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Dynamical thermal conductivity of argon crystal

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The thermal conductivity of a rare-gas crystal (Ar) is computed using equilibrium molecular dynamics in conjunction with the Green-Kubo linear response formalism, and the Lennard-Jones potential with an appropriately long cutoff (4σ). Besides predicting absolute values of the conductivity from low temperature up to the liquid, the approach allows heat conduction to be understood as a dynamical process through the temporal behavior of the heat current correlation function. At low temperatures the correlation function shows a characteristic two-stage decay, a short-time relaxation which we attribute to single-particle motions in a local environment, and a more extended component corresponding to collective atomic motions (phonons). As temperature increases the second correlation component diminishes much faster than the first component, indicating a transition from mainly phase-coherent phonon transport to mainly phase-incoherent interatomic energy transfer in solids. © *2007 American Institute of Physics*.

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I. INTRODUCTION

Theoretical analyses of the thermal conductivity of dielectric crystals have long been performed using the phonon Boltzmann equation.[1–5] A drawback of the phonon scattering approach is that the derivations and numerical computations become quite complicated when three-, four-, and higher-order phonon scattering processes are to be taken into account. In contrast, equilibrium molecular dynamics (MD) simulation[6] combined with the Green-Kubo formalism[7–10] is known to be effective in probing transport phenomena in liquids.[10,11] Since the numerical solution of Newton's equations of motion is no more difficult for solids, one would think MD is also appropriate for crystal lattices. With a few exceptions,[12–15] this approach for probing the dynamical processes of heat conduction in solids has not been discussed.

Crystal argon is a natural choice for a benchmark study of lattice thermal conductivity. The interatomic forces in this system are known to be adequately described by the Lennard-Jones pair potential. Second, experimental data[16,17] are available for validating the accuracy of the simulation results. In this article we present absolute conductivity values at zero pressure over the temperature range 10 to 70 K and compare with experimental data and previous MD results[14,15] to show the level of agreement one can expect from MD simulations. We then examine the temperature effects on heat current correlation $A(\tau) \equiv \langle \mathbf{J}(0)\cdot\mathbf{J}(\tau)\rangle$ as the system goes from low temperature to a liquid. As we will show, this allows one to assess the relative role of single-particle motions versus collective modes of lattice vibrations without any *a priori* assumptions concerning the many-body dynamics.

II. THERMAL CONDUCTIVITY DETERMINED FROM THE HEAT CURRENT CORRELATION FUNCTION

We apply the Green-Kubo formula,[7–10] which gives the thermal conductivity as the time integral of a current correlation function,

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \boldsymbol{J}(t)\cdot\boldsymbol{J}(0)\rangle dt, \tag{1}$$

where $\boldsymbol{J}$ is the heat current,

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

The heat current is evaluated by NVE-MD simulation of a periodic system of N argon atoms interacting through the pair potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{3}$$

with $\varepsilon = 119.8[\mathrm{K}]$, $\sigma = 3.405[\text{Å}]$. The Beeman method[18] is used to integrate the equations of motion with a time step of 2 fs. In a preliminary study[13] using a potential cutoff at 2.5σ, it was found that the pressure correction to the thermal

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[a)] Electronic mail: kaburaki.hideo@jaea.go.jp conductivity could not be ignored. In the present study we use a cutoff at 4σ, a sufficiently long range to make the pressure correction negligible.

Values of the thermal conductivity $\kappa(T)$ at constant pressure $(P=0)$ are determined over the temperature range 10 to 70 K under freestanding condition by applying the Nosé–Hoover thermostat[19] and the Parrinello–Rahman method[20] of maintaining the system at zero pressure. When equilibrium is reached at the desired condition, the simulation is changed to the microcanonical condition to calculate the heat current correlation function in the NVE ensemble. As a sensitivity test of system size, simulations are performed with the system size N varying from 256 to 1024 for 10^6 and 10^7 steps. The results are found to show little change from the $N=256$ case. The optimum condition for obtaining smooth correlation curves seems to be $N=864$ with 10^7 time steps; about 100 time origins are extracted from a single long trajectory and averaged to compute the heat flux correlation function. All the simulation results presented here are obtained in this manner. No attempt is made to account for quantum effects because zero-point motion effects are not significant even at the lowest temperature studied, $T=10$ K.[21]

To isolate the effects of harmonic interaction, we have expanded the total crystal potential in powers of the atomic displacements from the equilibrium positions, and keeping terms to second order in the displacements, $\Phi \approx \Phi_0 + \Phi_1 + \Phi_2$,[22] where Φ_0 is the total potential energy of the crystal with all particles at their equilibrium positions, Φ_1 is the linear energy term at equilibrium which vanishes by definition, and Φ_2 is the harmonic potential. For the harmonic system simulations, atom configurations from the full crystal potential simulations at different temperatures are used as an initial condition. Since there is no mixing among modes in the harmonic system, the data are averaged over five independent runs, each with a different initial configuration.

III. RESULTS

The absolute values of the thermal conductivity of crystal argon determined in the manner just described are shown in Fig. 1, along with available experimental data from the literature.[16,17] The numerical values are also given in Table I. Errors in the simulation results are estimated to be 5–10%. While we regard the agreement between predictions and experiments to be satisfactory at 10, 20, 30, and 70 K, one can discern an underestimate at 40 and 50 K. Also shown in Fig. 2 are the MD results reported by McGaughey and Kaviany for the same Lennard-Jones potential system of $N=256$ and a cutoff radius of about 2.5σ using the pressure correction,[14] and $N=864$ and a cutoff radius of 2.5σ without using the pressure correction,[15] and all other conditions being essentially the same. The fact that the former McGaughey–Kaviany results with a smaller system of $N=256$ using the pressure correction are in quite close agreement with our values, obtained entirely independent of each other, is reassuring for both studies. By the same token, the consequence of cutting off an interatomic potential prematurely in determining the thermal conductivity are clearly demonstrated by the comparison with the latter McGaughey-Kaviany results. Since presenting our initial results based on a cutoff of 2.5σ,[13] we have checked on the effects of potential truncation and found an underestimate of the conductivity, particularly at low temperatures, would result from a short cutoff radius.

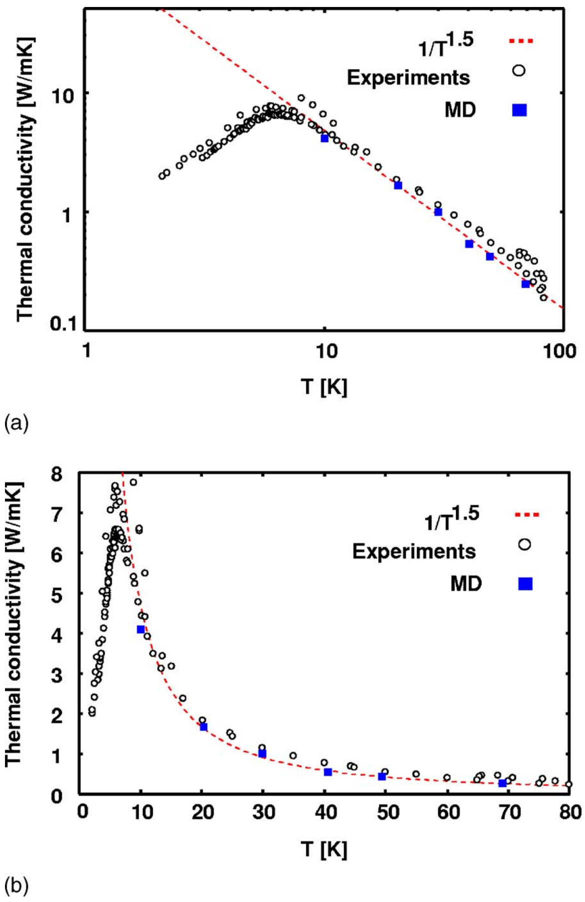

FIG. 1. (Color online) Thermal conductivity data for simulation and experiment (Refs. 16 and 17) as a function of temperature (a) in the doubly logarithmic scale, and (b) in the linear scale.

We note that in another study of absolute thermal conductivity of SiC,[12] which is a more complex crystal, the overall level of agreement between prediction and experiment is comparable to what is found here. Besides the potential cutoff effect, we are not aware of any systematic factor in the MD-linear response methodology itself that would lead to underestimating the conductivity. The present simulation results do not extend below 10 K, where quantum

TABLE I. Values of thermal conductivity of argon crystal obtained by MD simulation.

Temperature [K]	Thermal conductivity [W/mK]
10.0	4.12
20.4	1.63
30.0	0.99
40.5	0.53
49.3	0.42
69.2	0.25

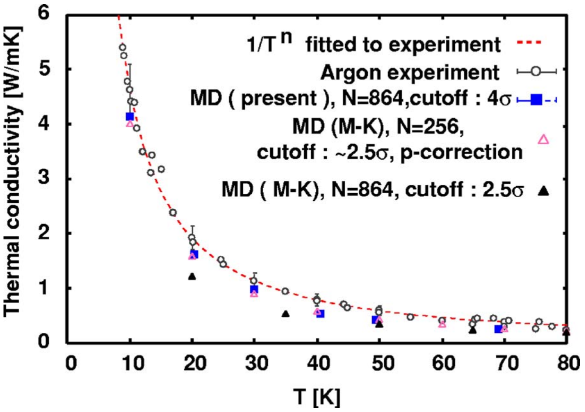

FIG. 2. (Color online) Experimental data of thermal conductivity (above 8 K) are fitted to a function of T^{-n}. The fitted value of n gives 1.27±0.02. The symbol M-K stands for the simulation data by McGaughey and Kaviany (Refs. 14 and 15).

effects would need to be considered. Also in this range there are boundary condition effects which depend on sample size and measurement conditions.

In Fig. 1 we see that in the high-temperature regime the calculations and the experimental data exhibit a temperature dependence varying more rapidly than T^{-1}, which is typically quoted in introductory text.[23] Both results seem to follow an exponent closer to −1.5. Fitting the calculations and experimental data (above 8 K) more precisely to T^{-n} gives $\boldsymbol{n} = 1.35 \pm 0.04$ and 1.27 ± 0.02, respectively, as shown in Fig. 2.

Figure 3(a) shows the temporal decay of the normalized heat current correlation function for the single crystal at each temperature, along with the result for the liquid at 90 K. The decay is seen to consist of two stages.[13,14] The initial rapid decay up to a time of 10^{-12} s, which we denote as stage I, can be regarded as driven mainly by single-particle motions. Beyond about 10^{-12} s the correlation function shows a plateau at low temperatures which diminishes almost entirely by $T = 70$ K. This is stage II behavior, which can be attributed to the collective motions of lattice vibrations or phonons. These results indicate a continuous transition from heat conduction in a low-temperature crystal to heat flow in the liquid. In the solid state, both relaxations are present, with the collective modes playing a more dominant role at low temperatures, whereas in the liquid state, the reverse holds. Figure 3(b) shows the same results on an expanded time axis. One can see a slight shoulder around 2×10^{-13} s, especially at 20, 30, and 40 K. This is a feature which has not been noted previously. We speculate that it may be associated with collective oscillations, possibly of a transverse or shear nature and highly damped. Figure 3(c) shows the liquid-phase heat current correlation function and the best single exponential fit to the MD results. One can see a discrepancy during initial decay which has to do with the inertial term in short-time

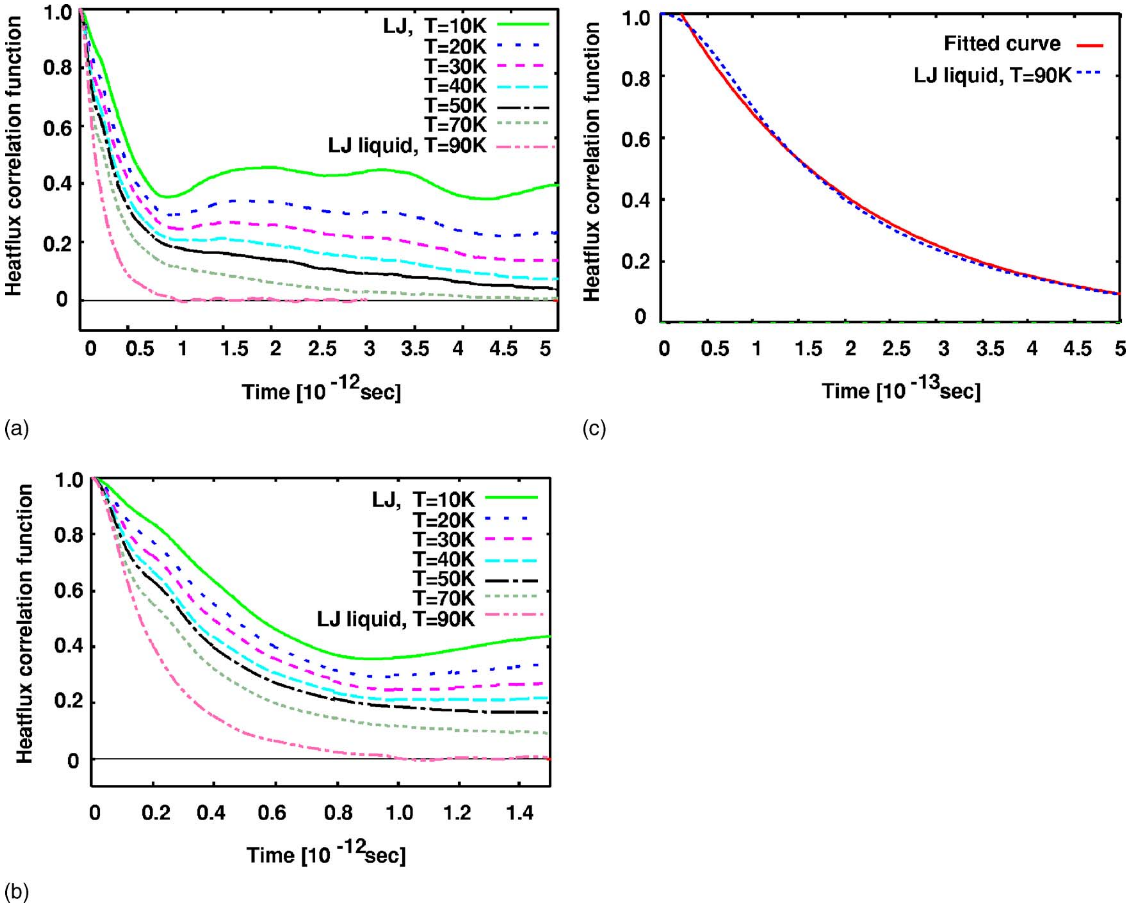

FIG. 3. (Color online) Normalized heat current correlation function at different temperatures (a) showing two stages of relaxation, and (b) showing stage I relaxation in greater detail on an expanded scale. The correlation function of liquid argon ($T = 90$ K) is fitted to (c) the single exponential decay function. The correlation mostly follows the exponential form except that the deviation occurs below 1.5×10^{-13} s.

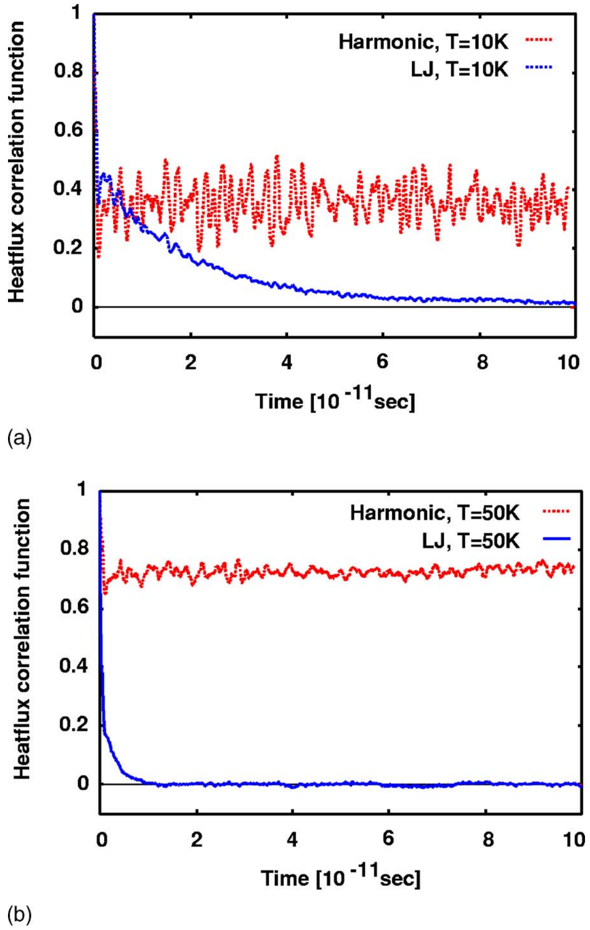

FIG. 4. (Color online) Heat current correlations from simulations using the harmonic approximation to the total potential at (a) $T=10$ K and (b) $T=50$ K. Also shown for comparison are the results obtained using the total potential.

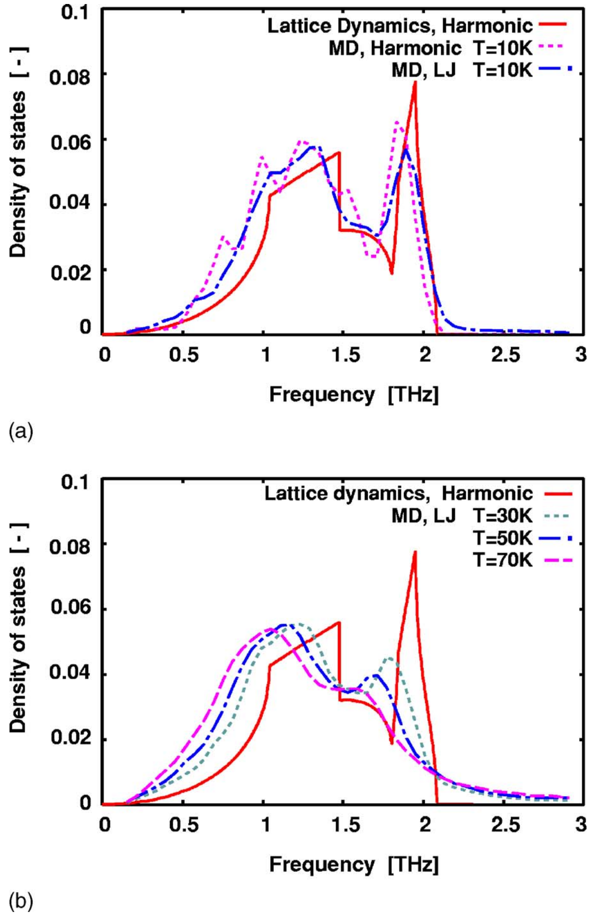

FIG. 5. (Color online) Effective density of states of argon crystal at (a) 10K and (b) at $T=30$, 50, and 70 K. Also shown in (a) are the results given by the harmonic approximation at $T=10$ K, and in (a) and (b) the density of states obtained from lattice dynamics.

expansion of classical autocorrelation functions which cannot be captured by any exponential.[9] On the other hand, the randomizing effects in liquid-state dynamics appear to be representable by a single stage.

Heat current correlation curves also have been presented and discussed by McGaughey and Kaviany.[14] Overall the two sets of results are in good agreement, which is another validation of the two independent simulations and data analyses. To get a sense of the effects of anharmonic interactions, we show in Fig. 4(a), the current correlation function at 10 K obtained using the harmonic approximation to the crystal potential, along with the results for the full potential. As to be expected, dissipation by phonon collisions is absent in the harmonic approximation, so stage II remains essentially flat, which implies an infinite thermal conductivity. This comparison is a clear-cut demonstration that the long-time decay of the heat current correlation is a consequence of anharmonic interactions. As Fig. 4(b) shows, the effects of anharmonic interactions are even more striking at higher temperatures. This suggests that treating a high-temperature crystal through a systematic correction to the harmonic approximation may not be appropriate whether it is to calculate the thermal conductivity or any other physical property.

Since molecular dynamics simulation is perfectly capable of probing crystal properties at high temperatures, we show in Figs. 5(a) and 5(b) the evolution of the effective density of states from low temperatures, where the harmonic approximation is applicable, to high temperatures, where anharmonic effects are certain to dominate. By effective density of states we mean the Fourier transform of the velocity autocorrelation function, a quantity which can be determined in a quite straightforward manner by MD simulation.[24] Besides the harmonic approximation result in Fig. 5(a), the phonon density of states calculated by diagonalizing the dynamical matrix, constructed using the Lennard-Jones potential, and using a simple Monte Carlo method to sample the **k**-points in the Brillouin zone,[25,26] is also shown. For the comparison between lattice dynamics and molecular dynamics spectra, increasing the number of particles of the latter is necessary because the data are intrinsically quite noisy. The MD results have been derived using 4000 particles. The spectra are further averaged by making a histogram with the frequency (0–3 THz) divided into 50 bins, and applying the Hanning window with area normalization.

In the low-temperature regime, Fig. 5(a), the spectra of effective density of states have the same overall profile as the phonon density of states given by lattice dynamics, with the latter having sharper peaks and displaying the characteristic van Hove singularities. Notice the harmonic approximation result at 10 K, aside from a slight frequency shift in the

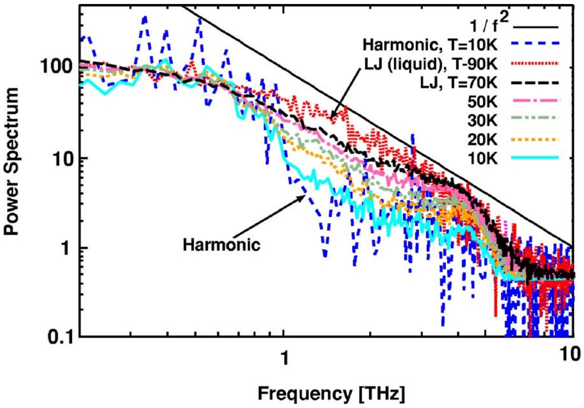

FIG. 6. (Color online) The power spectrum of the normalized heat current correlation of argon crystal and liquid at different temperatures.

high-frequency peak position, is in quite good agreement with the lattice dynamics result, particular in regard to the ω^2 classical behavior at low frequencies and the relative intensities of the features. This is a gratifying verification of the two types of calculations, performed independently of each other. There exists a systematic difference between the harmonic approximation and the full potential simulations at 10 K. It is reasonable to attribute this to the effects of anharmonic interactions, in particular the hard repulsive wall of the potential.

Turning to the high-temperature regime, Fig. 5(b), one can see a significant thermal softening effect in the shifting of the entire spectrum to lower frequencies and the smearing out of the high-frequency peak. At 70 K the lattice still retains sufficient ordering so that diffusive modes have not set in. As one approaches melting, one can expect the effective density of states to take on a zero-frequency component which, upon melting of the crystal, becomes the diffusive mode. This is expected because for a liquid the effective density of states at zero frequency is the self-diffusion coefficient.

Figure 6 shows the detailed structure of the power spectrum of the heat current correlation over the temperature range from solid to liquid. If a correlation function is decaying exponentially with a relaxation time τ_c, its power spectrum would be a Lorentzian $4\tau_c/\{1+(2\pi f\tau_c)^2\}$. Therefore, the spectral distribution would be a constant (white noise) up to a frequency $f \approx 1/(2\pi\tau_c)$, and at high frequencies it decays as $1/f^2$. In Fig. 6 the spectrum for the liquid most closely displays this behavior. One would expect that the effects of short-time contribution could be seen at high frequencies, above about 1–2 THz, coinciding with the Debye frequency, and collective motions at low frequencies below 1 THz. The high-frequency spectrum above 1 THz is interpreted to be mostly random. The spectrum for the harmonic solid consists of two flat regions above 1 THz. We see in Fig. 6 that the effects of temperature, from 10 K to melting, are most pronounced in the range of 1–5 THz, and the harmonic solid and the liquid constitute the lower and higher temperature limits of the LJ solid. The step around 5 THz in the spectrum, corresponding to the slight shoulder observed in Fig. 3(b), is typical of the lattice system and is not present in the liquid, indicating that this may be associated with collective motions of a transverse or shear nature. We may conclude that single-particle diffusive behavior (stage I) is not very different going from solid to liquid.

IV. DISCUSSION

We have shown that the thermal conductivity of crystal argon in the high-temperature region can be predicted with good accuracy by the method of molecular dynamics and using the Lennard-Jones potential with a sufficiently long cutoff radius. While the MD results presented here, particularly the absolute values of the conductivity and the two-stage relaxation of the heat current correlation, are in agreement with the results previously reported by McGaughey and Kiviany,[14,15] we differ from these authors in the interpretation and analysis of the heat current correlation. We attribute the first-stage relaxation to single-particle motions sampling the local environment of the system, whereas MK regard this relaxation to be associated with short-wavelength acoustic phonon. Based on our interpretation we expect this part of the current correlation to be relatively insensitive to temperature, because the local environment surrounding a particle does not change much even when the system goes from a low-temperature solid to the liquid phase and loses long-range ordering. Indeed, this is what we see in Fig. 3. It is noteworthy that the relaxation at very short times is not properly described by a single exponential for the reasons already discussed. Regarding stage II in the heat current correlation, we are in agreement with MK that the underlying process is lattice vibrations or phonons. This part is expected to be sensitive to temperature variations because long-range ordering is needed to sustain the collective motions. Adopting a phonon-based approach to determine the conductivity, MK fitted the MD heat current correlation over the entire temperature range to a sum of two exponentials, which they attribute to phonons of short and long wavelengths. We believe that committing to a description of dynamical relaxation in terms of only phonons neglects the role of single-particle motions, which should become dominant at temperatures near melting and collective modes become increasingly damped. Thus, it is behavior of stage I relaxation that holds the key to understanding the connection between the high-temperature behavior of a solid and that of the liquid and perhaps glassy solids. For this purpose an analysis in which the current correlation function is expressed in terms of memory functions may be useful.[9]

The features of the short-time contribution for the heat current autocorrelation or single-particle behavior are best illustrated by considering the various expressions of heat current, in particular, by focusing on the difference between the full atomistic expression of Eq. (2) and the Peierls expression,

$$\boldsymbol{J}_P = \sum_{\boldsymbol{k}} \sum_{\mu=1}^{D} E_\mu(\boldsymbol{k}) \boldsymbol{v}_\mu(\boldsymbol{k}), \tag{4}$$

where $E_\mu(\boldsymbol{k})$ and $\boldsymbol{v}_G^\mu(\boldsymbol{k})$ are the energy and group velocity of phonon mode $\boldsymbol{k}$ with branch number $\mu(=1,\ldots,D)$. This Peierls expression of heat flux is almost always taken as the exact starting point for the theoretical calculation of lattice thermal conductivity. As first noted in the Ladd, Moran, and Hoover's article,[27] the short-time contribution disappears using the Peierls expression of heat current. It should be noted here that the Peierls expression is only an approximation to the full atomistic expression, and one way to elucidate the nature of the short-time contribution is to analyze the range of validity of the Peierls expression. This has been discussed by one of the authors,[28] and the details of the calculations will be soon reported. Here, we briefly consider its connection with the single-particle motions as can be seen from the results of Fig. 6. The harmonic heat current, derived from the full atomistic expression of Eq. (2) by taking only the quadratic terms, is transformed into a complex form in terms of the normal or phonon coordinates. This expression roughly divides into a coherent, slowly varying component, corresponding to the Peierls expression, and an incoherent, slowly varying, and randomly fluctuating component, corresponding to the short-time contribution. In the latter component, randomness arises from the dephasing effect of cross terms consisting of the almost independent phonon coordinates, and its relaxation time is characterized roughly by the inverse of the Debye frequency. All these features of the short-time contribution, which are left out in the Peierls picture, can be discerned in Fig. 6 for the harmonic and the LJ solid at low temperatures, such as 10 K above nearly 1–2 THz. As the temperature approaches the melting point, single-particle motions behave more and more like typical motions characteristic of the liquid state.

The combination of MD with linear response formalism has been recently extended to a study of thermal transport mechanisms in nanofluids, dilute concentrations of nanosized clusters in a host fluid.[29] Significant conductivity enhancements over the pure fluid, up to about 40%, have been reported at volume fractions as low as 0.3%.[30] By decomposing the heat current vector into three modes, kinetic, potential, and virial (or collisional), one can systematically examine the resulting nine correlation functions. In this way it is possible to understand the variation of conductivity with volume fraction, without any prior assumption of a mechanism.[29] Given the results presented here, it would be interesting to see how the heat current correlation would behave in a two-component crystal.

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