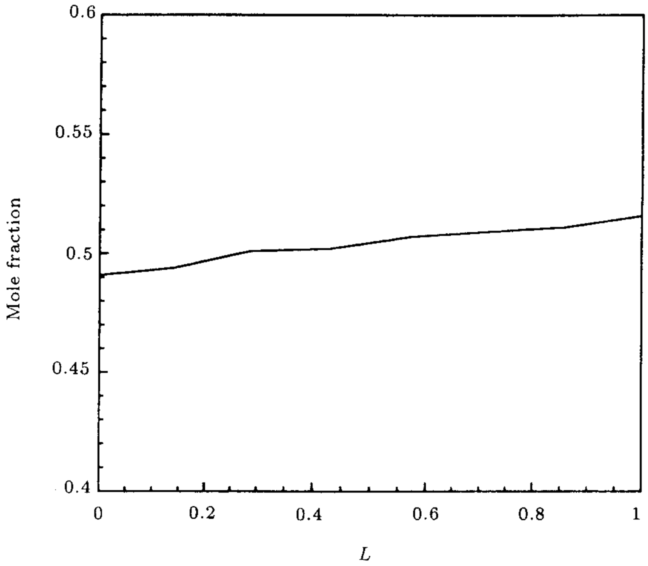

Figure 3. The variation of mole fraction of Ar along the simulation cell for Ar-Xe mixture.

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