The Second Relaxation Process for Thermal Conduction in Rare-Gas Crystals

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The thermal conductivity for solid Argon has been calculated by the equilibrium molecular dynamics method with the Green-Kubo formula. The results for the temperature dependence of thermal conductivity for the free standing condition agree well with experiments. We have found that the heat flux autocorrelation function consists of two stages which decrease exponentially and the presence of the second long time stage is significant in the lower temperature region and disappear as the temperature is increased toward the melting point.

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I. INTRODUCTION

We have performed equilibrimum molecular dynamics simulation to calculate the thermal conductivity for the Argon crystal using the Lennard-Jones potential. We have employed the Green-Kubo method to derive the temperature dependence of thermal conductiviy and compared the results with experiment, and also studied the behavior of heat flux autocorrelation function.

The present molecular dynamics simulation was carried out using the total number of particles of $N = 256$ with the periodic boundary condition. The fifth-order predictor-corrector (Gear) method was used to numerically integarte the equation of motion with the total time steps of 10^7. The time step was set as $10fs$ and the simulation was started from the initial f.c.c. crystal state with random velocities. The standard constants for the Lennard-Jones potential of $\epsilon = 119.8[K], \sigma = 3.405[\mathring{A}]$ were employed. The thermal conductivity was estimated by the time integration of the heat flux autocorrelation function using the following Green-Kubo formula

$$\kappa = \frac{1}{3Vk_BT^2} \int_0^\infty < \mathbf{J}(t) \cdot \mathbf{J}(0) > dt, \qquad (1.1)$$

where the heat flux $\mathbf{J}$ was

$$\mathbf{J} = \sum_i E_i \mathbf{v}_i + \frac{1}{2} \sum_{\substack{i>j \\ pairs}} \mathbf{r}_{ij} [\mathbf{F}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)]. \qquad (1.2)$$

The heat flux autocorrelation function was directly determined by taking averages during the time advancement. Firstly, the simulation with the total time step of 10^6 was performed to determine the thermal conductivity. In the case of $10K$ case, almost 10^4 time steps were needed for the heat flux autocorrelation function to converge to the zero value. However, the point of zero crossing value was found to change largely with each case. Therefore, the simulation with the total time step of 10^7 was performed to take ten ensemble averages to obtain the final smooth autocorrelation function.

II. THERMAL CONDUCTIVITY AND HEAT FLUX AUTOCORRELATION FUNCTION

Figure 1 shows the temperature dependence of thermal conductivity under the free standing condition, in which the comparison of molecular dynamics and experimental data was made. Here, in the molecular dynamics simulation, the free standing condition was achieved by varying the desity to realize the almost zero pressure condition. The errors incurred by determining the absolute values of thermal conductivity is between 5 to 10%. The temperature dependence of thermal conductivity was measured in the molecular dynamics simulation for six different temperatures at $10, 20, 35, 50, 70$ and $100K$. The numerical results of temperature dependence of thermal conductivity for the free standing case decrese more rapidly than T^{-1}, and show the same tendency as the experimental results. The absolute values of estimated thermal conductivity are found to be lower than experiments. The temperature dependence of thermal conductivity for the molecular dynamics data was fitted to the function T^{-n}, and the best fit value of the coefficient n was found to be 1.516 ± 0.006. The experimental data were well fitted to the function T^{-n} with $n = 1.5$ and the experimental absolute value of thermal conductivity was found to be 1.90 times larger than the molecular dynamics data. This fitted value was used for estimating the constant σ in the Lennard-Jones potential by keeping ϵ constant. The experimentally fitted σ was found to be $2.473[\AA]$. In order to check the size effects, the simulations with the total number of particle of $N = 512$ and $N = 1024$ were performed for the total time steps of 10^6 and 10^7. Since the $N = 512$ and 1024 case give almost the same results as the $N = 256$ case, the system with $N = 256$ particles is found to be large enough in the present temperature range. In estimating the temperatures, only the classical approximation is employed here and no distinction is made between the molecular dynamics temperature and the real temperature because the differece in temperatures due to the distribution of phonons is not significant even at the lowest temperature $T = 10K$. The thermal conductivity of Argon crystal is sesitively dependent on the molar volume, and the experiment by Clayton and Batchelder[2] was performed under the constant molar volume condition. The temperature dependence of thermal conductivity under this condition was also derived by the molecular dynamics method, and is found to follow the T^{-1} relation. However, in experiments, molar volumes slightly change as the temperature is varied, so that this case is inappropriate for comparison purposes.

All the theoretical calculations based on the three phonon interactions underestimate the thermal conductivity compared to experiments[3,4], except for the recent calculation by Omini and Sparavigna[5].

Figure 2 shows the heat flux autocorrelation function for the free standing condition at $20K$ and $70K$. The absolute values are rescaled by the maximum $t = 0$ value $< \mathbf{J}(0) \cdot \mathbf{J}(0) >$. The figure clearly indicates the existence of two stages, consisting of rapidly and slowly exponentially decaying stages. The first stage fitted to the exponential function is shown in Fig.2. This indicates that the second stage is more pronounced at the lower temperature. The heat flux autocorrelation function relaxes mostly by the rapidly decreasing first stage at the higher temperature. The second stage of the autocorrelation function at $20K$ shows the same oscillatory motion as observed in the paper using the pairwise-additive inverse-twelfth-power potential by Ladd, Moran, and Hoover[1].

Figure 3 shows the temperature dependence of the second long time stage for the free standing condition. Heat flux autocorrelation function corresponding to the measured temperatures $(10, 20, 35, 50, 70, 100$ K$)$ are shown in Fig.3. It is clearly seen that the two-stage process converges to the one-stage process as the temperature is increased. In the lower temperature region, the autocorrelation tends to have a long time exponentially decreasing second stage, and this second stage disappears as the temperature is increased. At 100 K, the correlation is relaxed almost by the single exponential process.

III. DISCUSSION

It is considered that the first stage, which persists even at higher temperatures, is related to the intrinsic anharmonic phonon scattering of the Umklapp process. On the other hand, the long time second stage, which tends to appear in the lower temperatures, is considered to be related to the normal three phonon process which tends to redistribute phonon energies and whose contribution becomes significant near the thermal conductivity peak.

ACKNOWLEDGMENTS

[1] A.J.C.Ladd, B.Moran, and W.G.Hoover, Phys.Rev.B **34**, 5058 (1986).

[2] F.Clayton and D.N.Batchelder, J. Phys. C **6**, 1213 (1973).

[3] C.L.Julian, Phys.Rev. **137**, A128 (1965).

[4] G.Niklasson, Phys.kondens.Materie 14,138(1972).

[5] M.Omini and A.Sparavigna, Phys.Rev.B **35**, 9064(1996-II).

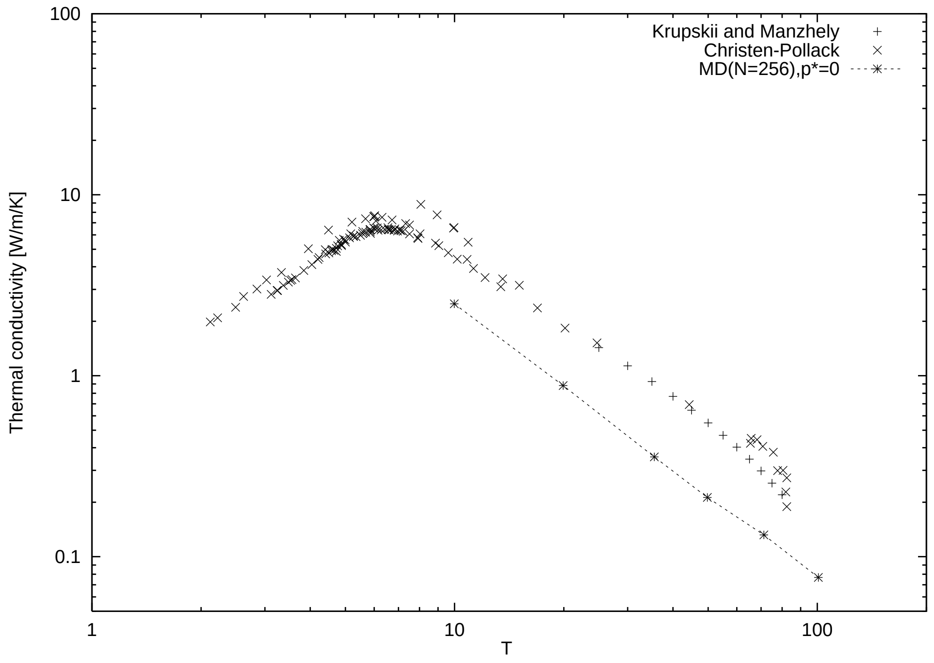

FIG. 1. Thermal conductivity of solid Argon as a function of temperature at free standing condition.

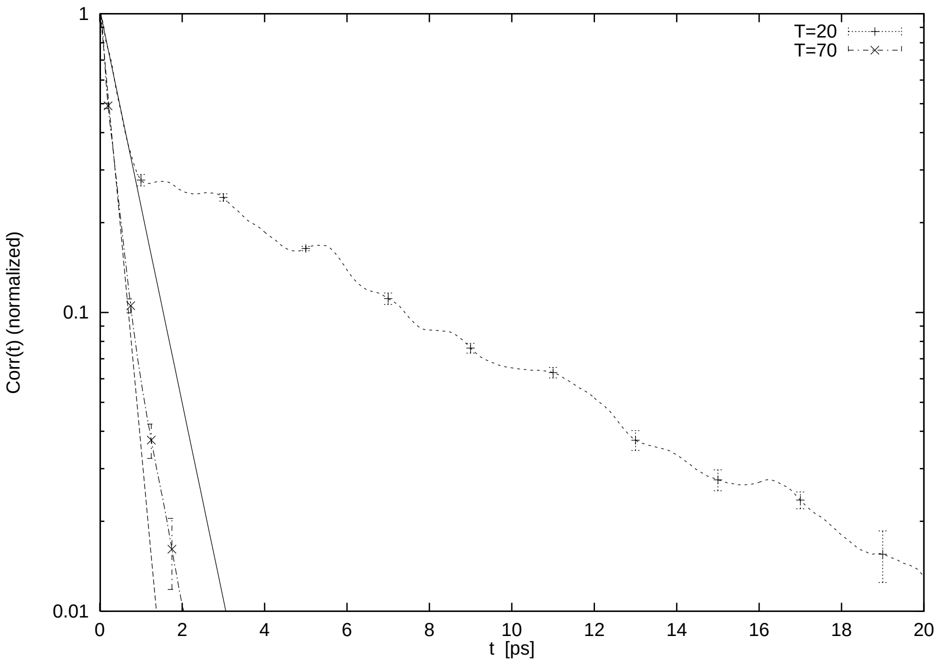

FIG. 2. Heat flux autocorrelation function at $T = 20K$ and $T = 70K$.

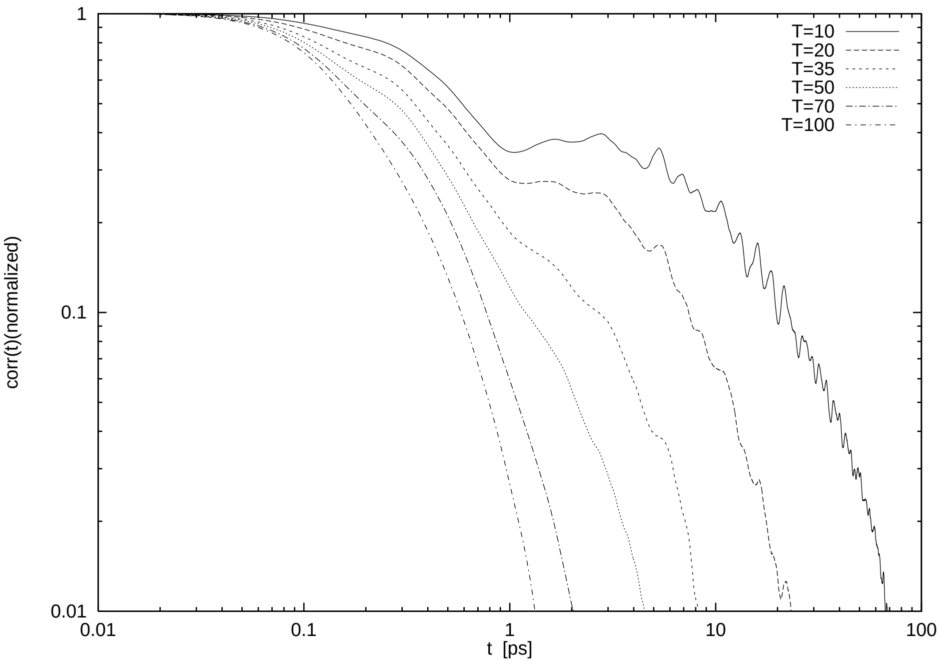

FIG. 3. Temperature dependence of the second stage for the heat flux autocorrelation function.

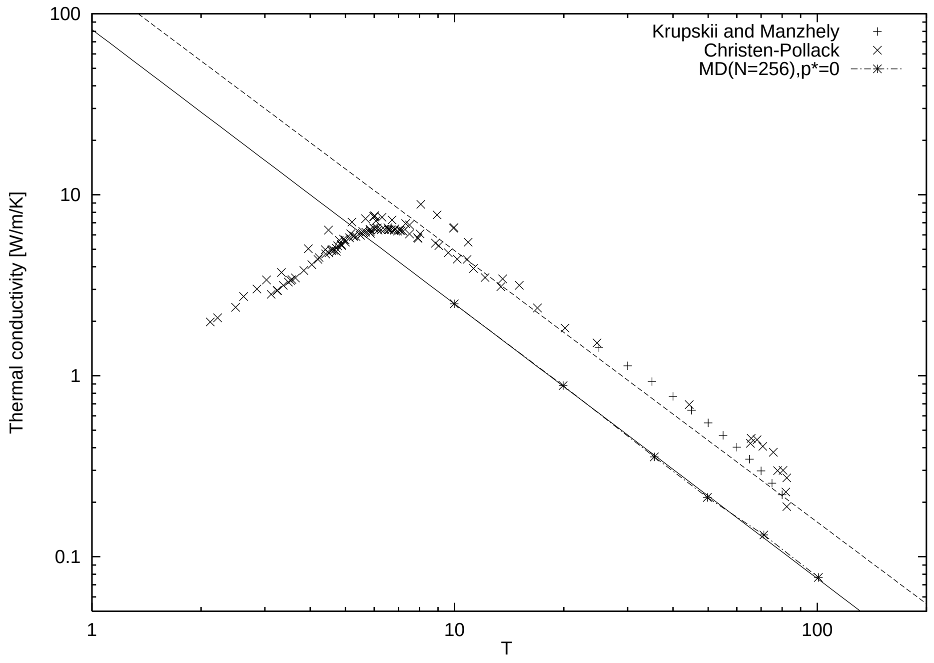

FIG. 4. For reference:Fitting the MD and experimental data for Argon.