

## Molecular Dynamics Simulation Study of Transport Properties of Diatomic Gases

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Received May 16, 2014, Accepted August 17, 2014

In this paper, we report thermodynamic and transport properties (diffusion coefficient, viscosity, and thermal conductivity) of diatomic gases ( $H_2$ ,  $N_2$ ,  $O_2$ , and  $Cl_2$ ) at 273.15 K and 1.00 atm by performing molecular dynamics simulations using Lennard-Jones intermolecular potential and modified Green-Kubo formulas. The results of self-diffusion coefficients of diatomic gases obtained from velocity auto-correlation functions by Green-Kubo relation are in good agreement with those obtained from mean square displacements by Einstein relation. While the results for viscosities of diatomic gases obtained from stress auto-correlation functions underestimate the experimental results, those for thermal conductivities obtained from heat flux auto-correlation functions overestimate the experimental data except  $H_2$ .

**Key Words** : Molecular dynamics simulation, Diffusion, Viscosity, Thermal conductivity, Diatomic gases

### Introduction

Molecular dynamics (MD) simulation is an effective supplement method to experiment. MD methods involve the solution of the equations of motion for a system of molecules that interact with each other through an intermolecular potential.<sup>1</sup> For this reason, MD has been widely employed in various areas, chemistry, biology, physics, engineering, and cancer research on studying the structural, functional and dynamic properties of molecular systems from microscopic to macroscopic models. MD methods provide both static (thermodynamic and structural) and dynamic (transport) properties, since they compute trajectories of a specified number of particles or dynamics using averages over time and particles. The system is generally considered to be of cubical shape, which makes it easier to implement periodic boundary conditions.<sup>2</sup> It assigns the total number of particles (atoms or molecules), density, which provides the system volume, and a temperature.

Molecular dynamics simulation adopts a classical approach in the molecular modeling and the intermolecular potential. In order to calculate the position and velocity of each molecule in the system every time step, the force on each of the molecule is required. These forces are derived from the intermolecular potentials. Transport coefficients can be computed either by the use of Green-Kubo formulas and Einstein relations during equilibrium molecular dynamics (EMD) simulations,<sup>3</sup> or by conducting non-equilibrium molecular dynamics (NEMD) simulations.<sup>4</sup> The aim of this study is to calculate the transport properties of diatomic gases,  $H_2$ ,  $N_2$ ,  $O_2$ , and  $Cl_2$ , using the Green-Kubo formulas through MD simulation.

To the best of our knowledge this study is the first computational effort for the transport properties (diffusion, viscosity, and thermal conductivity) of real diatomic gases at

273.15 K and 1 atm. Previously MD simulation studies were performed for the calculation of transport properties for an ideal model of diatomic molecule on the effect of the elongation of diatomic molecule by us.<sup>5,6</sup>

### Green-Kubo Formulas

Translational diffusion constant ( $D_t$ ) is evaluated by two different ways: the Green-Kubo formula that is the integral of velocity auto-correlation functions (VAC):

$$D_t = \frac{1}{3} \int_0^\infty \langle v_i(t) \cdot v_i(0) \rangle dt. \quad (1)$$

Alternatively, the Einstein formula evaluates  $D_t$  as the long-time limit of the slope of mean-square displacement (MSD):

$$D_t = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d \langle |r_i(t) - r_i(0)|^2 \rangle}{dt}. \quad (2)$$

The contribution to diffusion by rotational motion of diatomic molecule is represented by rotational diffusion constant<sup>5,6</sup>:

$$D_r = \frac{l^2}{2} \int_0^\infty \langle w_i(t) \cdot w_i(0) \rangle dt \quad (3)$$

and

$$D_r = \frac{l^2}{4} \lim_{t \rightarrow \infty} \frac{d \langle |e_i(t) - e_i(0)|^2 \rangle}{dt}. \quad (4)$$

Here  $w_i(t)$  and  $e_i(t)$  are the angular velocity and the unit orientation vector of diatomic molecule  $i$ , respectively. The denominators of 2 and 4 in Eqs. (3) and (4) are due to 2 degrees of freedom of rotational motion of diatomic molecule.

The shear viscosity is given a revised Green-Kubo formula for better statistical accuracy<sup>7</sup>:

$$\eta_t = \frac{V}{k_B T} \int_0^\infty dt \sum_i \langle P'_{i\alpha\beta}(0) P'_{i\alpha\beta}(t) \rangle, \quad (5)$$

where

$$P'_{i\alpha\beta}(t) = \frac{1}{V} \left[ m v_{i\alpha}(t) v_{i\beta}(t) + \sum_{j \neq i} r_{ij\alpha}(t) f_{ij\beta}(t) \right] \quad (6)$$

with  $\alpha\beta = xy, xz, yx, yz, zx,$  and  $zy$ .

Similarly thermal conductivity is calculated by a revised Green-Kubo formula for better statistical accuracy<sup>7</sup>:

$$\lambda = \frac{V}{k T^2} \int_0^\infty dt \sum_i \langle \dot{q}_{i\alpha}(0) \dot{q}_{i\alpha}(t) \rangle, \quad (7)$$

where  $\alpha = x, y,$  and  $z,$  and the total heat flux by molecule  $i$  is

$$\dot{q}_{i\alpha}(t) = \frac{1}{V} \left\{ \varepsilon_i(t) v_{i\alpha}(t) + \frac{1}{2} \sum_{j \neq i} r_{ij\alpha}(t) [v_j(t) \cdot f_{ij}(t) + \omega_i^p(t) \cdot N_{ij}^p(t)] \right\}. \quad (8)$$

Here  $N_{ij}$  is the torque exerted on molecule  $i$  by molecule  $j,$  and the superscript  $p$  indicates the principle axis frame. The total energy of molecule  $i$  is given by the sum of the translational, rotational and potential energies:

$$\varepsilon_i(t) = \frac{1}{2} m_i v_i(t)^2 + \frac{1}{2} I \omega_i(t)^2 + \frac{1}{2} \sum_{j \neq i} \Phi[r_{ij}(t)], \quad (9)$$

where  $I$  is moment of inertia and  $\Phi(r_{ij})$  denotes the potential energy between molecules  $i$  and  $j$  at time  $t.$

In our MD simulations, four diatomic molecules in gas phase,  $H_2, N_2, O_2,$  and  $Cl_2,$  are considered at  $T = 273.15$  K and  $p = 1.00$  atm as two centered Lennard-Jones (LJ) potential.<sup>8</sup> The total interaction is a sum of pairwise contributions from distinct atoms  $a$  in molecule  $i$  at position  $r_{ia},$  and  $b$  in molecule  $j$  at position  $r_{jb}$  as follows:

$$u_{ij}(r_{ij}) = \sum_{a=1}^2 \sum_{b=1}^2 u_{ab}(r_{ab}), \quad (10)$$

where  $r_{ab}$  is the inter-site separation  $r_{ab} = |r_{ia} - r_{jb}|$  and  $u_{ab}$  is the pair potential acting between sites  $a$  and  $b:$

$$u_{ab}(r_{ab}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ab}} \right)^{12} - \left( \frac{\sigma}{r_{ab}} \right)^6 \right] \quad (11)$$

Here  $\varepsilon_d$  and  $\sigma_d$  are the Lennard-Jones (LJ) parameters for each site of the diatomic molecule. The values of  $\sigma_d$ (nm) and  $\varepsilon_d/k_B$ (K) for the gases are shown in Table 1.

## Molecular Models and Molecular Dynamics Simulation

The MD simulation begins with collection of molecules,  $N = 1728$  molecules, in a cubic box of length  $L = 40.072, 40.057, 40.066,$  and  $40.067$  nm for  $H_2, N_2, O_2,$  and  $Cl_2,$  respectively, which are obtained from density ( $\rho_m$ )<sup>9</sup> and molecular mass ( $M$ ). Nosé-Hoover thermostat<sup>10,11</sup> is used to keep the temperature constant (the Nosé-Hoover thermostat relaxation constant is given as  $Q = 10 f k_B$  with  $f$  as the number of degrees of freedom). The usual periodic boundary condition is applied in the  $x-, y-,$  and  $z-$ directions, and the minimum image convention for pair potential were applied. The potential is truncated at 8.0 nm for all molecules, which is the cut-off distance in many MD simulations for the LJ potential. Long-range corrections are applied to the energy, pressure, and *etc.* due to the potential truncation.<sup>12</sup> The equation of translational motion was solved using a velocity Verlet algorithm<sup>13</sup> for NVT-fixed MD simulations with the determined volumes from the density of each system.<sup>9</sup> The time step was chosen as  $10^{-14}$  second for the systems of  $N_2, O_2,$  and  $Cl_2,$  and  $0.25 \times 10^{-14}$  second for that of  $H_2.$  The diatomic molecules are assumed as a rigid body with fixed inter-nuclear distances,  $d,$  as shown in Table 1. A quaternion formulation<sup>14,15</sup> is employed to solve the equations of rotational motion about the center of mass of rigid diatomic molecule. The configurations of the diatomic gases are stored every 10 time steps (40 for  $H_2$ ) for further analysis. The systems are fully equilibrated and the equilibrium properties are averaged over three blocks of 400,000 time steps for the systems of gaseous  $N_2, O_2, Cl_2$  and  $H_2.$

## Results and Discussion

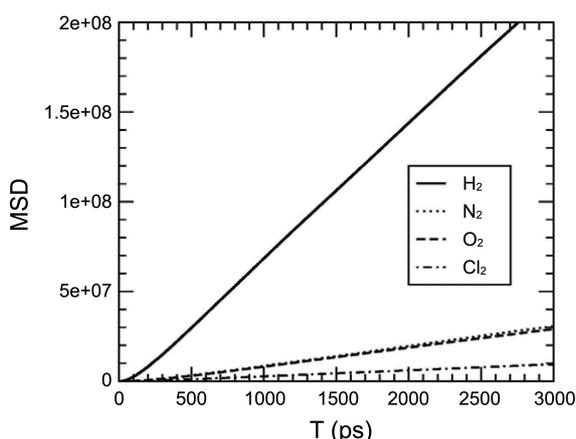
The values of  $(M/\rho_m)$  calculated from the length of the simulation box  $L$  (40.072, 40.057, 40.066, and 40.067 nm for  $H_2, N_2, O_2$  and  $Cl_2,$  respectively) are given in Table 1 which are almost the same as Avogadro's hypothesis (22.414 l/mol). Pressures,  $p$ (atm), obtained from NVT-fixed MD simulations are also given in Table 1. The obtained compressibility factor ( $Z = pV/RT$ ) for  $H_2, N_2, O_2$  and  $Cl_2$  at 273.15 K and 1 atm are 1.0018, 0.9996, 0.9994, and 0.9858, respectively. As agreed with the experimental trend,  $Z(H_2)$  is larger than,  $Z(N_2)$  and  $Z(O_2)$  are smaller than, and  $Z(Cl_2)$  is much smaller than the unity at 1 atm.

Energetic properties for diatomic molecules at 273.15 K and 1 atm obtained from our MD simulations are shown in

**Table 1.** Lennard-Jones parameters, and  $\rho_m$  at 273.15 K and 1 atm,  $M,$  and  $d$  are density, molecular mass, and inter-nuclear distance, respectively

Gases	LJ parameters <sup>a</sup>		$\rho_m$ (kg/m <sup>3</sup> )	$M/\rho_m$ (l/mol)	$d^b$ (nm)	P (atm) NVT	-E <sub>LJ</sub> (kJ/mol)	E <sub>total</sub> (kJ/mol)
	$\sigma_d$ (nm)	$\varepsilon_d/k_B$ (K)						
H <sub>2</sub>	0.281	8.6	0.0899	22.424	0.074	1.0013	0.0005	5.6772
N <sub>2</sub>	0.331	61.6	1.2506	22.400	0.110	1.0002	0.0067	5.6710
O <sub>2</sub>	0.295	37.3	1.4276	22.414	0.121	0.9994	0.0089	5.6688
Cl <sub>2</sub>	0.335	173.5	3.1632	22.416	0.199	0.9857	0.0592	5.6185

<sup>a</sup>Ref. 18. <sup>b</sup>Ref. 19 for H<sub>2</sub>, Ref. 20 for N<sub>2</sub>, Ref. 21 for O<sub>2</sub>, and Ref. 22 for Cl<sub>2</sub>.

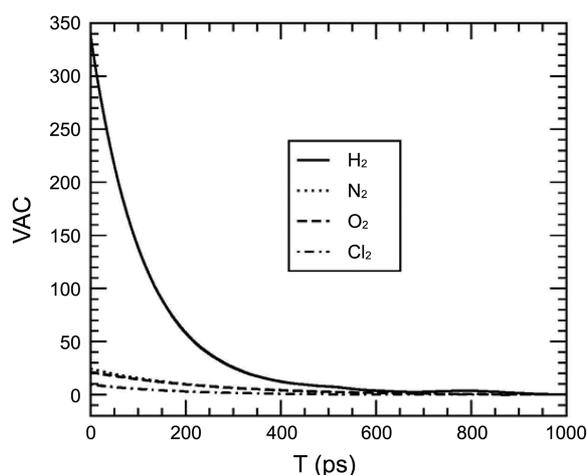


**Figure 1.** Mean square displacements (MSD, Å<sup>2</sup>) of diatomic gases at 273.15 K and 1.00 atm.

Table 1. The Lennard-Jones (LJ) potential of each system is negligibly small compared to the total energy, which reflects that the most portion of the total energy is the kinetic energy. The LJ energy for the system of gaseous H<sub>2</sub> is almost zero, those for N<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub> increase negatively with increasing inter-nuclear distance. The sum of the translational and rotational (2 degrees of freedom) kinetic energy is exactly  $\frac{5}{2}RT = 5.6777$  kJ/mol, and total energy decreases slightly with increasing inter-nuclear distance.

Mean square displacements (MSD) and velocity auto-correlation (VAC) of the diatomic gases at 273.15 K and 1 atm are plotted in Figures 1 and 2. The behaviors of MSD and VAC are remarkably different from those of diatomic liquid at 78.2 K and 1 atm.<sup>16</sup> While the mean square displacement (MSD) of diatomic liquid shows a linear behavior within 3 ps, the MSD of diatomic gas increases nonlinearly over 200 ps and shows a straight line between 500 and 3000 ps (Fig. 1). The velocity auto-correlation (VAC) function also shows a dramatic difference. The VAC of diatomic liquid decays to 0 within 0.5 ps and has a negative value due to the collision with the neighboring particle,<sup>16</sup> but the VAC of diatomic gas decays very slowly to 0 over 1000 ps (Fig. 2). MSD and VAC of diatomic gases are very similar to those of noble gases.<sup>17</sup>

Diffusion coefficients of the diatomic gases,  $D_r$ , at 273.15 and 1 atm obtained from MSD's using Eq. (1) and VAC's using Eq. (2) are listed in Table 2 and those are in good agreement each other. As expected,  $D_r$  decreases with increasing molecular mass. Unfortunately the experimental



**Figure 2.** Velocity auto-correlation (VAC, (10 Å/ps)<sup>2</sup>) functions of diatomic gases at 273.15 K and 1.00 atm.

measures for  $D_r$  of diatomic gases are hardly found in the literature except N<sub>2</sub>. The agreement for  $D_r$  of N<sub>2</sub> obtained from MSD and VAC with the experimental result is excellent as shown in Table 2 and from this observation it could be expected that the agreement of  $D_r$  is good for the other diatomic gases.

MD simulation result for  $D_r$  of gaseous N<sub>2</sub> and O<sub>2</sub> is order of  $\sim 0.18$  cm<sup>2</sup>/s which is much larger than those of liquid N<sub>2</sub> and O<sub>2</sub> ( $1.7\sim 3.2 \times 10^{-5}$  cm<sup>2</sup>/s)<sup>16</sup> at 78.2 K. These diffusion coefficients of diatomic molecules are consistent with those for gaseous argon (0.16 cm<sup>2</sup>/s)<sup>17</sup> at 273.15 K and liquid argon ( $2.4 \times 10^{-5}$  cm<sup>2</sup>/s)<sup>7</sup> at 94.4 K.

In order to calculate the rotational diffusion coefficient,  $D_r$ , one may rewrite Eq. (3) as

$$D_r = \frac{I^2}{2} \langle w^2 \rangle \int_0^\infty \frac{\langle w_i(t) \cdot w_i(0) \rangle}{\langle w_i(0) \cdot w_i(0) \rangle} dt. \quad (12)$$

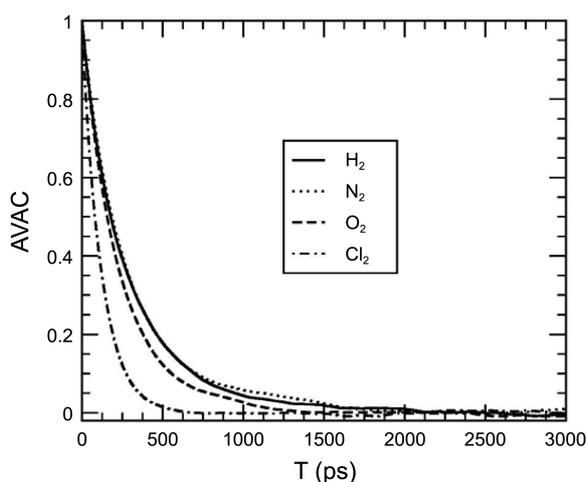
We plot the normalized angular velocity auto-correlation functions for H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub> in Figure 3, which decrease exponentially to zero around 1000-2000 ps. Since the rotational temperature,  $RT_r = Iw^2/2N$  ( $R$ : gas constant), is a constant and the inertia of momentum for diatomic molecules is given by  $I = 2m/(1/2)^2 = m^2/2$ ,  $I^2 \langle w^2 \rangle / 2 = 2RT_r / mN$  is equal to  $0.938 \times 10^6$  cm<sup>2</sup>/s<sup>2</sup> for N<sub>2</sub>. Here  $dt$  is 0.1 ps and the value of integral is calculated as  $3.01 \times 10^{-10}$  s. Hence the order of  $D_r$  is  $10^{-3}$  cm<sup>2</sup>/s, which is negligibly small compared to  $D_r$ .

In Einstein formula, Eq. (4), the mean square displace-

**Table 2.** Comparison of diffusion coefficients, viscosities, and thermal conductivities of diatomic gases at T = 273.15 K and 1.00 atm from NVT-fixed MD simulations with experiment. Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis

Gases	$D_r$ (cm <sup>2</sup> /s)		$\eta_t$ ( $\mu$ P)		$\lambda$ (J/m·s·K)	
	MSD/VAC	Exp. <sup>a</sup>	SAC	Exp. <sup>b</sup>	HFAC	Exp. <sup>b</sup>
H <sub>2</sub>	1.246(0)/1.316(0)	–	73.3(0)	84.0	0.0748(0)	0.168
N <sub>2</sub>	0.185(2)/0.183(5)	0.18	136(4)	166	0.0309(8)	0.0240
O <sub>2</sub>	0.178(2)/0.173(3)	–	145(6)	191	0.0295(5)	0.0245
Cl <sub>2</sub>	0.057(2)/0.056(1)	–	105(5)	125	0.0103(4)	0.0079

<sup>a</sup>Ref.23 and <sup>b</sup>Ref.24.



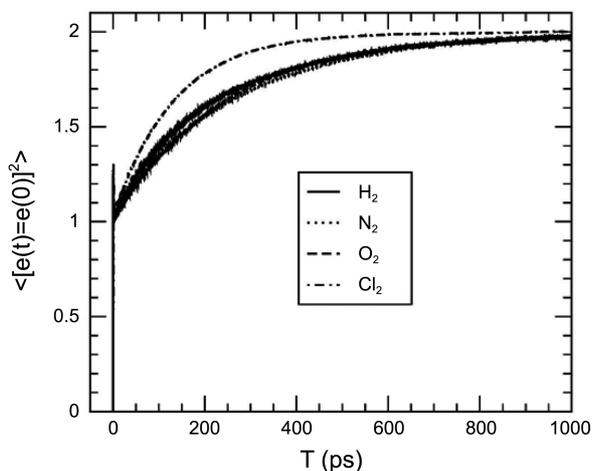
**Figure 3.** Normalized angular velocity auto-correlation (AVAC) functions of diatomic gases at 273.15 K and 1.00 atm.

ments of unit orientation vector  $e_i(t)$  are not a linear function of time as seen in Figure 4 because the value of  $e_i(t)$  is unit. As a result, we were not able to calculate the rotational diffusion coefficients from Eq. (4). The value of the mean square displacements of unit orientation vector approaches to 2 as time goes infinity since in the following equation:

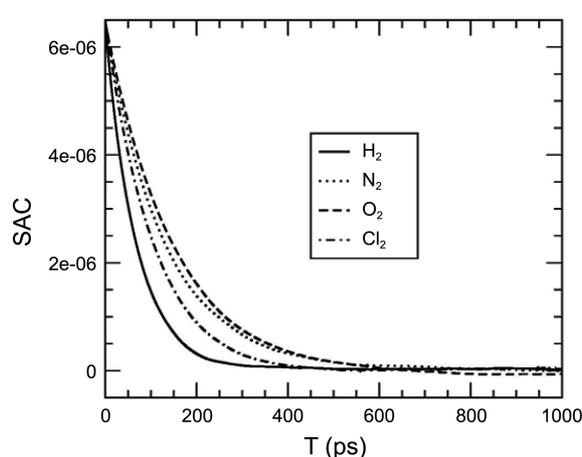
$$\begin{aligned} \lim_{t \rightarrow \infty} \langle |e_i(t) - e_i(0)|^2 \rangle &= \lim_{t \rightarrow \infty} [\langle |e_i(t)|^2 \rangle + \langle |e_i(0)|^2 \rangle - 2\langle e_i(t) \cdot e_i(0) \rangle] \\ &= 2 - 2 \lim_{t \rightarrow \infty} \langle e_i(t) \cdot e_i(0) \rangle \end{aligned} \quad (13)$$

The second term in the last equation goes zero as time goes infinity.

Stress auto-correlation (SAC) and heat-flux auto-correlation (HFAC) functions of the diatomic gases at 273.15 K and 1atm are presented in Figures 5 and 6. One can see that SAC functions monotonically fast decrease and decay very slowly to zero around 600-1000 (ps). In Figure 5, the curve of HFAC for H<sub>2</sub> shows only a rapid fall until 200 ps, the two curves of HFAC for N<sub>2</sub> and O<sub>2</sub> are hardly distinguishable



**Figure 4.** Mean square displacements of unit orientation vector at 273.15 K and 1.00 atm.

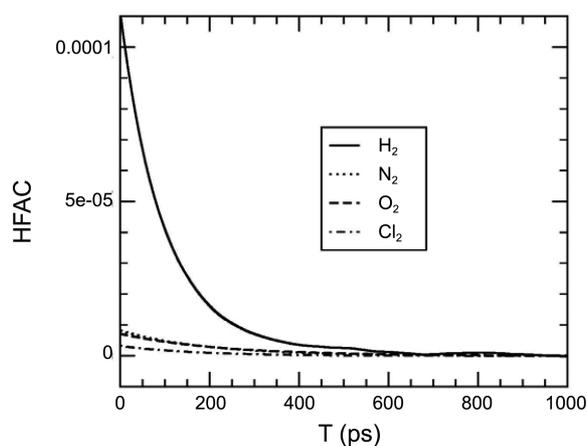


**Figure 5.** Stress auto-correlation (SAC, (J/mol·Å<sup>3</sup>)<sup>2</sup>) functions of diatomic gases at 273.15 K and 1.00 atm.

over entire time steps, and the curve for Cl<sub>2</sub> presents the lowest value close to 0. This behavior of SAC and HFAC of diatomic gas is completely different from that of diatomic liquid at 78.2 K which undergoes a decrease-increase in the short time and decay to zero in 4-10 ps.

Shear viscosities by translational motions calculated from our MD simulations are listed in Table 2. The viscosities ( $\eta_t$ ) of diatomic gases show close results with the experimental data with relative errors,  $(\eta_{MD} - \eta_{Exp})/\eta_{Exp} = -12.7, -18.1, -24.1,$  and  $-16.0\%$  for H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub>, respectively. The results for viscosity of diatomic gases estimated from SAC functions underestimate the experimental results. In comparison with the results for viscosity of diatomic liquid from MD simulation,<sup>16</sup>  $\eta$  of gaseous N<sub>2</sub> and O<sub>2</sub> (170-190  $\mu$ P) is much smaller than those of liquid N<sub>2</sub> and O<sub>2</sub> (1600-2900  $\mu$ P)<sup>16</sup> at 78.2 K. These viscosities of diatomic molecules are consistent with those for gaseous argon (210  $\mu$ P)<sup>17</sup> at 273.15 K and liquid argon (3100  $\mu$ P)<sup>7</sup> at 94.4 K.

Thermal conductivities by translational and rotational motions calculated from our MD simulations are also listed in Table 2. The relative errors to the experimental data,  $(\lambda_{MD} - \lambda_{Exp})/\lambda_{Exp}$ , are  $-55.5, 28.8, 20.4$  and  $30.4\%$  for H<sub>2</sub>, N<sub>2</sub>,



**Figure 6.** Heat-flux auto-correlation (HFAC, (10 J/mol·Å<sup>2</sup>·ps)<sup>2</sup>) functions of diatomic gases at 273.15 K and 1.00 atm.

O<sub>2</sub>, and Cl<sub>2</sub>, respectively. The results for thermal conductivity of diatomic gases estimated from HFAC functions overestimate the experimental results except H<sub>2</sub>. This disagreement might be related to the intermolecular LJ parameters for diatomic gases in very low density. MD simulation results for viscosities and thermal conductivities of diatomic gases are hardly found in the literature. Comparing with the results for thermal conductivity of diatomic liquid from MD simulation,<sup>16</sup>  $\lambda$  of gaseous N<sub>2</sub> and O<sub>2</sub> (0.024 J/m·s·K) is much smaller than those of liquid N<sub>2</sub> and O<sub>2</sub> (0.15 J/m·s·K)<sup>16</sup> at 78.2 K. The thermal conductivities for gaseous argon at 273.15 K and for liquid argon at 94.4 K from MD simulations are 0.016 J/m·s·K<sup>17</sup> and 0.065 J/m·s·K,<sup>7</sup> respectively.

### Conclusion

We have performed molecular dynamics simulations of diatomic gases (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub>) in order to calculate transport properties at 273.15 K and 1.00 atm. Translational diffusion coefficients of N<sub>2</sub> obtained from velocity auto-correlation functions (VAC) by Green-Kubo relation and from mean square displacements (MSD) by Einstein relation are in good agreement with the experimental measure. Rotational diffusion coefficients ( $D_r$ ) obtained from the angular velocity auto-correlation functions (AVAC) for diatomic gases are negligibly small compared to  $D_r$ . The viscosities of diatomic molecules show close results with the experimental data with acceptable relative errors. Thermal conductivities also show good agreement with the experimental data except H<sub>2</sub>. Overall, the difference between the results from our MD simulations and the experimental ones of the viscosities and thermal conductivities is not more than 30% relative error except H<sub>2</sub> in thermal conductivity. However, we note that the results for viscosities and thermal conductivities of diatomic gases at 273.15 K and 1.00 atm obtained from our MD simulations show insufficient agreement with the experimental data. This can be at least partly attributed to the accuracy of the MD simulation algorithm or

simulation settings such as intermolecular LJ parameters for diatomic gases.

**Acknowledgments.** This research was supported by Kyungshung University Research Grants in 2014 for SHL.

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