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Equilibrium and Non-equilibrium Molecular Dynamics Simulations of Thermal Transport Coefficients of Liquid Argon

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The thermal transport coefficients—the self-diffusion coefficient, shear viscosity, and thermal conductivity—of liquid argon at 94.4 K and 1 atm are calculated by non-equilibrium molecular dynamics (NEMD) simulations of a Lennard-Jones potential and compared with those obtained from Green-Kubo relations using equilibrium molecular dynamics (EMD) simulations and with experimental data. The time-correlation functions—the velocity, pressure, and heat flux auto-correlation functions—of liquid argon obtained from the EMD simulations show well-behaved smooth curves which are not oscillating and decaying fast around 1.5 ps. The calculated self-diffusion coefficient from our NEMD simulation is found to be approximately 40% higher than the experimental result. The Lagrange extrapolated shear viscosity is in good agreement with the experimental result and the asymptotic formula of the calculated shear viscosities seems to be an exponential form rather than the square-root form predicted by other NEMD studies of shear viscosity. The agreement for thermal conductivity between the simulation results (NEMD and EMD) and the experimental result is within statistical error. In conclusion, through our NEMD and EMD simulations, the overall agreement is quite good, which means that the Green-Kubo relations and the NEMD algorithms of thermal transport coefficients for simple liquids are valid.

Introduction

Molecular theory of transport through gases and liquids is now very active area of research and it has been only in the 1960s that this field has been set on a basis comparable to equilibrium statistical mechanics. There are various theories of transport 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 (this is essentially the thermodynamic background for non-equilibrium statistical mechanics), 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 the 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 relations) which is probably the most successful theory for transport 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 nonequilibrium statistical mechanics that the partition function plays in equilibrium statistical mechanics. The

Table 1. Green-Kubo Relations for Thermal Transport Coefficients

$$D_s = \frac{1}{3} \int_0^\infty dt \langle v_i(0) \cdot v_i(t) \rangle \text{ self-diffusion coefficient} \quad (1)$$

$$\eta = \frac{V}{kT} \int_0^\infty dt \langle P_{xy}(0)P_{xy}(t) \rangle \text{ shear viscosity} \quad (2)$$

$$\lambda = \frac{V}{kT^2} \int_0^\infty dt \langle J_{Qx}(0)J_{Qx}(t) \rangle \text{ thermal conductivity} \quad (3)$$

where v_i is the velocity of particle i , P_{xy} is an off-diagonal ($x \neq y$) of the viscous pressure tensor:

$$P_{xy} V = \sum_i m v_i x_i v_i + \sum_i r_i F_i \quad (4)$$

and J_{Qx} is a component of the energy current:

$$J_{Qx} V = \sum_i E_i v_i + \frac{1}{2} \sum_i \sum_j r_{ij} (v_i \cdot F_{ij}) \quad (5)$$

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 nonequilibrium 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 Green-Kubo relations (Table 1) are the formal expres-

sions 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 hydrodynamics 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 simulation, a convenient starting point for constructing analytic theories for nonequilibrium processes, and an essential information for designing non-equilibrium molecular dynamics (NEMD) algorithm.

In practice of performing an equilibrium molecular dynamics simulation of an N-particle system to calculate transport coefficients directly from the Green-Kubo relations, it is found that since the time-correlation functions 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 , then 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 For these and other reasons, new method to calculate transport coefficients was appeared in the early 1970's which would be more efficient than the equilibrium Green-Kubo method.

The development of non-equilibrium molecular dynamics (NEMD) technique in recent years has made it possible to calculate theoretically a wide variety of thermal transport coefficients essentially exactly from a given potential model for the interactions between the molecules at the microscopic level. These quantities include the shear (η) and bulk (k) viscosities, thermal conductivity (λ), and self-diffusion coefficient (D_s) of both simple and molecular fluids.⁴⁻²³ The general principle of the NEMD method²⁴ is to introduce a (possibly fictitious) external field X into the equations of motion of the system, which derives the corresponding thermodynamic flux J . The first requirement for this applied field is that it should be consistent with the periodic boundary conditions to ensure that the simulation box remains homogeneous. The second requirement is that the transport coefficient β of interest can be calculated from the constitutive relation

$$\beta = \lim_{X \rightarrow 0} \left[\lim_{t \rightarrow \infty} \frac{J(t)}{X} \right] \quad (6)$$

where t is time. The formal proof that an algorithm satisfies these two requirements is given by linear response theory.^{18,25,26} In many cases the value of the thermal transport coefficient at non-zero fields has no physical meaning since the field used to derive the thermodynamic flux is fictitious, but the slod algorithm for planar Couette flow^{18,26} used to calculate shear viscosity can be shown to be exact for all values of the field as noted in Sec. II. (2).

In this paper, we perform equilibrium and nonequilibrium molecular dynamics simulations to calculate the thermal

transport coefficients (we restrict ourselves to calculate only the self-diffusion coefficient D_s , shear viscosity η , and thermal conductivity λ) of argon at 94.4 K and 1 atm. In Sec. II, the NEMD algorithm derived from the linear response theory and details of simulations of liquid argon are briefly described. Results and discussion is presented in Sec. III. Finally in Sec. IV, concluding remarks are presented.

Non-Equilibrium Molecular Dynamics

Hamiltonian Algorithm for Self-diffusion Coefficient. The Hamiltonian for a many-body system

$$H_0 = \sum_i^N \frac{p_i^2}{2m} + \Phi(r) \quad (7)$$

has added to it a perturbing external field at time 0

$$H = H_0 + \sum_i^N c_i x_i F(t), \quad t \geq 0 \quad (8)$$

where c_i are colour charges analogous to electric charges and $F(t)$ is the applied colour field. For simplicity c_i is given by $(-1)^i$ for an even number of particles N . The external field F stimulates a current density J_x

$$J_x = \frac{1}{V} \sum_i^N c_i \dot{x}_i \quad (9)$$

analogous to an electric current density where V is the volume. The linear response theory^{18,25,26} predicts that in the linear small field limit,

$$\lim_{t \rightarrow \infty} \langle J_x(t) \rangle = - \int_0^t ds \chi(t-s) F(s) \quad (10)$$

where the susceptibility, χ , is

$$\chi(t) = \frac{-V}{kT} \langle J_x(t) J_x(0) \rangle \quad (11)$$

Because the unperturbed Hamiltonian H_0 and the propagator e^{Lt} are both colour blind where L is the Liouville operator, and when Eq. (9) is substituted into Eq. (11) for $J_x(0)$ and $J_x(t)$, the colour current auto-correlation function can be written in terms of the velocity auto-correlation function in the Green-Kubo relations, Eq. (1):

$$\chi(t) = \frac{-N^2}{(N-1)VkT} \langle v_{xi}(t)v_{xi}(0) \rangle \quad (12)$$

Taking the integration over time t in Eq. (12) and using Eq. (10) with constant field F ($\int_0^t \chi(t-s) ds = \int_0^\infty \chi(s) ds$, as $t \rightarrow \infty$), thus the self-diffusion coefficient can be determined by carrying out a series of constant field simulations and extrapolating the resulting conductivities to the zero field limit

$$D_s = \frac{(N-1)VkT}{N^2} \lim_{F \rightarrow 0} \left[\lim_{t \rightarrow \infty} \frac{\langle J_x(t) \rangle}{F} \right] \quad (13)$$

The equations of translational motion for atomic molecule are given by

$$\dot{r}_i = p_i/m \quad (14)$$

$$\dot{p}_{xi} = F_{xi} + c_i F - \alpha p_{xi} \quad (15a)$$

$$\dot{p}_{yi} = F_{yi} - \alpha p_{yi} \quad (15b)$$

$$\dot{p}_{zi} = F_{zi} - \alpha p_{zi} \quad (15c)$$

where the external field is applied to only the x -direction and α is a parameter from the translational temperature constraint of systems of canonical ensemble (N, V, T fixed). The derivation of the terms containing α in the equations of motion is obtained using Gauss's principle of least constraint.^{13,27} The constant translational temperature constraint requires that

$$\frac{1}{2m} \sum_{i=1}^N \dot{p}_i^2 = \frac{3NkT}{2} \quad (16)$$

The parameter can be identified explicitly by multiplying the equations of motion (15) by \dot{p}_{ix} , \dot{p}_{iy} , and \dot{p}_{iz} and summing over all particles

$$\begin{aligned} \frac{d}{dt} \left[\frac{1}{2m} \sum_i \dot{p}_i^2 \right] &= \frac{1}{m} \sum_i \dot{p}_i \cdot \dot{p}_i = \frac{d}{dt} \frac{3nkT}{2} \\ &= \sum_i \dot{p}_i \cdot F_i + F \sum_i c_i \dot{p}_{ix} - \alpha \sum_i \dot{p}_i \cdot \dot{p}_i = 0 \end{aligned}$$

Thus the parameter α is function of time which depend upon the particle colours charges, velocities, and forces.

$$\alpha = \left[\sum_i \dot{p}_i \cdot F_i + F \sum_i c_i \dot{p}_{ix} \right] / \sum_i \dot{p}_i \cdot \dot{p}_i \quad (17)$$

Shear Viscosity from Steady Planar Couette Flow.

The simulation for the shear viscosity closely mimics real viscous flow a fluid under a steady uniform shearing motion, i.e., with two plates moving in opposite x directions located at $y = \pm \infty$, characterized by a velocity gradient of the form $du_x/dy = \gamma$ where γ is the constant strain rate. Among many methods for simulating a steady planar Couette flow, the most efficient technique appears to be the Slod algorithm.¹⁸ This algorithm uses the usual periodic boundary conditions in the x and z directions but in the y direction the periodic image cubes move in the positive and negative x directions according to the strain rate γ . This is the well-known "sliding brick" boundary condition²⁸ the row of bricks immediately above the central simulation cube slide with constant velocity γL in the positive x direction and the row of bricks below the central cube slide with equal velocity but the opposite direction where L is the length of the side of the simulation cube. In this boundary condition, a molecule leaving the top (bottom) of the central cube reenters at the bottom (top) shifted to the left (right) by an amount $\gamma L t$ and with the x component of its velocity reduced (increased) by an amount γL . The "sliding brick" boundary condition also alters the usual minimum image convention.

The linear response theory^{18,25,26} may be applied to the equation of motion as in the applied colour field in Sec. III. (1) and in the linear small strain rate γ ,

$$\langle P_{xy}(t) \rangle = - \lim_{t \rightarrow \infty} \int_0^t ds \chi(t-s) \gamma(s) \quad (18)$$

where P_{xy} is the xy component of the viscous pressure tensor, Eq. (4), and

$$\chi(t) = - \frac{V}{kT} \langle P_{xy}(t) P_{xy}(0) \rangle \quad (19)$$

is the susceptibility. As the same process in Eq. (12) and (13), taking the integration over time t in Eq. (19), $\chi(t)$ becomes precisely the Green-Kubo integrand for the shear visco-

sity, Eq. (2). Being constant strain rate $\gamma(s)$ in the limit of $t \rightarrow \infty$ in Eq. (18), when this is combined with the integrated form of Eq. (19) the shear viscosity can be calculated by

$$\eta = \lim_{\gamma \rightarrow 0} \left[\lim_{t \rightarrow \infty} \frac{\langle P_{xy}(t) \rangle}{\gamma} \right] \quad (20)$$

The slod equations^{19,24} of translational motion for atomic molecule are given by

$$\dot{x}_i = \dot{p}_{ix}/m + \gamma y_i \quad (21a)$$

$$\dot{y}_i = \dot{p}_{iy}/m \quad (21b)$$

$$\dot{z}_i = \dot{p}_{iz}/m \quad (21c)$$

$$\dot{p}_{ix} = F_{ix} - \dot{p}_{ix} \gamma - \alpha \dot{p}_{ix} \quad (22a)$$

$$\dot{p}_{iy} = F_{iy} - \alpha \dot{p}_{iy} \quad (22b)$$

$$\dot{p}_{iz} = F_{iz} - \alpha \dot{p}_{iz} \quad (22c)$$

The constant translational temperature constraint parameter α can be derived in the same process for Eq. (17) under the same requirement, Eq. (16)

$$\alpha = \sum_i \left[(\dot{p}_{ix} \cdot F_{ix} - \dot{p}_{ix} \dot{p}_{ix} : \nabla u) \right] / \sum_i \dot{p}_i^2 \quad (23)$$

NEMD Algorithm for Thermal Conductivity.

The NEMD algorithm for thermal conductivity has been developed by Evans^{12,20} and involves the use of fictitious vector field F as the deriving force for a heat flux J_Q , Eq. (5). In the linear small external field F_x , the ensemble average of corresponding thermodynamic heat flux at time t is given by

$$\langle J_Q(t) \rangle = - \lim_{F_x \rightarrow 0} \int_0^t ds \chi(t-s) F_x(s) \quad (24)$$

where the susceptibility, χ is

$$\chi(t) = \frac{-V}{kT} \langle J_Q(t) J_Q(0) \rangle \quad (25)$$

Integrating over time t in Eq. (25) and using Eq. (3), we obtain

$$\lambda = - \frac{1}{T} \int_0^\infty dt \chi(t) \quad (26)$$

Further using Eq. (24) in the limit of $t \rightarrow \infty$ with constant $F_x(s)$, the thermal conductivity is derived as

$$\lambda = \frac{1}{T} \lim_{F_x \rightarrow 0} \left[\lim_{t \rightarrow \infty} \frac{\langle J_Q(t) \rangle}{F_x} \right] \quad (27)$$

Consider the equations of motion for atomic molecule:

$$\dot{r}_i = \dot{p}_i/m \quad (28)$$

$$\dot{p}_i = F_i + (E_i - \bar{E}) F(t) + \frac{1}{2} \sum_j F_{ij} \tau_{ij} \cdot F(t)$$

$$- \frac{1}{2N} \sum_{i,j} F_{ij} \tau_{ij} \cdot F(t) - \alpha \dot{p}_i \quad (29)$$

where E_i and \bar{E} are, respectively, the instantaneous energy of molecule i and the average energy of the system, the constant translational temperature constraint parameter, α , is

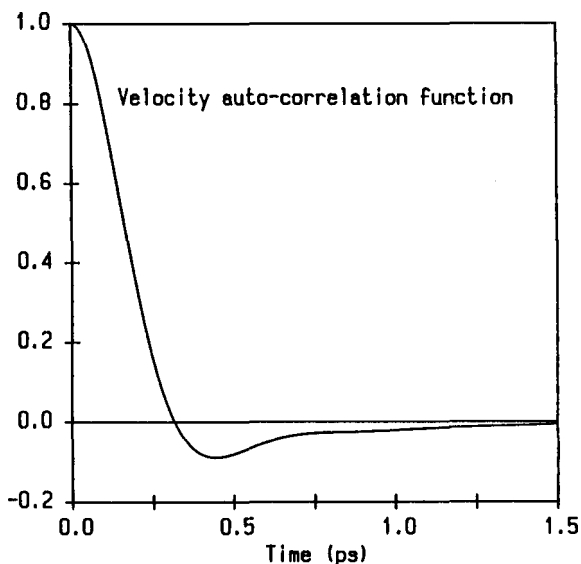


Figure 1. Normalized velocity auto-correlation function of liquid argon at 94.4 K and 1 atm.

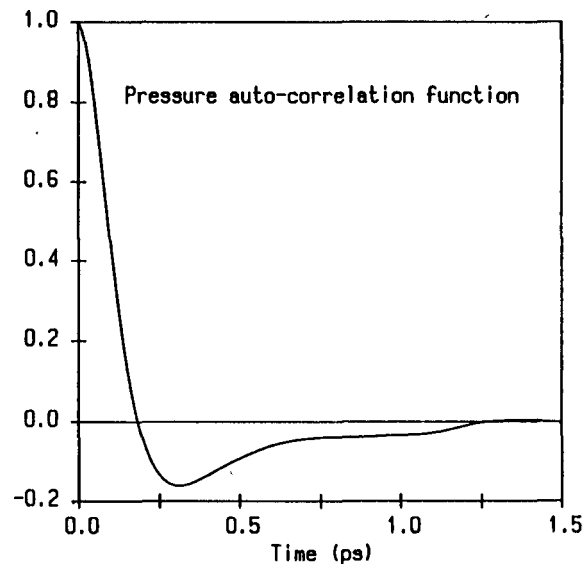


Figure 2. Normalized pressure auto-correlation function of liquid argon at 94.4 K and 1 atm.

$$\alpha = \frac{\sum_i [F_i + (E_i - \bar{E})F(t) - \frac{1}{2} \sum_j F_{ij} \tau_{ij} \cdot F(t) + \frac{1}{2N} \sum_{j,k} F_{jk} \tau_{jk} \cdot F(t)] \cdot P_i}{\sum_i p_i \cdot p_i} \quad (30)$$

and F_{ij} is the force on particle i due to j .

Details of EMD and NEMD Simulations of Liquid Argon. The usual Lennard-Jones 12-6 potential for the interaction between atoms is used with LJ parameters, $\alpha = 3.4$ Å and $\epsilon/k_B = 120$ K. The interatomic potential is truncated at 8.5 Å, the cut-off distance used in many other simulations. The preliminary canonical ensemble (NVT fixed) MD simulation of 216 argon atoms was started in the cubic box of length $L = 2.191$ Å, of which the density is equal to 1.374 g/cm³ at 94.4 K and 1 atm. The equations of motion are solved using a fifth-order predictor-corrector Gear integration²⁹ with a time step of 10^{-14} second.

Results and Discussion

In equilibrium molecular dynamics simulations, the thermal transport coefficients of gases and liquids may be calculated by using the Green-Kubo relations from various correlation functions as given in Table 1. The integrands in Eqs. (1), (2), and (3) are called the velocity, pressure, and heat flux auto-correlation functions respectively. In spite of the difficulties of calculation of correlation functions as mentioned in Sec. I, these time-correlation functions are calculated. To average the velocity auto-correlation function, the trajectories (positions and momenta) of all the particles are stored every time steps (0.01 ps). This run ends after 1,000 time steps due to the difficulty of storing a huge number of data. A set of correlation function of 0 ps to 1.5 ps is obtained from the trajectories of 1~151 time steps, another set is obtained from 2~152 time steps, and so on. The curve in Figure 1 is averaged over these 850 sets of individual curves. The curves in Figure 2 and 3 are averaged over 1850 sets of those curves which needs 2,000 time steps run.

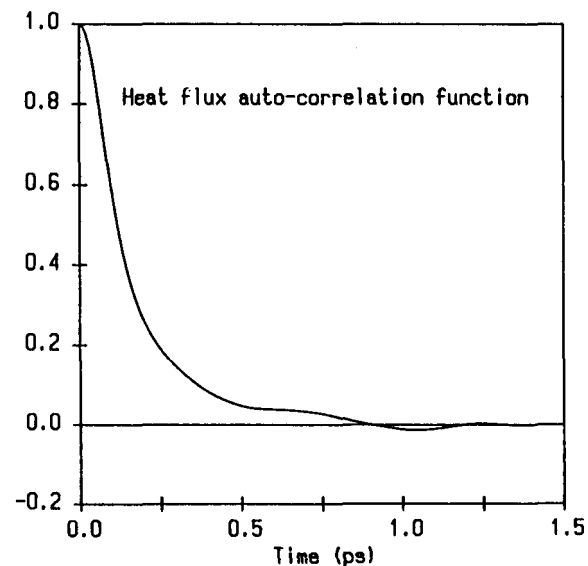


Figure 3. Normalized heat flux auto-correlation function of liquid argon at 94.4 K and 1 atm

As the factor 3 for the x -, y -, and z -components of the velocity in calculation of the self-diffusion coefficient of Eq. (1), the shear viscosity and thermal conductivity need the factors, respectively, 6 and 3 for averaging over the xy -, yx -, xz -, zx -, yz -, and zy -components of the pressure tensor P and the x -, y -, and z -components of the heat flux vector J_Q in Eqs. (2) and (3) due to the isotropic property of bulk argon.

In Figure 1-3 we have plotted the normalized velocity, pressure, heat flux auto-correlation functions of liquid argon at 94.4 K and 1 atm. In contrast to the failure to obtain the pressure and heat flux auto-correlation functions of liquid water at 298.15 K and 1 atm as reported in our later study,³⁰ these time-correlation functions show well-behaved smooth curves which are not oscillating and decaying rapidly to zero around 1.5 ps. The velocity auto-correlation function has almost the same features appeared in other Lennard-Jones

Table 2. Comparison of the Results Obtained from the Green-Kubo Relations for Thermal Transport Coefficients of Liquid Argon at 94.4 K and 1.374 g/cm³ with Those Values Obtained from Lagrange Interpolation³² of Experimental Results³³

| Transport properties | Green-Kubo results | Experimental results |
|--|--------------------|----------------------|
| Self-diffusion coefficients (10 ⁻⁵ cm ² /sec) | 2.44 | 2.83 |
| Shear viscosity (mp.) | 2.29 | 1.97 |
| Thermal conductivity (10 ⁻⁴ cal/sec · cm · K) | 1.84 | 2.74 |

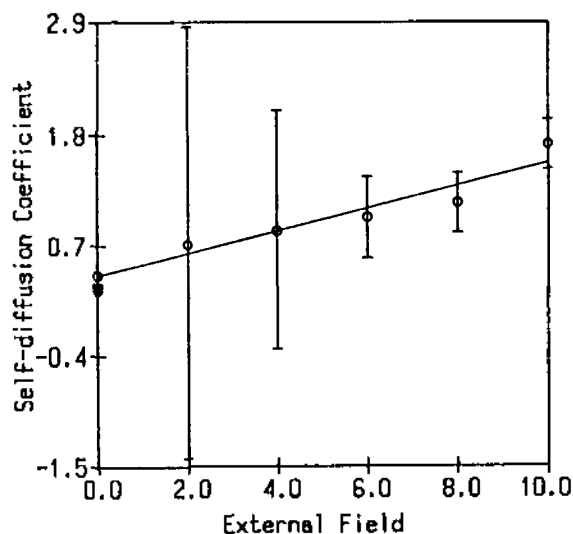


Figure 4. NEMD simulation results for the self-diffusion coefficient, in the unit of 10⁻⁴ cm²/sec, of liquid argon at 94.4 K and 1 atm as a function of external field (g·nm/mol·ps²). The white circle at zero external field is obtained by least squares fit of the results to a straight line. □ is an experimental result and the black circle represents the EMD result obtained from the Green-Kubo relation. The error bars indicate the standard deviation.

particle computer simulation.³¹ The negative region of this correlation function indicates that it is probable that the particle changes its movement to a direction opposite that which it had at $t=0$, due to a collision with the nearest particle. The pressure auto-correlation function shows the same behavior as the velocity auto-correlation function with faster and deeper rebound of correlation even though the pressure is a collective property against a wall of the system not like the velocity of individual particles. On the other hand, the heat flux auto-correlation function is somewhat different from the correlation of mechanical quantities; there is no rebound of the energy current but just vanishment.

The upper integration limit $t \rightarrow \infty$ in the Green-Kubo relations, Eqs. (1)-(3), may be replaced by a finite value since the time-correlation functions decay rapidly to zero. The EMD results for the self-diffusion coefficient, shear viscosity, and thermal conductivity of liquid argon at 94.4 K and 1 atm are given in Table 2 with those values obtained for the same temperature and pressure from Lagrange interpo-

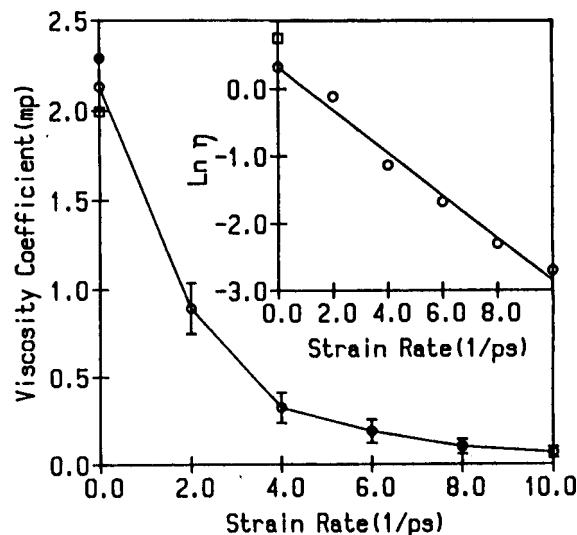


Figure 5. NEMD simulation results for the shear viscosity, in the unit of mp of liquid argon at 94.4 K and 1 atm as a function of strain rate (ps⁻¹). The white circle at zero external field is obtained by Lagrange extrapolation.³² □ is an experimental result and the black circle represents the EMD result obtained from the Green-Kubo relation. The error bars indicate the standard deviation.

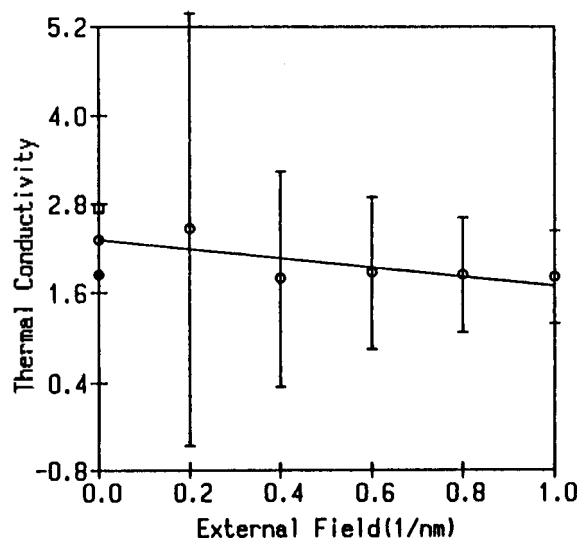


Figure 6. NEMD simulation results for the thermal conductivity, in the unit of milli-watt/cm·K, of liquid argon at 94.4 K and 1 atm as a function of external field (nm⁻¹). The white circle at zero external field is obtained by least squares fit of the results to a straight line. □ is an experimental result and the black circle represents the EMD result obtained from the Green-Kubo relation. The error bars indicate the standard deviation.

lation³² of experimental data.³³ The overall agreement is quite good. This means that the Green-Kubo relations are valid for simple liquids and that our equilibrium molecular dynamics (EMD) simulation works properly.

The results of non-equilibrium molecular dynamics simulations for the self-diffusion coefficient, shear viscosity, and thermal conductivity of argon at 94.4 K and 1 atm are shown

Table 3. NEMD Simulation Results for the Self-diffusion Coefficient (D_s), Shear Viscosity (η), and Thermal Conductivity (λ) of Liquid Argon at 94.4 K and 1.374 g/cm³. D_s and λ at Zero External Field are Obtained by Least Squares Fit of the Results to a Straight Line and η is Obtained by Lagrange Extrapolation³²

| External field (g·nm/mol·ps ²) | 10.0 | 8.0 | 6.0 | 4.0 | 2.0 | 0.0 |
|---|--------------|-------------|-------------|-------------|-------------|-------|
| Self-diffusion coefficients (10 ⁻⁵ cm ² /sec) | 17.12 ± | 11.36 ± | 9.91 ± | 8.55 ± | 7.18 ± | 4.02 |
| Strain rate (ps ⁻¹) | 10.0 | 8.0 | 6.0 | 4.0 | 2.0 | 0.0 |
| Shear viscosity (mp.) | 0.06715 ± | 0.1002 ± | 0.1877 ± | 0.3224 ± | 0.8927 ± | 2.133 |
| External field (nm ⁻¹) | 10.0 | 8.0 | 6.0 | 4.0 | 2.0 | 0.0 |
| Thermal conductivity (10 ⁻⁴ cal/sec·cm·K) | 1.819 ± | 1.848 ± | 1.876 ± | 1.798 ± | 2.460 ± | 2.309 |
| | 0.615 | 0.764 | 1.016 | 1.447 | 2.919 | |

in Figures 4-6 and in Table 3. Each NEMD simulation result is averaged over 20,000 time steps after simulation runs of 10,000~20,000 time steps to reach a steady state. The self-diffusion coefficient and the thermal conductivity at zero external field are obtained by least squares fit of the non-zero external field results to a straight line, and the shear viscosity is obtained by Lagrange extrapolation at zero external field.³²

As shown in Figure 4, the standard deviation tells us huge fluctuations of simulation results especially in small external fields. Nevertheless, the average values of self-diffusion coefficients at non-zero external field are almost on a straight line and the least-square-fitted self-diffusion coefficient at zero external field is found to be approximately 40% higher than the experimental result (□). Comparing with the EMD result (●) obtained from the Green-Kubo relation, the NEMD result is less accurate.

Figure 5 shows that the Lagrange extrapolated shear viscosity at zero strain rate is within only 8% error when compared with the corresponding experimental result (□). It appears that as the strain is decreased the shear viscosity increases but it does not seem that the shear viscosity shows the square-root behaviour, as Cummings and coworkers expected in their NEMD studies.²¹⁻²³ Rather the asymptotic relation of the calculated shear viscosity may have an exponential form, $\eta = b \cdot \exp(-a\gamma)$. As shown in the inserted figure, the logarithm of η , $\ln \eta$, is plotted against γ and a strain line ($a=0.3172$ and $b=1.376$) is obtained by least squares fit. The shear viscosity (●) at zero strain is underestimated by 30% in comparison with the experimental result (□).

Many studies of NEMD of Lennard-Jones particles for

thermal conductivity calculation at various temperatures²⁰ including the triple-point region¹² are reported. Our result at 94.4 K and 1 atm is agreed with those results. As shown in Figure 6, the agreement between our results (NEMD and EMD) and the experimental result is quite good. This means that the Green-Kubo relation and the Evans algorithm (Sec. II. (3)) for thermal conductivity calculation of simple liquids are reliable.

Concluding Remarks

In this study, we purpose to perform the equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations to determine the thermal transport coefficients (the self-diffusion coefficient, shear viscosity, and thermal conductivity) of liquid argon at 94.40 K and 1 atm, by using a simple Lennard-Jones potential model for the interactions between the argon atoms at the microscopic level. The results obtained from the EMD simulations of Lennard-Jones model using the Green-Kubo relations (Sec. I) indicate that the time-correlation functions show well-behaved smooth curves which is integrated to give the reasonable thermal transport coefficients directly. The results of the NEMD simulations of the same model give quite good overall agreements even though there are more or less statistical errors. During simulations, it is also observed that the Gauss's principle of least constraint for constant translational temperatures works excellent, which means the achievement of $\pm 0.01\%$ accuracy in temperatures.

To conclude, what is clear is that based on this work, the application of the Green-Kubo relations and the NEMD algorithm for thermal transport coefficients of simple liquids is successful. Further study should assess the ability of calculation of another transport coefficient, the bulk viscosity κ , this would not be easily done because of the unknown external field applied to the system to calculate κ or because it may need NPT ensemble NEMD simulation.

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Non-equilibrium Molecular Dynamics Simulations of Thermal Transport Coefficients of Liquid Water

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In a recent paper¹ we reported equilibrium (EMD) and non-equilibrium (NEMD) molecular dynamics simulations of liquid argon using the Green-Kubo relations and NEMD algorithms to calculate the thermal transport coefficients—the self-diffusion coefficient, shear viscosity, and thermal conductivity. The overall agreement with experimental data is quite good. In this paper the same technique is applied to calculate the thermal transport coefficients of liquid water at 298.15 K and 1 atm using TIP4P model for the interaction between water molecules. The EMD results show difficulty to apply the Green-Kubo relations since the time-correlation functions of liquid water are oscillating and not decaying rapidly enough except the velocity auto-correlation function. The NEMD results are found to be within approximately $\pm 30\sim 40\%$ error bars, which makes it possible to apply the NEMD technique to other molecular liquids.

Introduction

In recent years, the non-equilibrium molecular dynamics (NEMD) simulations have emerged as a powerful tool for the study of thermal transport coefficients - self-diffusion coefficient, shear and bulk viscosities, and thermal conductivity of both simple and molecular fluids. Recent development include the sllod algorithm^{2,3} for shear viscosity, the color current technique⁴ for self-diffusion coefficient, the Evans algorithm^{5,6} for thermal conductivity, and the use of Gauss's principle^{4,7} of least constraint for isokinetic and/or isobaric ensemble simulations. More recently a homogeneous NEMD simulation⁸ to investigate the nature of liquid sulfur under extreme shear using the potential model developed by Stil-

linger and Weber⁹ which involves three-body interaction is reported. Furthermore the principle of the color current algorithm is applied to non-equilibrium Brownian dynamics (NEBD) simulations,¹⁰ in which the non-equilibrium state is achieved by including a constant electric field in the Smoluchowski dynamics, to calculate the self-diffusion coefficients of the ions in a model electrolyte solutions.

In a recent paper¹ we reported equilibrium molecular dynamics (Green-Kubo relations¹¹) and non-equilibrium molecular dynamics simulations of liquid argon at 94.4 K and 1 atm to determine the thermal transport coefficients. The overall agreement of the EMD and NEMD results is quite good in comparison with experimental data. This means that the Green-Kubo relations and the NEMD algorithms are re-