MD Simulation of Diatomic Gases

Bull. Korean Chem. Soc. **2014**, Vol. 35, No. 12   3527

Molecular Dynamics Simulation Study of Transport Properties of Diatomic Gases

Song Hi Lee and Jahun Kim[*]

*Department of Chemistry, Kyungsung University, Busan 608-736, Korea. *E-mail: jhkim7@ks.ac.kr*

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.[1] 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.[2] 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,[3] or by conducting non-equilibrium molecular dynamics (NEMD) simulations.[4] 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.[5,6]

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):

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

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

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

The contribution to diffusion by rotational motion of diatomic molecule is represented by rotational diffusion constant[5,6]:

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

and

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

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[7]:

Jahun Kim and Song Hi Lee

$$\eta_t = \frac{V}{k_B T} \int_0^\infty dt \sum_i \langle P^t_{i\alpha\beta}(0) P^t_{i\alpha\beta}(t) \rangle, \tag{5}$$

where

$$P^t_{i\alpha\beta}(t) = \frac{1}{V}\left[m v_{i\alpha}(t) v_{i\beta}(t) + \sum_{j\neq i} r_{ij\alpha}(t) f_{ij\beta}(t) \right] \tag{6}$$

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[7]:

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

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

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

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:

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

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.[8] 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:

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

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:

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

Here ε_d and σ_d are the Lennard-Jones (LJ) parameters for each site of the diatomic molecule. The values of σ_d(nm) and ε_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 (ρ_m)[9] and molecular mass (M). Nosé-Hoover thermostat[10,11] 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.[12] The equation of translational motion was solved using a velocity Verlet algorithm[13] for NVT-fixed MD simulations with the determined volumes from the density of each system.[9] The time step was chosen as 10^{-14} second for the systems of N_2, O_2, and Cl_2, and 0.25×10^{-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[14,15] 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/ρ_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 Avogardo'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, 09996, 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 ρ_m at 273.15 K and 1 atm, M, and d are density, molecular mass, and inter-nuclear distance, respectively

Gases	LJ parameters[a]		ρ_m (kg/m³)	M/ρ_m (l/mol)	d[b] (nm)	P (atm) NVT	$-E_{LJ}$ (kJ/mol)	E_{total} (kJ/mol)
	σ_d (nm)	ε_d/k_B (K)						
H_2	0.281	8.6	0.0899	22.424	0.074	1.0013	0.0005	5.6772
N_2	0.331	61.6	1.2506	22.400	0.110	1.0002	0.0067	5.6710
O_2	0.295	37.3	1.4276	22.414	0.121	0.9994	0.0089	5.6688
Cl_2	0.335	173.5	3.1632	22.416	0.199	0.9857	0.0592	5.6185

[a]Ref. 18. [b]Ref. 19 for H_2, Ref. 20 for N_2, Ref. 21 for O_2, and Ref. 22 for Cl_2.
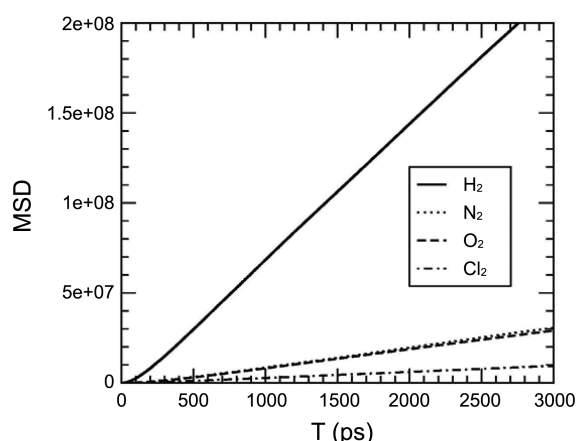
Figure 1. Mean square displacements (MSD, Å^2) of diatomic gases at 273.15 K and 1.00 atm.

Figure 2. Velocity auto-correlation (VAC, $(10 \text{ Å/ps})^2$) functions 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_2 is almost zero, those for N_2, O_2, and Cl_2 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.[16] 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,[16] 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.[17]

Diffusion coefficients of the diatomic gases, D_t, 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_t decreases with increasing molecular mass. Unfortunately the experimental
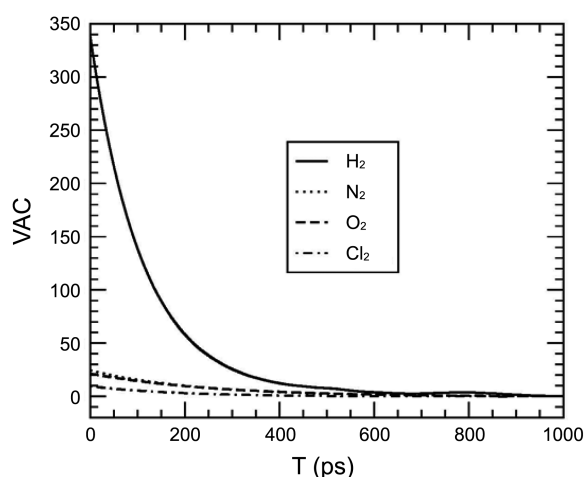
measures for D_t of diatomic gases are hardly found in the literature except N_2. The agreement for D_t of N_2 obtained from MSD and VAC with the experimental result is excellent as shown in Table 2 and from this observation it could be expected that the agreement of D_t is good for the other diatomic gases.

MD simulation result for D_t of gaseous N_2 and O_2 is order of ~0.18 cm^2/s which is much larger than those of liquid N_2 and O_2 (1.7~3.2 × 10^{-5} cm^2/s)[16] at 78.2 K. These diffusion coefficients of diatomic molecules are consistent with those for gaseous argon (0.16 cm^2/s)[17] at 273.15 K and liquid argon (2.4 × 10^{-5} cm^2/s)[7] at 94.4 K.

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

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

We plot the normalized angular velocity auto-correlation functions for H_2, N_2, O_2, and Cl_2 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 $I = 2m/(l/2)^2 = ml^2/2$, $l^2\langle w^2\rangle/2 = 2RT_r/mN$ is equal to 0.938×10^6 cm^2/s^2 for N_2. Here dt is 0.1 ps and the value of integral is calculated as 3.01×10^{-10} s. Hence the order of D_r is 10^{-3} cm^2/s, which is negligibly small compared to D_t.

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

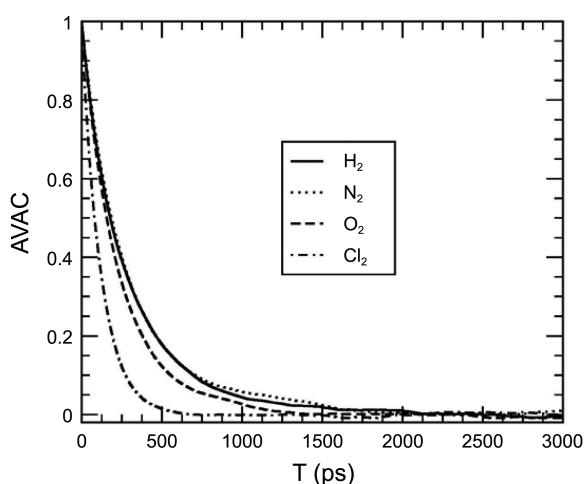| Gases	D_t (cm^2/s)		η_t (μP)		λ (J/m·s·K)	
	MSD/VAC	Exp.[a]	SAC	Exp.[b]	HFAC	Exp.[b]
H_2	1.246(0)/1.316(0)	–	73.3(0)	84.0	0.0748(0)	0.168
N_2	0.185(2)/0.183(5)	0.18	136(4)	166	0.0309(8)	0.0240
O_2	0.178(2)/0.173(3)	–	145(6)	191	0.0295(5)	0.0245
Cl_2	0.057(2)/0.056(1)	–	105(5)	125	0.0103(4)	0.0079

[a]Ref.23 and [b]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:

$$\lim_{t \to \infty} \langle |e_i(t) - e_i(0)|^2 \rangle = \lim_{t \to \infty} [\langle |e_i(t)|^2 \rangle + \langle |e_i(0)|^2 \rangle - 2\langle |e_i(t) \cdot e_i(0)|^2 \rangle]$$

$$= 2 - 2 \lim_{t \to \infty} \langle |e_i(t) \cdot e_i(0)| \rangle \qquad (13)$$

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_2 shows only a rapid fall until 200 ps, the two curves of HFAC for N_2 and O_2 are hardly distinguishable

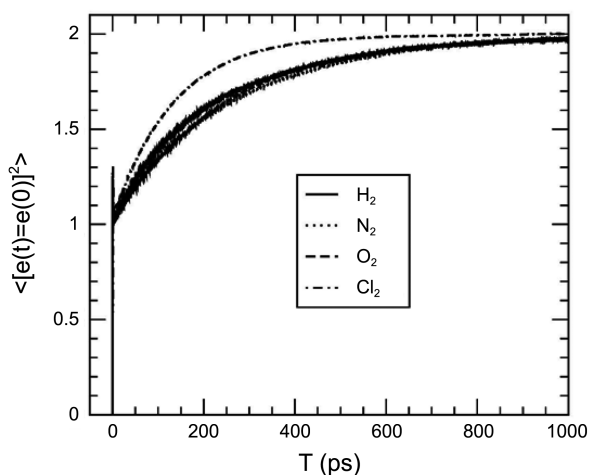**Figure 4.** Mean square displacements of unit orientation vector at 273.15 K and 1.00 atm.
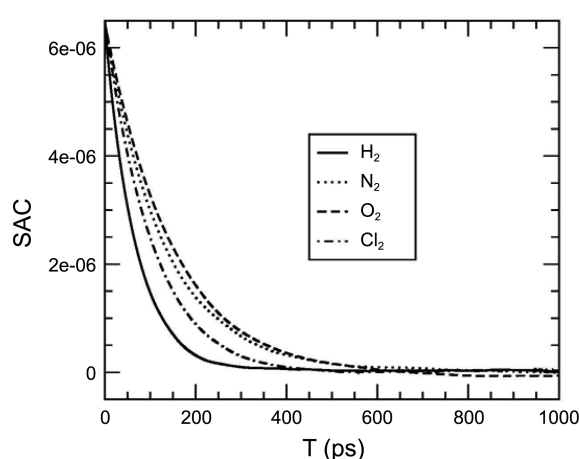

Figure 5. Stress auto-correlation (SAC, (J/mol·Å^3)^2) functions of diatomic gases at 273.15 K and 1.00 atm.

over entire time steps, and the curve for Cl_2 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 (η_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_2, N_2, O_2, and Cl_2, 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,[16] η of gaseous N_2 and O_2 (170-190 μP) is much smaller than those of liquid N_2 and O_2 (1600-2900 μP)[16] at 78.2 K. These viscosities of diatomic molecules are consistent with those for gaseous argon (210 μP)[17] at 273.15 K and liquid argon (3100 μP)[7] 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_2, N_2,
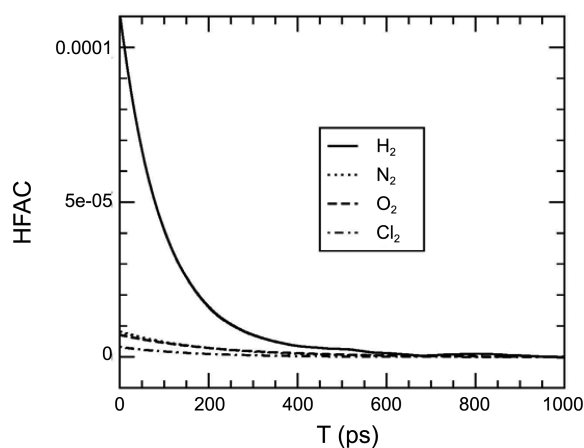

Figure 6. Heat-flux auto-correlation (HFAC, (10 J/mol·Å^2·ps)^2) functions of diatomic gases at 273.15 K and 1.00 atm.

O_2, and Cl_2, respectively. The results for thermal conductivity of diatomic gases estimated from HFAC functions overestimate the experimental results except H_2. 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,[16] λ of gaseous N_2 and O_2 (0.024 J/m·s·K) is much smaller than those of liquid N_2 and O_2 (0.15 J/m·s·K)[16] 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[17] and 0.065 J/m·s·K,[7] respectively.

Conclusion

We have performed molecular dynamics simulations of diatomic gases (H_2, N_2, O_2, and Cl_2) in order to calculate transport properties at 273.15 K and 1.00 atm. Translational diffusion coefficients of N_2 obtained from velocity autocorrelation 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_t. 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_2. 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_2 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.

References

1. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press: Oxford, 1987; p 2.
2. Xiong, D. X.; Xu, Y. S.; Guo, Z.Y. *J. of Thermal Science* **1996**, 5, 196.
3. Nwobi, O. C.; Long, L. N.; Micci, M. M. *J. of Thermodynamics and Heat Transfer* **1999**, *13*, 351.
4. Evans, D. J.; Morriss, G. P. *Comput. Phys. Rep.* **1984**, *1*, 297.
5. Lee, S. H. *Bull. Korean Chem. Soc.* **2004**, *25*, 737.
6. Lee, S. H. *Bull. Korean Chem. Soc.* **2007**, *28*, 1697.
7. Lee, S. H. *Bull. Korean Chem. Soc.* **2007**, *28*, 1371.
8. Singer, K.; Taylor, A.; Singer, J. V. L. *Mol. Phys.* **1977**, *33*, 1757.
9. Gas Encyclopedia, "http://encyclopedia.airliquide.com/encyclopedia.asp"
10. Nosé, S. *J. Chem. Phys.* **1984**, *81*, 511.
11. Hoover, W. G. *Phys. Rev. A* **1985**, *31*, 1695.
12. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press: Oxford, 1987; p 64.
13. Swope, W. C.; Andersen, H. C.; Beren, P. H.; Wilson, K. R. *J. Chem. Phys.* **1982**, *76*, 637.
14. Evans, D. J. *Mol. Phys.* **1977**, *34*, 317.
15. Evans, D. J.; Murad, S. *Mol. Phys.* **1977**, *34*, 327.
16. Kim, J. H.; Lee, S. H. *in preparation.*
17. Lee, S. H. *Bull. Korean Chem. Soc.* **2013**, *34*, 2931.
18. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press: Oxford, 1987; p 21.
19. DeKock, R. L.; Gray, H. B. *Chemical Structure and Bonding*; University Science Books: 1989; p 199.
20. Moore, E. A. *Molecular Modelling and Bonding*; Royal Society of Chemistry: 2002; p 64.
21. http://en.wikipedia.org/wiki/Oxygen
22. Verma, N. K.; Khanna, S. K.; Kapila, B. *Comprehensive Chemistry XI*; Laxmi Publications: p 466, ISBN 8170085969.
23. McQuarrie, D. A. *Statistical Mechanics*, 2nd ed.; Happer & Row: NY, 1976; p 365.
24. Atkins, P. W.; de Paula, J. *Physical Chemistry. Vol. 1 Thermodynamics and Kinetics*, 8th ed.; Oxford Univ Press: Oxford, 2006; p 453.