

Molecular Dynamics Simulation Study of the Transport Properties of Liquid Argon: The Green-Kubo Formula Revisited

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The velocity auto-correlation (VAC) function of liquid argon in the Green-Kubo formula decays quickly within 5 ps to give a well-defined diffusion coefficient because the velocity is the property of each individual particle, whereas the stress (SAC) and heat-flux auto-correlation (HFAC) functions for shear viscosity and thermal conductivity have non-decaying, long-time tails because the stress and heat-flux appear as system properties. This problem can be overcome through N (number of particles)-fold improvement in the statistical accuracy, by considering the stress and the heat-flux of the system as properties of each particle and by deriving new Green-Kubo formulas for shear viscosity and thermal conductivity. The results obtained for the transport coefficients of liquid argon obtained are discussed.

Key Words : Diffusion, Shear viscosity, Thermal conductivity, Liquid argon, Molecular dynamics simulation

Introduction

Transport coefficients - self-diffusion coefficient, shear viscosity, and thermal conductivity - are defined in terms of the system response to a perturbation. For example, the diffusion coefficient relates the particle flux to a concentration gradient, whereas the shear viscosity is a measure of the shear stress induced by an applied velocity gradient. By introducing such perturbations into the Hamiltonian, or directly into the equations of motion, their effect on the distribution function may be calculated. By retaining the linear terms in the perturbation, and comparing the equation for the response with a macroscopic transport equation, we can identify the transport coefficient.

This is usually the infinite time integral of an equilibrium correlation function of the form known as the Green-Kubo formula:

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

where γ is the transport coefficient and A is a variable appearing in the perturbation term in the Hamiltonian.

The problem in the calculation of transport properties using the equilibrium molecular dynamics (EMD) simulation is the non-decaying, long-time tail of the time correlation functions in Eq. (1). The velocity auto-correlation (VAC) function of liquid argon in the Green-Kubo formula decays quickly within 5 ps to give a well-defined diffusion coefficient because the velocity is the property of each particle. On the other hand, the stress (SAC) and the heat-flux auto-correlation (HFAC) functions for shear viscosity and thermal conductivity have non-decaying long-time tails because the stress and the heat-flux appear as the system properties.

In the present paper, we examine the Green-Kubo formula for the calculation of transport properties of liquid argon

using the EMD simulation. The primary study goal is to seek an alternate route for the non-decaying, long-time tail of the time correlation functions in Eq. (1). This paper is organized as follows: We present the technical details of MD simulation in the following section, some theoretical aspects in Section III, our results in Section IV, and concluding remarks in Section V.

Molecular Dynamics Simulation Details

The usual Lennard-Jones (LJ) 12-6 potential for the interaction between argon atoms was used with LJ parameters, $\sigma = 0.34$ nm and $\epsilon/k = 120$ K, where k is the Boltzmann constant. The inter-atomic potential was truncated at 0.85 nm, which is the cut-off distance used in many other simulations. Long-range corrections were applied to the energy and pressure due to the potential truncation.¹ The preliminary canonical ensemble (NVT fixed) EMD simulation of 1728 argon atoms was initiated in a cubic box of length $L = 4.3696$ nm, with a density of 1.374 g/cm³ at 94.4 K and 1 atm. The equations of motion were solved using a velocity Verlet algorithm² for NVT EMD simulation and a fifth-order, predictor-corrector, Gear integration³ for NpT EMD simulation with a time step of 10^{-14} second. Both systems were fully equilibrated and the equilibrium properties were averaged over five blocks of 10,000 time steps. A brief summary of thermodynamic averages is given in Table 1. The configurations of argon atoms were stored at every time step for further analysis.

Table 1. Liquid argon system at 94.4 K

Methods	ρ (g/cm ³)	p (atm)	$-E_{LJ}$ (kJ/mol)
Verlet NVT EMD	1.374	38.11	5.382
Gear NpT EMD	1.361	-0.41	5.338

Theorem

As dynamic properties, we calculate the self-diffusion coefficient (D_s), shear viscosity (η), and thermal conductivity (λ) of liquid argon system using the Green-Kubo formulas.

Diffusion coefficient. The self-diffusion coefficient D_s can be obtained through the Green-Kubo formula :

$$D_s = \frac{1}{3} \int_0^{\infty} dt \langle v_i(t) \cdot v_i(0) \rangle. \quad (2)$$

Here the integrand of Eq. (2) is called the VAC function, which is obtained with very high statistical accuracy by time-averaging over N particles of the system.

Shear viscosity. The Green-Kubo formula for shear viscosity η is given by

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

where $\alpha\beta = xy, xz, yx, yz, zx, \text{ or } zy$ and $P_{\alpha\beta}$ is the $\alpha\beta$ component of the molecular stress tensor \mathbf{P} of the system :

$$P_{\alpha\beta}(t) = \frac{1}{V} \left[\sum_i m_i v_{i\alpha}(t) v_{i\beta}(t) + \sum_i r_i v_{i\alpha}(t) f_{i\beta}(t) \right]. \quad (4)$$

There is another formula for $P_{\alpha\beta}$:

$$P_{\alpha\beta}(t) = \frac{1}{V} \left[\sum_i m_i v_{i\alpha}(t) v_{i\beta}(t) + \sum_i \sum_j r_i v_{i\alpha}(t) f_{ij\beta}(t) \right]. \quad (5)$$

The equality of Eqs. (4) and (5) without potential truncation is fully discussed in Ref. [4]. It is recommended to use Eq. (5) in a simulation that employs the periodic boundary condition. The stress auto-correlation (SAC) functions, the integrand of Eq. (3), obtained from Eqs. (4) and (5), do not decay to zero in the long-term, as shown in Figure 1, and the resulting running integrals of SAC for shear viscosity are not well-defined, as seen in Figure 2.

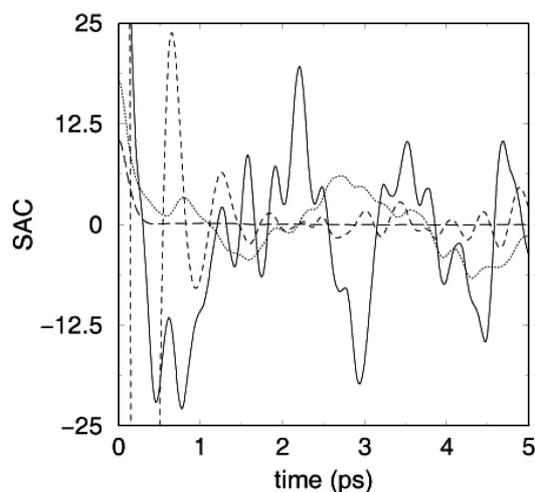


Figure 1. Stress auto-correlation (SAC) functions of liquid argon. Solid line: Eq. (4), dotted line: Eq. (5), dashed line: Eq. (6), and long dashed line: Eq. (8).

Though the stress is a property of the system, it can be considered as a property of each particle i , by writing $P_{i\alpha\beta}$ on the analogy of Eq. (4) as

$$P_{i\alpha\beta}(t) = \frac{1}{V} [m_i v_{i\alpha}(t) v_{i\beta}(t) + r_{i\alpha}(t) f_{i\beta}(t)]. \quad (6)$$

The new shear viscosity η is defined as

$$\eta = \frac{V}{kT} \int_0^{\infty} dt \sum_i \langle P_{i\alpha\beta}(0) P_{i\alpha\beta}(t) \rangle. \quad (7)$$

In our previous paper,⁵ this equation was first introduced and the result was discussed. There is another formula for $P_{i\alpha\beta}$, through the analogy of Eq. (5):

$$P_{i\alpha\beta}(t) = \frac{1}{V} \left[m_i v_{i\alpha}(t) v_{i\beta}(t) + \sum_{j \neq i} r_{ij\alpha}(t) f_{ij\beta}(t) \right]. \quad (8)$$

Of course, the newly derived Green-Kubo formulas are different from the original Green-Kubo formulas. In order to improve the results for the transport properties using the Green-Kubo formula, applying the newly derived Green-Kubo formulas by EMD simulation is our study goal. Regarding the difference between Eqs. (3) and (7), in Eq. (3) the stress of the system is calculated using Eq. (4) or (5) and the SAC of the system is time-averaged, while in Eq. (7) each particle's stress is obtained using Eq. (6) or (8), each particle's SAC is time-averaged, and the system SAC is summed over the SAC of N particles. Then the statistical accuracy is improved, being N (number of particles)-fold larger than that using Eq. (4) or (5). Figure 1 shows the perfect decay of the SAC of Eq. (8), but the SAC of Eq. (6) still suffers fluctuation. In Figure 2, the resulting running integral of the SAC of Eq. (8) gives a constant plateau value, whereas that of Eq. (6) is not a constant. This kind of treatment in calculating shear viscosity has already been applied to solute molecular dynamics in a mesoscopic solvent. Since there is no interaction between solvent

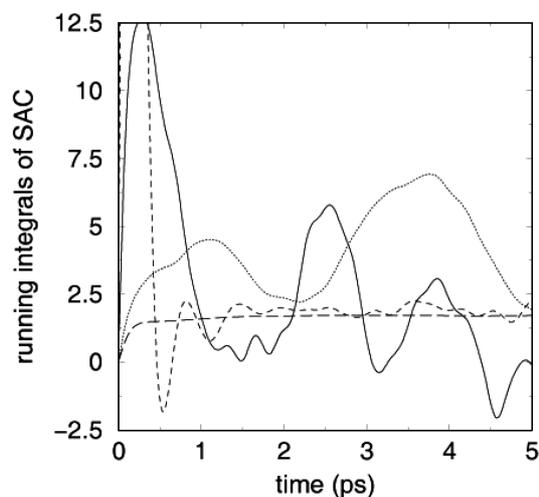


Figure 2. Running integrals of stress-correlation (SAC) functions of liquid argon. Solid line: Eq. (4), dotted line: Eq. (5), dashed line: Eq. (6), and long dashed line: Eq. (8).

particles in a mesoscopic solvent, the second term of Eq. (6) or (8) vanishes, and $v_{i\beta}$ is treated as the cell-jump velocity.⁶

Thermal conduction. The discussion here is exactly the same as in the previous section for shear viscosity. The Green-Kubo formula for thermal conductivity λ is given by

$$\lambda = \frac{V}{kT^2} \int_0^\infty dt \langle \dot{q}_\alpha(0) \dot{q}_\alpha(t) \rangle, \quad (9)$$

where $\alpha = x, y,$ and z and the heat flux by the system is

$$\dot{q}_\alpha(t) = \frac{1}{V} \left\{ \sum_i \in_i v_{i\alpha}(t)^2 + \frac{1}{2} \sum_i \sum_{j \neq i} r_{ij\alpha}(t) [v_i(t) \cdot f_{ij}(t)] \right\} \quad (10)$$

Here, the energy of molecule i is given by

$$\in_i(t) = \frac{1}{2} m_i v_i(t)^2 + \frac{1}{2} \sum_{j \neq i} \Phi[r_{ij}(t)], \quad (11)$$

where $\phi(r_{ij})$ denotes the potential energy between molecules i and j .

Again the heat flux is considered as a property of each particle i , writing $\dot{q}_{i\alpha}$ on the analogy of Eq. (8) as

$$\dot{q}_{i\alpha}(t) = \frac{1}{V} \left\{ \in_i(t) v_{i\alpha}(t) + \frac{1}{2} \sum_{j \neq i} r_{ij\alpha}(t) [v_i(t) \cdot f_{ij}(t)] \right\}. \quad (12)$$

This is the heat flux by molecule i . Then the new shear viscosity η is defined as

$$\lambda = \frac{V}{kT^2} \int_0^\infty dt \sum_i \langle \dot{q}_{i\alpha}(0) \dot{q}_{i\alpha}(t) \rangle. \quad (13)$$

The heat flux by each molecule, Eq. (12), with the energy of molecule, Eq. (11), consists of three contributions:

$$\dot{q}_{i\alpha} = \dot{q}_{i\alpha}^{tm} + \dot{q}_{i\alpha}^{pm} + \dot{q}_{i\alpha}^{ti} \quad (14)$$

where

$$\dot{q}_{i\alpha}^{tm} = \frac{1}{V} \left[\frac{1}{2} m_i v_i^2 \right] v_{i\alpha}, \quad (15)$$

$$\dot{q}_{i\alpha}^{pm} = \frac{1}{V} \left[\frac{1}{2} \sum_{j \neq i} \Phi(r_{ij}) \right] v_{i\alpha} \quad (16)$$

and

$$\dot{q}_{i\alpha}^{ti} = \frac{1}{V} \left[\frac{1}{2} \sum_{j \neq i} r_{ij\alpha} (v_i \cdot f_{ij\alpha}) \right], \quad (17)$$

$\dot{q}_{i\alpha}^{tm}$ and $\dot{q}_{i\alpha}^{pm}$ are the translational and the potential energy transport due to molecular motion, respectively, and $\dot{q}_{i\alpha}^{ti}$ is the translational energy transfer due to molecular interaction. Hence, the thermal conductivity, Eq. (13), consists of three contributions :

$$\lambda_{tot} = \lambda_{tm} + \lambda_{pm} + \lambda_{ti}. \quad (15)$$

Results and Discussion

The calculated velocity auto-correlation (VAC) function of liquid argon in the Green-Kubo formula, the integrand of

Eq. (2), decays to zero quickly within 5 ps (data not shown) and the resulting self-diffusion coefficient is well-defined. The self-diffusion coefficients obtained from our Verlet NVT EMD and Gear NpT EMD simulations are listed in Table 2 and the agreement with the experimental results⁷ is quite good with only very small standard deviations being observed.

Figures 1 and 2 show four different stress auto-correlation (SAC) functions of liquid argon and the resulting running integral of the SAC, respectively. The SAC functions with the stress as a property of the system in Figure 1 do not decay to zero in the long-term and the resulting running integrals of the SAC in Figure 2 are not well-defined. As a result we were not able to calculate the shear viscosity. The SAC function obtained using one of the newly derived Green-Kubo formulas (Eq. (6)) and the resulting running integral of the SAC function still suffered fluctuation, as seen in Figures 1 and 2. The final SAC function obtained using the other newly derived Green-Kubo formula (Eq. (8)) shows the perfect decay of the correlation in Figure 1 and the resulting running integral of the SAC gives a constant plateau value in Figure 2. As a result, the calculated shear viscosities of liquid argon using the two newly derived Green-Kubo formulas are similar in both Verlet NVT EMD and Gear NpT EMD simulations, but are notable for the large difference of standard deviation in the calculated shear viscosity, reflecting the behavior of each SAC function, as listed in Table 2. The calculated shear viscosities of liquid argon overestimate the experimental measure.⁸

The related formulas for the thermal conductivity of liquid argon have a very similar situation to those for the shear viscosity. Since the calculated heat-flux auto-correlation (HFAC) functions and its resulting running integrals (data not shown) show a very similar behavior to the calculated SAC and its running integrals, we consider only the final

Table 2. Comparison of self-diffusion constant (D_s in 10^{-5} cm²/sec), shear viscosity (η in mp), and thermal conductivities (λ in 10^{-4} cal/K-cm-sec) of liquid argon at 94.4 K obtained from the Green-Kubo formulas with the experimental measures

Transport properties	Verlet NVT	Gear NpT	Experimental
D_s (Eq. (2))	2.42 ± 0.03	2.55 ± 0.04	2.43^a
η (Eqs. (7) and (6))	3.04 ± 0.35	3.09 ± 0.31	1.97^b
η (Eqs. (7) and (8))	3.16 ± 0.02	3.08 ± 0.01	–
λ (Eqs. (13) and (12))	1.55 ± 0.03	1.56 ± 0.05	2.74^b

^aAt 90 K and 1.374 g/cm³. ^bObtained from Lagrange interpolation of experimental results at 94.4 K.⁸

Table 3. Thermal conductivities (λ in 10^{-4} cal/K-cm-sec) of liquid argon at 94.4 K as contributed from each term of Eqs. (15), (16), and (17)

Thermal conductivities	Verlet NVT	Gear NpT
λ_{tm} (Eqs. (13) and (15))	0.14 ± 0.01	0.15 ± 0.01
λ_{pm} (Eqs. (13) and (16))	0.77 ± 0.04	0.79 ± 0.05
λ_{ti} (Eqs. (13) and (17))	0.79 ± 0.02	0.77 ± 0.02
λ_{total}	1.70 ± 0.06	1.71 ± 0.07

form of the newly derived Green-Kubo formula on the analogy of Eq. (8). In Table 2 the thermal conductivities of liquid argon obtained from our Verlet NVT EMD and Gear NpT EMD simulations are in good agreement with each other. The calculated thermal conductivities of liquid argon underestimate the experimental measure.⁸

Assuming the contributions of the three heat fluxes to the total heat flux (Eq. (14)) are independent of each other, the calculated thermal conductivities of liquid argon by each contribution are listed in Table 3. The assumption of the independence of the three contributions is valid within 91% (=1.55/1.70). The thermal conduction by translational energy transport due to molecular motion has a small portion of about 8.2%, while that by potential energy transport due to molecular motion and translational energy transfer due to molecular interaction has an equal portion of 45.9% each. The energy transport by molecular motion is proportional to each energy - the average translational (1.18 kJ/mol from 94.4 K) and potential energies (-5.34 ~ -5.38 kJ/mol).

Conclusion

In the present paper, we examine the Green-Kubo formula to calculate the calculation of the transport properties of liquid argon at 94.4 K, using the equilibrium molecular dynamics (EMD) simulation. No complication is introduced in the calculation of the self-diffusion coefficient since the velocity auto-correlation (VAC) function decays to zero fast within 5 ps, because the velocity of each particle is a property of particle. However, for the shear viscosity and thermal conductivity, the stress (SAC) and the heat-flux auto-correlation (HFAC) functions in the Green-Kubo formulas have non-decaying, long-time tails because the stress and the heat flux are system properties, rather than particle properties. By considering the stress and heat-flux of

the system as properties of each particle, this problem can be overcome through an N (number of particles)-fold improvement in the statistical accuracy. The results for shear viscosity and thermal conductivity of liquid argon obtained through the Green-Kubo formula by using a velocity Verlet algorithm for NVT EMD and a fifth-order predictor-corrector Gear integration for NpT EMD simulations give a reasonable agreement with the experimental results. The applications of this method to the simulation study of various molecular liquids, such as diatomic molecules, H₂O, CH₄, and C₄H₁₀ is presently under study. However, the validity of the application of the newly derived Green-Kubo formulas for molecular liquids should be verified. For example, two shear viscosities obtained from different translational stresses, Eq. (6) and (8), for diatomic molecules show a difference in order of magnitude each other.⁹

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