

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

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There are various theories of transport properties in gases and liquids: the elementary kinetic theory of gases and molecular collisions, the macroscopic equations of continuum mechanics or hydrodynamics such as the continuity equation, the momentum balance equation, and the energy balance equation, the concept of phase space and Liouville equation which result in the reduced distribution function and BBGKY hierarchy for fluid distribution function, the Boltzmann equation and Chapman-Enskog method which are respectively the central equation of the rigorous kinetic theory of gases and the standard method for solving this Boltzmann integrodifferential equation, and finally the time-correlation function method (Green-Kubo (GK) relation) which is probably the most successful theory for the transport properties of liquids.

Green and Kubo¹ showed that the phenomenological coefficients describing many transport processes and time-dependent phenomena in general could be written as integrals over a certain type of function called a time-correlation function. These time-correlation functions play a somewhat similar role in non-equilibrium statistical mechanics that the partition function plays in equilibrium statistical mechanics. The analogy breaks down in one respect. Since the state of thermal equilibrium is unique, a single partition function gives all the thermodynamic properties, but since there are many different kinds of non-equilibrium states, a different time-correlation function for each type of transport process is needed. Determining the appropriate time-correlation function to use for a particular transport process of interest is very important.

The GK relations (section II) are the formal expressions for hydrodynamic field variables and some of the thermodynamic properties in terms of the microscopic variables of an N-particle system. The identification of microscopic expressions for macroscopic variables is made by a process of comparison of the conservation equations of hydrody-

namics with the microscopic equations of change for conserved densities. The importance of these relations is three-fold: they provide an obvious method for calculating transport coefficients using computer simulations, a convenient starting point for constructing analytic theories for non-equilibrium processes, and an essential information for designing non-equilibrium molecular dynamics (NEMD) algorithms.

In practice of performing an equilibrium molecular dynamics (EMD) simulation of an N-particle system to calculate transport coefficients directly from the GK relations, it is found that since the time-correlation decay in a slow algebraic fashion ($t^{-d/2}$ in d dimensions),² a large portion of the transport coefficient is determined by the long time tail of the correlation functions. This is probably the most difficult part of the correlation function to calculate. Another problem relating to the calculation of the correlation function is the size of simulation box. If one wishes to calculate a time correlation over a time span t , one must ensure that the system simulated is sufficiently large for a sound wave not to be able to traverse the system in a time less than t . If this condition is not fulfilled the periodic image convention used in simulation means that the damping of the sound wave will be modified as an image sound wave propagates across the system.³

In a recent study, we have examined the Green-Kubo formula for the calculation of transport properties (diffusion coefficient, viscosity, and thermal conductivity) of liquid Argon by carrying out a series of equilibrium molecular dynamics (EMD) simulations for the system of $N = 1728$ at 94.4 K and 1.374 g/cc and the error estimates, $(X_{MD} - X_{Exp})/X_{Exp}$, were reported as -0.4, 54.3, and -43.4% for $X = D, \eta,$ and λ of liquid argon, respectively.⁴ 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 liquid argon of the systems of $N = 1728$, 6912, 13824, 27648 and 110592 at 94.4 K and 1.374 g/cc. The primary goal of this study is to examine the size effect on the transport properties (D , η , and λ) of liquid argon.

Green-Kubo Formulas 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 accuracy:⁴

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

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 by⁴

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

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

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

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

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

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

We have chosen argon systems of $N = 1728$, 6912, 13824, 27648 and 110592 to carry out MD simulations at $T = 94.4$ and $\rho = 1.374$ g/cc. 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 liquid 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 interatomic potential is truncated at 1.0 nm, which is the cut-off distance used in many other simulations. Long-range corrections are 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 time step for further analysis. The systems were fully equilibrated and the equilibrium properties are averaged over 10 blocks of 5,000 time steps (50 ps).

RESULTS AND DISCUSSION

The mean square displacement (MSD) and the velocity auto-correlation (VAC) function of liquid argon show a normal behavior (not shown) as Rahman depicted them first time in 1964.⁸ The MSD of liquid argon shows a linear behavior within 3 ps with the initial dent within 0.3 ps,⁸ and the VAC of liquid argon decays rapidly to 0 within 0.5 ps, has a negative value due to the collision with the neighboring particle, and fluctuates near zero after 1.5 ps.⁸

Table 1 lists diffusion coefficients of the liquid argon for

Table 1. Comparison of diffusion coefficients, viscosities, and thermal conductivities of liquid argon at 94.4 K and 1.374 g/cc in NVT MD simulations with experiment. L is the length of cubic simulation box

N of argon molecules	L (nm)	D (10^{-5} cm ² /s)	η (mP)	λ (10^{-4} cal/cm-s-K)
		MSD/VAC	SAC	HFAC
1728	4.370	2.393(25)/2.401(21)	2.912(29)	1.783(17)
6912	6.936	2.427(15)/2.430(13)	2.905(10)	1.795(14)
13824	8.739	2.429(14)/2.435(15) [3.885(19)/3.881(17)] ^a	2.895(12)[1.712(15)] ^a	1.800(6)[2.205(5)] ^a
27648	11.010	2.422(10)/2.428(10)	2.899(9)	1.796(4)
110592	17.478	2.435(2)/2.435(4)	2.901(6)	1.798(3)
Exp.	–	2.43 ^b	1.97 ^c	2.74 ^c

^aUsing other LJ parameters: $\sigma = 0.3268$ nm and $\varepsilon/k_B = 119.8$ K. ^bAt 90 K and 1.374 g/cc. ^cObtained from Lagrange interpolation of experimental results at 94.4 K and saturated vapor pressure.¹²

$N = 1728, 6912, 13824, 27648$ and 110592 at 94.4 K and 1.374 g/cc obtained from MSD's using Eq. (1) and VAC's using Eq. (2) which are in good agreement with the experimental measures (2.43×10^{-5} cm²/s at 90 K and 1.374 g/cc).⁹ As the number of argon molecules increases, D obtained from MSD approaches the experimental measure ($2.393 \rightarrow 2.427 \rightarrow 2.429 \rightarrow 2.422 \rightarrow 2.435$) and D obtained from VAC also shows a good accuracy ($2.401 \rightarrow 2.403 \rightarrow 2.435 \rightarrow 2.428 \rightarrow 2.435$). The previously reported results for D of liquid argon at the same state were 2.44 ,¹⁰ 2.48 ,¹¹ and 2.42×10^{-5} cm²/s⁴ by EMD, and 4.02×10^{-5} cm²/s by NEMD.¹⁰ The results using other LJ parameters [$\sigma = 0.3268$ nm and $\epsilon/k_B = 119.8$ K] for $N = 13824$ are much poorer than those using the original LJ parameters [$\sigma = 0.3405$ nm and $\epsilon/k_B = 119.8$ K] as shown in Table 1. Obviously, the larger diffusion coefficients (D) are attributed to the smaller size LJ parameter (σ).

Stress auto-correlation (SAC) and heat-flux auto-correlation (HFAC) functions of the liquid argon for $N = 1728, 13824$, and 110592 at 94.4 K and 1.374 g/cc are plotted in Figs. 1 and 2. Both correlation functions are fluctuating near zero after 5 ps. In the inset of Fig. 1, we plot the detailed SAC functions in the very narrow y-axis around the zero correlation. For $N = 1728$, the fluctuation of the SAC function is very high, but it lowered with increasing number of argon molecules. The SAC function for $N = 13824$ is acceptable and that for $N = 110592$ is more perfect.

Running integrals for $\eta(t)$ of liquid argon for $N = 1728, 13824$, and 110592 at 94.4 K and 1.374 g/cc are plotted as a function of time in Fig. 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. As shown in the

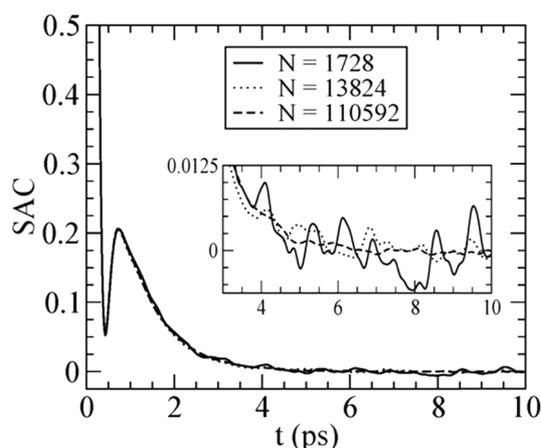


Figure 1. Stress auto-correlation functions $SAC = \frac{V}{kT} \sum_i \langle P_{i\alpha\beta}(0) \cdot P_{i\alpha\beta}(t) \rangle$ (kJ/mol·K·Å·ps³) of liquid argon at 94.4 K and 1.374 g/cc. The inset shows the detailed behavior of SAC functions.

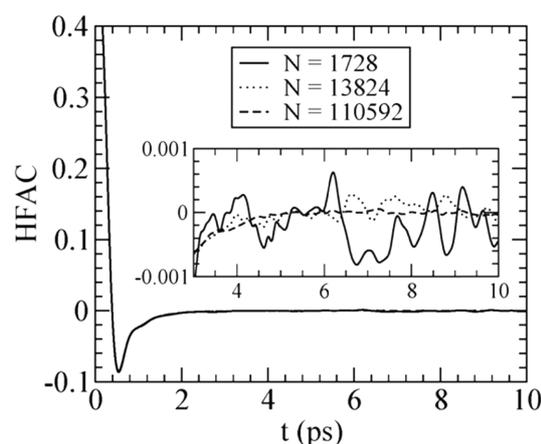


Figure 2. Heat-flux auto-correlation functions $HFAC = \frac{V}{kT} \sum_i \langle \dot{q}_{ia}(0) \cdot \dot{q}_{ia}(t) \rangle$ (kJ/mol·Å³) of liquid argon at 94.4 K and 1.374 g/cc. The inset shows the detailed behavior of HFAC functions.

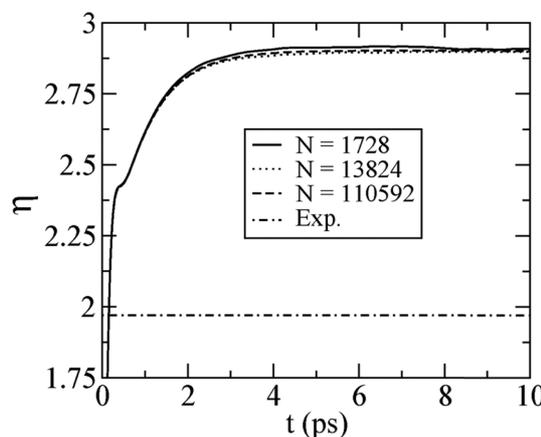


Figure 3. Running integrals for $\eta(t)$ (mP) of liquid argon at 94.4 K and 1.374 g/cc.

inset of Fig. 1, all the SAC functions reach zero at about 5 ps and we report the shear viscosities for $N = 1728, 6912, 13824, 27648$, and 110592 at 94.4 K and 1.374 g/cc in Table 1 by averaging the running integrals for shear viscosity in Fig. 3 for $5 \sim 10$ ps. As the number of argon molecules increases, η obtained from SAC decreases to the experimental and then increases slightly.

The shear viscosities, η , obtained by MD simulations at 94.4 K and 1.374 g/cc overestimate the experimental measure for all the values of N . η for $N = 13824$ is closer to the experimental measure¹² than those for larger N 's as shown in Table 1 and Fig. 3, but the result for $N = 1728$ is unreliable due to the high fluctuation of the SAC function as seen in the inset of Fig. 1. Increasing further in N makes the result slightly worse. $\eta = 2.895$ mP for $N = 13824$ is better than the previously reported results for η of liquid argon at

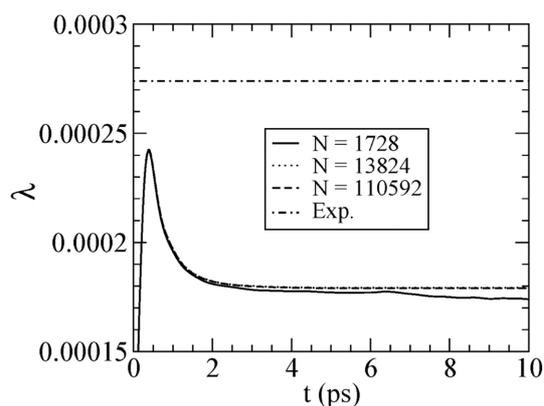


Figure 4. Running integrals for $\lambda(t)$ (cal/cm·s·K) of liquid argon at 94.4 K and 1.374 g/cc.

the same state, 3.08^{11} and 3.04 mp^4 by EMD, but not for 2.29 mp^{10} by EMD and 2.13 mp by NEMD.¹⁰ η obtained for $N = 13824$ using other LJ parameters [$\sigma = 0.3268 \text{ nm}$ and $\epsilon/k_B = 119.8 \text{ K}$] is much better than that using the original LJ parameters [$\sigma = 0.3405 \text{ nm}$ and $\epsilon/k_B = 119.8 \text{ K}$] as shown in *Table 1*.

The situation for HFAC is very similar to that for SAC. In the inset of *Fig. 2*, the detailed HFAC function in the very narrow y-axis around the zero correlation shows the high fluctuation of the HFAC function for $N = 1728$, but it lowered with increasing number of argon molecules. The HFAC function for $N = 13824$ is better than that for $N = 1728$, and that for $N = 110592$ is more reliable.

Running integrals for $\lambda(t)$ of liquid argon for $N = 1728$, 13824 , and 110592 at 94.4 K and 1.374 g/cc are plotted as a function of time in *Fig. 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 *Fig. 2*, all the HFAC functions reach zero at about 5 ps and we report the thermal conductivities for $N = 1728$, 6912, 13824, 27648, and 110592 at 94.4 K and 1.374 g/cc in *Table 1* by averaging the running integrals for thermal conductivity in *Fig. 3* for 5–10 ps.

The thermal conductivities, λ , obtained by MD simulations at 94.4 K and 1.374 g/cc underestimate the experimental measure¹² for all the values of N . η for $N = 13824$ is the best among all the values of N in *Table 1* and *Fig. 4*. λ for $N = 1728$ is unreliable due to the high fluctuation of the HFAC function as seen in the inset of *Fig. 2*. λ for $N = 13824$ is better than λ for $N = 110592$ and increasing N also makes the result slightly worse. The previously reported results for λ of liquid argon at the same state were 1.84 ,¹⁰

3.05 ,¹¹ and $1.55 \times 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{K}^4$ by EMD, and $2.31 \times 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{K}$ by NEMD.¹⁰ λ obtained for $N = 13824$ using other LJ parameters [$\sigma = 0.3268 \text{ nm}$ and $\epsilon/k_B = 119.8 \text{ K}$] is much better than that using the original LJ parameters [$\sigma = 0.3405 \text{ nm}$ and $\epsilon/k_B = 119.8 \text{ K}$] as the same for the case of η .

In summary, we have carried out a series of equilibrium molecular dynamics (EMD) simulations of liquid argon at 94.4 K and 1.374 g/cc 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 the experimental values with increasing N , the viscosities (η) and thermal conductivities (λ) obtained for $N = 1728$ are unreliable due to the high fluctuation of the time correlation functions, but those for $N = 13824$ are rather acceptable. Increasing N further to 110592 brings the EMD results a slightly worse for η and λ . The EMD results for η overestimate and those for λ underestimate the experimental measurements,¹⁰ respectively, and it is not expected that further increase in N would give results closer to the experimental measurements. The use of the smaller size LJ parameter (σ) could improve the results for η and λ of liquid argon at 94.4 K and 1.374 g/cc but not for D . Therefore a systematic EMD simulation using various values for LJ parameters (σ and ϵ) is currently under study.

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