# THERMAL CONDUCTIVITY OF SOLID ARGON BY CLASSICAL MOLECULAR DYNAMICS

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## ABSTRACT

Following the Green-Kubo formalism in linear response theory, the lattice thermal conductivity of solid argon is determined by using classical molecular dynamics simulation to calculate the heat current correlation function. Comparing the absolute conductivities obtained using the Lennard-Jones potential with experiments, we find the predicted results to uniformly underestimate the measurements in magnitude, whereas the calculated temperature dependence corresponds well with the data. The temporal behavior of the heat current autocorrelation function shows that while a single exponential decay description is appropriate at elevated temperatures, below the half of the Debye temperature, the heat current relaxation clearly consists of two stages, an initial rapid decay associated with local dynamics followed by a slower component associated with the dynamics of lattice vibrations (phonons).

## INTRODUCTION

Molecular dynamics simulation is by now a well established method for calculating transport properties of liquids, especially when a reliable interatomic potential model is available [1]. For rare-gas systems the Lennard-Jones pair potential has long been in use as a reference model. While generally useful for qualitative purposes, it is known to have limitations associated with the neglect of many-body or quantum effects [2, 3].Thermal conductivity happens to be a property for which the Lennard-Jones potential has given results for liquid argon which are in quite good agreement with experiment [4]. Thus it may be expected that using this model to describe solid argon should meet with similar success.

In contrast to liquid-state studies, the use of molecular dynamics simulation to analyze thermal conduction in solids has been relatively limited [5, 6, 7, 8, 9]. None of these studies to date can claim to provide an unambiguous demonstration of the quantitative accuracy of this method against experimental data. On the other hand, several attempts at phonon scattering calculations in the analysis of thermal conduction in rare-gas crystals have been reported [10, 11, 12], showing varying degrees of agreement with experiments. Because each calculation involves certain approximations, it is at present unclear how one can separate the issue of validity of the potential model from that of the theoretical assumptions.

In this work we report the calculation of thermal conductivity of single crystal argon using classical molecular dynamics in conjunction with the conventional model of Lennard-Jones interatomic pair potential. Besides the goal of establishing a benchmark for the prediction of thermal conductivity of a solid, our motivation also includes understanding further the dynamical details of thermal conduction in a crystalline lattice. We have obtained results at constant pressure (P=0) which span the entire temperature range down to 10 K. Fitting our simulation data to $T^{-n}$, we find, whereas fitting the experimental data in the same way gives n = 1.5. For the magnitude of the conductivity coefficient, we find the experimental values to be uniformly greater by about a factor of 1.9. As indicated below, we regard this discrepancy as largely associated with the interatomic potential model.

According to the Green-Kubo formalism [5], the thermal conductivity is given by the time interval of the heat current autocorrelation function $< \mathbf{J}(t)\mathbf{J}(0) >$. In this approach, besides the numerical value of the thermal conductivity, one can probe the dynamics of thermal conduction through the temporal decay of the correlation function. Our results show that near the melting point the relaxation of $< \mathbf{J}(t)\mathbf{J}(0) >$ can be reasonably well described as a single exponential decay. As temperature is lowered past the half of the Debye temperature (about 80-90K), a second (slower) relaxation component becomes discernible.

## THERMAL CONDUCTIVITY AND HEAT CURRENT AUTOCORRELATION FUNCTION

Our simulations were carried out using a periodic cell containing $N$ argon atoms which interact through the Lennard-Jones 6-12 potential with constants $\epsilon = 119.8[K], \sigma = 3.405[\AA]$. While most runs were made with $N = 256$, a few runs also have been made with $N = 500$. Fifth-order predictor-corrector (Gear) method was used to integrate the equations of motion with a time step size of $10fs$. The thermal conductivity is given by

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

where the heat current $\mathbf{J}$ is

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

The heat current autocorrelation function was obtained by averaging over a number of time origins. Typically a simulation run of $10^6$ time steps was performed to determine the thermal conductivity. In the case of $10K$, almost $10^4$ time steps were needed for the autocorrelation function to decay to zero value. Also, the point of zero crossing was found to vary appreciably from one run to another . Therefore, a long run of $10^7$ steps was made to obtain ten samples which were then averaged to give the final smooth autocorrelation function.

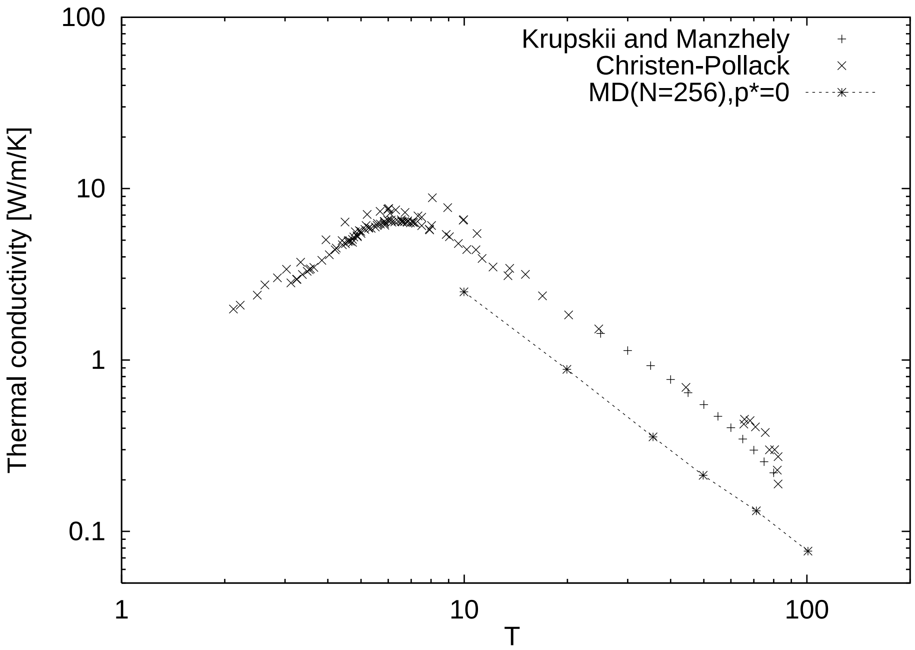


Figure 1: Temperature dependence of thermal conductivity of solid argon under the free standing condition.

Figure 1 shows the calculated thermal conductivity at six temperatures, $10, 20, 35, 50, 70$ and $100K$, under the free standing condition, achieved in each case by varying the density to maintain effectively zero pressure. Errors incurred in determining the absolute values of the conductivity are estimated to be between $5$ to $10\%$.It is found that these data exhibit a temperature dependence varying more rapidly than $T^{-1}$. Fitting the data to $T^{-n}$ gives $n$ = $1.516 \pm 0.006$.

Figure 1 also shows two sets of experimental data [13, 14]. We first note that the temperature variation of simulation results is very similar to that observed. A good fit of the experimental results is obtained with $n = 1.5$. Secondly the magnitude of the calculated conductivity is uniformly low compared to the experiments, by a factor of about 0.52.

As a test of system size effects, additional simulations with $N = 500$ were performed for $10^6$ and $10^7$ steps. As shown in Figure 2, there appears to be little change in going from $N = 256$ to $N = 500$. It should be noted that we have made no attempt to introduce any correction for quantum effects [6, 9]. This is because zero-point motion effects are not significant in the thermal conductivity of argon, even at the lowest temperature studied, $T = 10K$.

The thermal conductivity of argon crystal is known to be sensitive to variations in molar volume. We have performed several constant volume simulations , obtaining the conductivity values shown in Figure 3. From these results we find a $T^{-1}$ temperature variation which is sometimes taken to be a rough estimate of the phonon lifetime at high temperatures. Also shown in Figure 3 are the measurements at constant molar volume [15]. A comparison of the simulation results with these data over the range of molar volume studied at 70K, given in Figure 4, shows the same trend of increasing conductivity with decreasing volume.

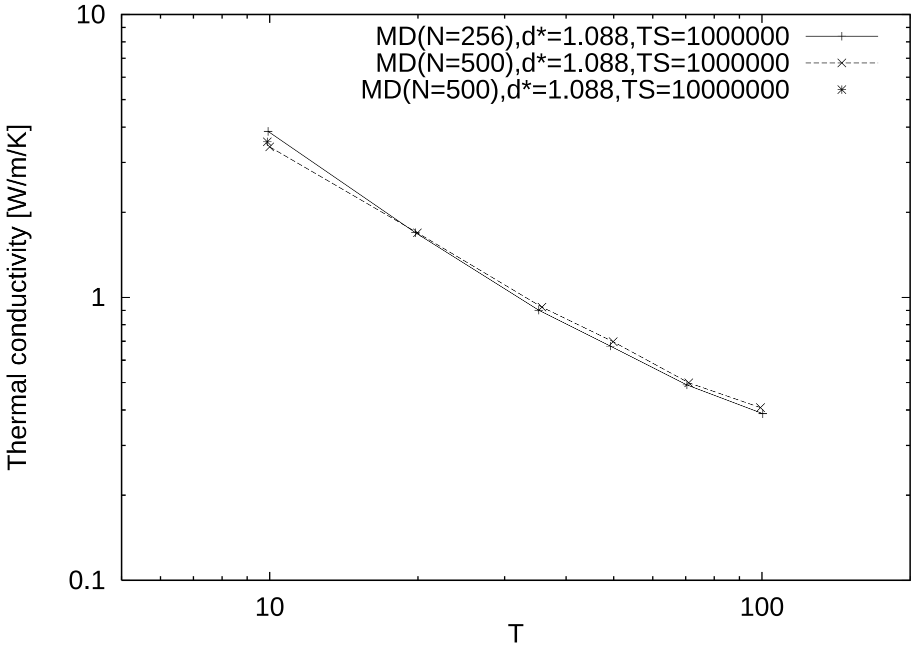


Figure 2: System size effect of thermal conductivity of solid argon.

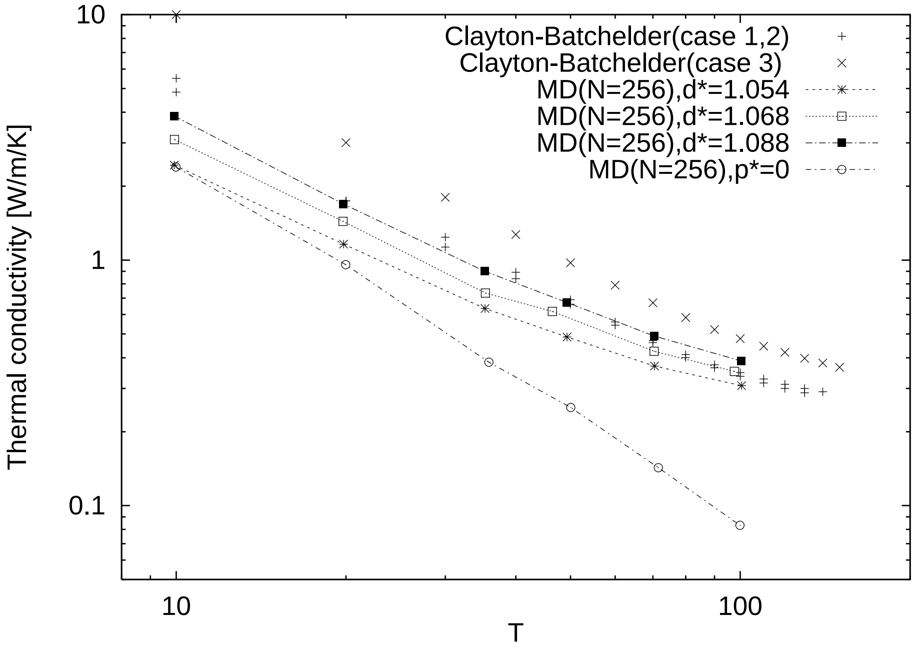


Figure 3: Temperature dependence of thermal conductivity of solid argon under constant molar volume conditions.

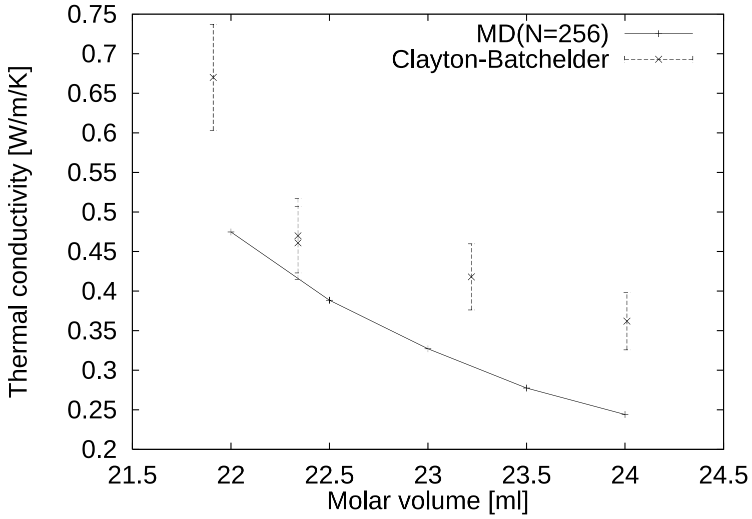


Figure 4: Molar volume dependence of thermal conductivity of solid argon at 70K.

Figure 5 shows the heat current 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 existence of a two-stage decay at the lower temperature can be seen clearly. In the composite of the six temperatures we have studied, Figure 6, the systematic appearance of the second relaxation component becomes increasingly more pronounced as the temperature is lowered. We interpret the initial rapid decay as characteristic of local dynamics, while the slower decay is associated with the dynamics of phonon transport, the collective effects of lattice vibrations.

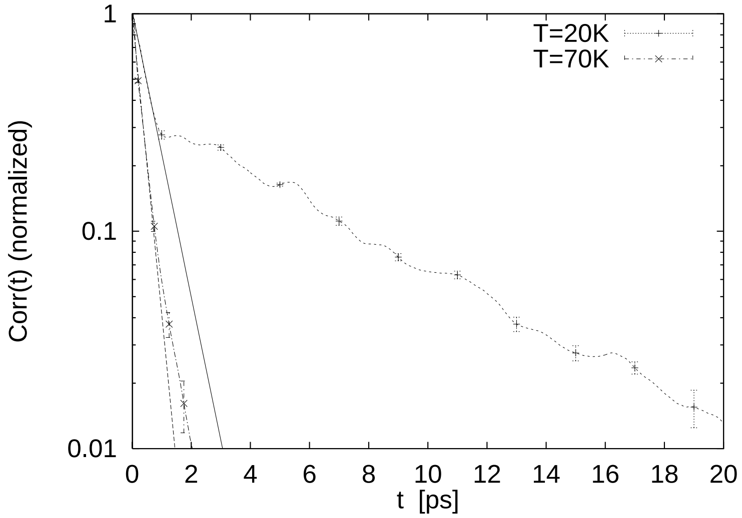


Figure 5: The heat current autocorrelation function for the free standing condition at 20K and 70K.

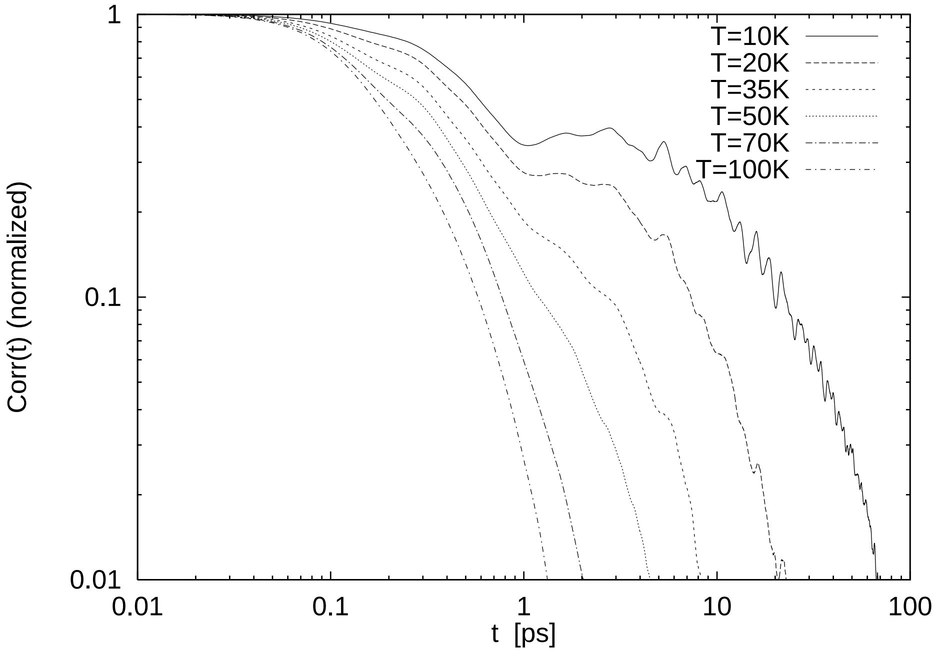


Figure 6: Temperature dependence of the second relaxation component for the heat current autocorrelation function.

## DISCUSSION

This work has a two-fold purpose. The first is to establish how well one can predict the thermal conductivity of a simple solid such as argon for which a reasonably well established interatomic potential model is available. We find that the conventional Lennard-Jones potential gives results which are lower than the experiment. In view of the fact that the same potential gives quite good agreement in the case of liquid argon [4], this discrepancy may be interpreted as an inadequacy of the model potential. We have confirmed that this is indeed the case by performing the same thermal conductivity calculation using a recently improved pair potential [16]. Our second purpose is to probe the dynamics of thermal conduction through a study of the decay of the heat current correlation function. This is felt to be useful since the theoretical analyses to date [10, 11, 12] are concerned with the direct calculation of the thermal conductivity, or equivalently an effective relaxation time, in which case the dynamics are revealed only indirectly through the temperature dependence. In the results presented here we have seen that the relaxation of the heat current correlation at moderate to low temperatures exhibits two stages. It would be worthwhile to analyze the simulation results further to clarify the role of phonon interactions which are of a collective nature as opposed to the short-time relaxation which necessarily reflects the short-range or local interatomic interactions. This work is in progress and will be reported in the near future.

## ACKNOWLEDGMENTS

Work of J. Li and S. Yip is supported by AFOSR Grant No. F49620-1-0447.

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