

Size Effect on Transport Properties of Gaseous Argon: A Molecular Dynamics Simulation Study

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Received December 15, 2013, Accepted January 19, 2014

Key Words : Molecular dynamics simulation, Gaseous argon, Green-Kubo formula, Transport properties

In a recent study, we have examined the Green-Kubo formula for the calculation of transport properties (diffusion coefficient, viscosity, and thermal conductivity) of noble gases (He, Ne, Ar, Kr, and Xe) by carrying out a series of equilibrium molecular dynamics (EMD) simulations for the system of N=1728 at 273.15 K and 1.00 atm.¹ While the diffusion coefficients (D) of noble gases were obtained through the original Green-Kubo formula, the viscosities (η) and thermal conductivities (λ) were obtained by utilizing the revised Green-Kubo formulas.^{2,3} The structural and dynamic properties of gaseous argon are completely different from those of liquid argon at 94.4 K and 1.374 g/cm³. The results for transport properties (D, η , and λ) at 273.15 K and 1.00 atm obtained from our EMD simulations are in general agreement with the experimental data and superior to the rigorous results of the kinetic theory.⁴

The error estimates, $(X_{MD}-X_{Exp})/X_{Exp}$, were reported as -0.6, -21.4, and -12.3% for X = D, η , and λ of gaseous argon for the system of N = 1728 at 273.15 K and 1.00 atm, respectively.¹ While the agreement between the MD results and the experimental measure for D is excellent, those for η and λ are acceptable but rather unsatisfied. In this note, we perform EMD simulations for gaseous argon of the systems of N = 432, 1728, and 6912 at 273.15 K and 1.00 atm. The primary goal of this study is to examine the size effect on the transport properties (D, η , and λ) of gaseous argon.

Green-Kubo Formula and Molecular Dynamics Simulation. The diffusion coefficient is obtained through two routes: the Green-Kubo formula from velocity auto-correlation (VAC) function:

$$D = \frac{1}{3} \int_0^{\infty} dt \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle, \quad (1)$$

and the Einstein formula from mean square displacement (MSD):

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle. \quad (2)$$

The shear viscosity is given by a modified Green-Kubo formula for better statistical accuracy³:

$$\eta = \frac{V}{kT} \int_0^{\infty} dt \sum_i \langle P_{i\alpha\beta}(0) \cdot P_{i\alpha\beta}(t) \rangle, \quad (3)$$

where

$$P_{i\alpha\beta}(t) = \frac{1}{V} \left[m v_{i\alpha}(t) \cdot v_{i\beta}(t) + \frac{1}{2} \sum_{j \neq i} r_{ij\alpha}(t) \cdot f_{ij\beta}(t) \right]. \quad (4)$$

with $\alpha\beta = xy, xz, yx, yz, zx,$ and zy . Similarly the thermal conductivity is given by

$$\lambda = \frac{V}{3kT^2} \int_0^{\infty} dt \sum_j \langle \dot{q}_{i\alpha}(0) \cdot \dot{q}_{i\alpha}(t) \rangle, \quad (5)$$

where $\dot{q}_{i\alpha}$ is the heat flux:

$$\dot{q}_{i\alpha}(t) = \frac{1}{V} \left[\varepsilon_i(t) \cdot v_{i\alpha}(t) + \frac{1}{2} \sum_{j \neq i} r_{ij\alpha}(t) \cdot [v_j(t) \cdot \mathbf{f}_{ij}(t)] \right], \quad (6)$$

with $\alpha = x, y,$ and z . The energy of molecule i is given by

$$\varepsilon_i(t) = \frac{p_i(t)^2}{2m_i} + \frac{1}{2} \sum_{j \neq i} \phi[r_{ij}(t)], \quad (7)$$

where $\phi[r_{ij}(t)]$ is the potential energy between particles i and j at time t .

We have chosen argon systems of N = 432, 1728, and 6912 to carry out MD simulations at T = 273.15 K and p = 1.00 atm. The length of cubic simulation box of each system is given in Table 1. The usual Lennard-Jones (LJ) 12-6 potential for the interaction between gaseous argon is used with the LJ parameters,⁵ $\sigma = 0.3405$ nm and $\varepsilon/k_B = 119.8$ K, where k_B is the Boltzmann constant. The inter-atomic potential is truncated at 1.0 nm, which is the cut-off distance used in many other simulations. Long-range corrections are

Table 1. Comparison of diffusion coefficients, viscosities, and thermal conductivities of gaseous argon at T = 273.15 K and 1.00 atm in NVT MD simulations with experiment. L is the length of cubic simulation box. Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis

N of argon molecules	L (nm)	D (cm ² /s)	η (μ P)	λ (J/m·s·K)
		MSD/VAC	SAC	HFAC
432	25.23	0.153(6)/0.165(4)	179(12)	0.0170(12)
1728	40.05	0.156(2)/0.154(8) [0.156(1)/0.158(4)] ^a	165(4) [166(4)] ^a	0.0143(6) [0.0155(9)] ^a
6912	63.58	0.157(1)/0.156(4)	169(2)	0.0158(3)
Exp.	—	0.157 ^b	210 ^c	0.0163 ^c

^aUsing other LJ parameters. ^bRef.4. ^cRef.9.

applied to the energy, pressure, *etc.* due to the potential truncation.⁶ The equations of motion were solved a velocity Verlet algorithm⁷ with a time step of 10^{-14} second for NVT MD simulations with the determined volumes from the system density. The configurations of argon molecules were stored every 10 time steps for further analysis. The systems were fully equilibrated and the equilibrium properties are averaged over five blocks of 400,000 time steps (4000 ps) since the autocorrelation functions decay very slowly over 3000 ps.

Results and Discussion

The mean square displacement (MSD) of gaseous argon increases nonlinearly over 500 ps and shows a straight line between 1000 and 3000 ps,¹ but the MSD of liquid argon shows a linear behavior within 3 ps (see the inset of Figure 2 in Ref. 1). The velocity auto-correlation (VAC) function also shows a dramatic difference. The VAC of liquid argon decays to 0 within 0.5 ps and has a negative value due to the collision with the neighboring particle (see the inset of Fig.3 in Ref. 1), but the VAC of gaseous argon decays very slowly to 0 over 3000 ps.¹

Table 1 lists diffusion coefficients of the gaseous argon for $N = 432$, 1728, and 6912 at 273.15 K and 1 atm obtained from MSD's using Eq. (1) and VAC's using Eq. (2) which are in good agreement with the experimental measures⁴ and are superior to the predictions of the kinetic theory from molecular collision⁴ as discussed in Ref.1. As the number of argon molecules increases, D obtained from MSD approaches the exact experimental measure ($0.153 \rightarrow 0.156 \rightarrow 0.157$) but D obtained from VAC lacks the accuracy ($0.165 \rightarrow 0.154 \rightarrow 0.156$). The results using other LJ parameters⁸ for $N = 1728$ are slightly better than those using the original LJ parameters.

Stress auto-correlation (SAC) and heat-flux auto-correlation (HFAC) functions of the gaseous argon at 273.15 K and 1 atm are plotted in Figures 1 and 2. Both correlation functions are monotonically decreased and decays very

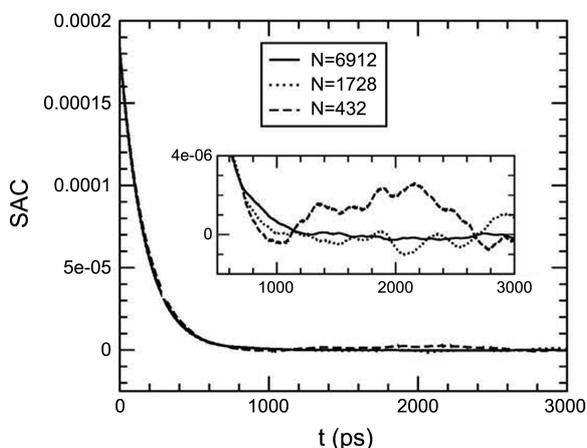


Figure 1. Stress auto-correlation functions ($\text{kJ/mol}\cdot\text{K}\cdot\text{\AA}\cdot\text{ps}^3$) of gaseous argon at 273.15 K and 1.00 atm. The inset shows the detailed behavior of SAC functions.

slowly to 0 over 3000 ps. In the inset of Figure 1, we plot the detailed SAC functions in the very narrow y-axis around the zero correlation. For $N = 432$, the fluctuation of the SAC function is very high, but it lowered with increasing number of argon molecules. The SAC function for $N = 1728$ is acceptable and that for $N = 6912$ is more perfect.

Running integrals for $\eta(t)$ of gaseous argon for $N = 432$, 1728, and 6912 at 273.15 K and 1 atm are plotted as a function of time in Figure 3. All the running integrals for viscosity clearly show plateaus which signify that the corresponding SAC functions have decayed to zero and are fluctuating along the horizontal time axis except for $N = 432$. As shown in the inset of Figure 1, all the SAC functions reach zero at about 1200 ps and we report the shear viscosities for $N = 432$, 1728, and 6912 at 273.15 K and 1 atm in Table 1 by averaging the running integrals for shear viscosity in Figure 3 for 1200-3000 ps.

The shear viscosities, η , obtained by MD simulations at 273.15 K and 1 atm underestimate the experimental measure for all the values of N . η for $N = 432$ is closer to the experi-

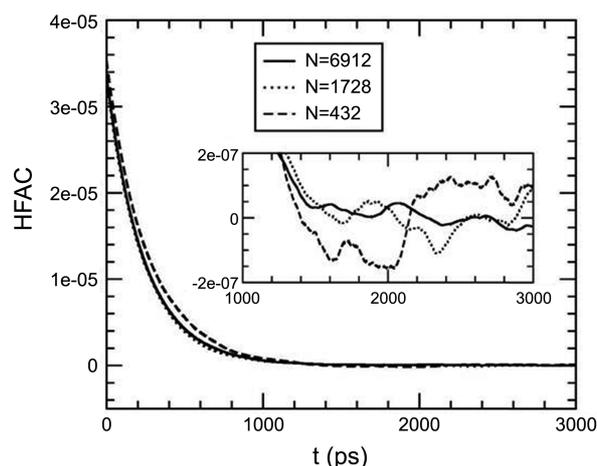


Figure 2. Heat-flux auto-correlation functions ($\text{kJ/mol}\cdot\text{\AA}^3$) of gaseous argon at 273.15 K and 1.00 atm. The inset shows the detailed behavior of SAC functions.

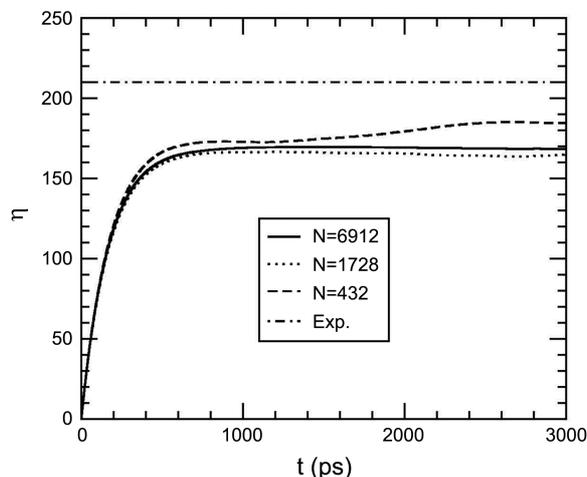


Figure 3. Running integrals for $\eta(t)$ (μP) of gaseous argon at 273.15 K and 1 atm.

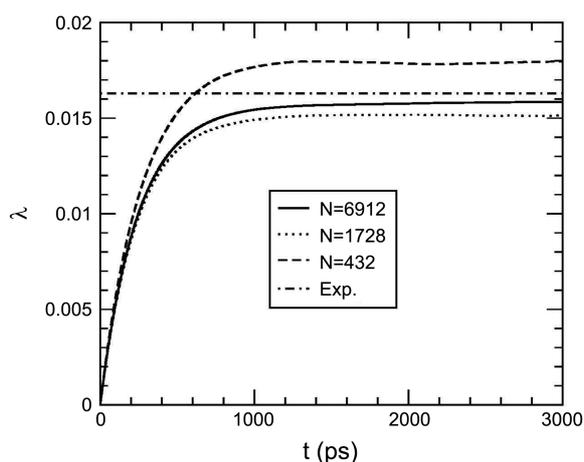


Figure 4. Running integrals for $\lambda(t)$ ($\text{J}/\text{m}\cdot\text{s}\cdot\text{K}$) of gaseous argon at 273.15 K and 1 atm.

mental measure than those for larger N 's in Figure 3, but the result for $N = 432$ is unreliable due to the high fluctuation of the SAC function as seen in the inset of Figure 1. η for $N = 6912$ is better than η for $N = 1728$ and increasing N makes the result slightly better. η obtained for $N = 1728$ using other LJ parameters⁸ is also comparable to that using the original LJ parameters.

The situation for HFAC is very similar to that for SAC. In the inset of Figure 2, the detailed HFAC functions in the very narrow y-axis around the zero correlation show the high fluctuations of the HFAC function for $N = 432$ and 1728, but it lowered with increasing number of argon molecules. The HFAC function for $N = 1728$ is better than that for $N = 432$, and that for $N = 6912$ is more reliable.

Running integrals for $\lambda(t)$ of gaseous argon for $N = 432$, 1728, and 6912 at 273.15 K and 1 atm are plotted as a function of time in Figure 4. All the running integrals for thermal conductivity clearly show plateaus which signify that the corresponding HFAC functions have decayed to zero and are fluctuating along the horizontal time axis. As shown in the inset of Figure 2, all the HFAC functions reach zero at about 1500 ps and we report the thermal conductivities for $N = 432$, 1728, and 6912 at 273.15 K and 1 atm in Table 1 by averaging the running integrals for thermal conductivity in Figure 3 for 1500–3000 ps.

The thermal conductivities, λ , obtained by MD simulations at 273.15 K and 1 atm overestimate the experimental measure for $N = 432$ and underestimate for $N = 1728$ and

6912. λ for $N = 432$ is too high compared to the experimental measure and this result is unreliable due to the high fluctuation of the HFAC function as seen in the inset of Figure 2. λ for $N = 6912$ is better than λ for $N = 1728$ and increasing N makes the result closer to the experimental measure. λ obtained for $N = 1728$ using other LJ parameters⁸ is much better than that using the original LJ parameters.

In summary, we have carried out a series of equilibrium molecular dynamics (EMD) simulations of gaseous argon at 273.15 K and 1.00 atm for the calculation of transport properties as a function of the number of argon molecules (N). While the diffusion coefficients (D) of gaseous argon approach to the experimental measure with increasing N , the viscosities (η) and thermal conductivities (λ) obtained for $N = 432$ are unreliable due to the high fluctuation of the time correlation functions and those for $N = 1728$ are rather acceptable. Increasing further to $N = 6912$ has improved the MD results a little closer to the experimental measures for η and λ . Both the EMD results for η and λ for $N = 6912$ underestimate the experimental measures and it is not expected that the more increasing N makes the closer results to the experimental measures. One possible explanation for the large disagreement between MD results and the experimental measures for η and λ may be due to the use of LJ parameters which were used for liquid argon.

Acknowledgments. This research was supported by Kyungshung University Research Grants in 2014. The computation for this work has been achieved by four PC clusters (Intel Xeon64 5620) for 2 months.

References

1. Lee, S. H. *Bull. Korean Chem. Soc* **2013**, *34*, 2931.
2. Lee, S. H.; Park, D. K.; Kang, D. B. *Bull. Korean Chem. Soc.* **2003**, *24*, 178.
3. Lee, S. H. *Bull. Korean Chem. Soc* **2007**, *28*, 1371.
4. McQuarrie, D. A. *Statistical Mechanics*, 2nd ed.; Happer & Row: NY, 1976; pp 364–365.
5. Hirschfelder, J. O.; Curtiss, C. F.; Birds, R. B. *Molecular Theory of Gases and Liquids*; John Wiley: NY, 1954; p 1212.
6. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press: Oxford: 1987; p 64.
7. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press: Oxford: 1987; p 81.
8. $\sigma = 0.3542$ nm and $\epsilon/k_B = 93.3$ K.
9. Atkins, P. W.; de Paula, J. *Physical Chemistry. Vol. 1 Thermodynamics and Kinetics*, 8th ed; Oxford Univ Press: Oxford, 2006; p 452.