Thermal Insulating Behavior in Crystals at High Frequencies

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When solving heat-conduction problems with periodic temperature perturbations, the thermal conductivity is assumed to remain frequency independent. We, however, show by using the molecular dynamics technique and the fluctuation-dissipation theorem a decrease of the effective thermal conductivity of 2 orders of magnitude when the excitation frequency approaches or exceeds the reverse of the phonon mean relaxation time. Most of the dielectric and semiconductor materials have to be considered as strongly insulating in those conditions. The comparison between molecular-dynamics simulations performed in Si crystals and theoretical predictions reveals a clear agreement.

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Clock frequencies of present microprocessors based on silicon technology reach the gigahertz (10^9 Hz), and roadmaps suggest that devices with clock rates of 100 GHz will be produced in the next few years. Understanding heat transfer mechanisms at high frequencies, when local nonequilibrium regimes appear, can therefore not be dismissed. Short time heat conduction in solids has generated much interest for four decades, and extended reviews can be found in the literature [1]. The basic modeling consists in adding an inertia term in the Fourier law linking the temperature gradient $\overrightarrow{\mathrm{grad}}T$ and the heat flux $\vec{q}$ [2,3]:

$$\tau \frac{\partial \vec{q}}{\partial t} + \vec{q} = -\lambda \overrightarrow{\mathrm{grad}}T\,, \tag{1}$$

where τ denotes the heat flux relaxation time, and λ is the thermal conductivity. The Boltzmann transport equation written in terms of the phonon occupation number confirms the intuitive derivation of Eq. (1) and leads to the equality between τ and the phonon mean relaxation time [4]. Equation (1) is coherent with the fact that phonons, i.e., heat carriers in solids, rarely scatter together in time intervals smaller than τ. Combining Eq. (1) with the energy balance equation allows one to derive the well-known hyperbolic heat conduction equation:

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \alpha \Delta T\,, \tag{2}$$

where α represents the thermal diffusivity. The right-hand side term, however, implies a diffusive heat transport which cannot appear in the involved spatial scales. Heat flux or temperature fields calculation actually requires the solving of the Boltzmann equation that can be reformulated as a radiative transport equation [2,3]. Note that a simpler approach was recently proposed based on the decomposition of this last equation into ballistic and diffusive equations [5].

We report a direct way to derive the dissipated heat flux when a high frequency AC temperature perturbation is generated in bulk materials. We predict a decrease of 2 orders of magnitude for this quantity when the excitation frequency approaches or exceeds the reverse of the phonon mean relaxation time. We then prove the relevance of this result based on molecular dynamics (MD) simulations performed in Si crystals. Results show accordance between predicted and computed heat fluxes concerning frequency and temperature dependence.

The fluctuation-dissipation theorem derived in the frame of the linear response theory allows one to express the heat flux q created by an AC temperature disturbance of frequency ω, denoted $\overrightarrow{\mathrm{grad}}Te^{i\omega t}$, in terms of the equilibrium fluctuations of the heat flux $\mathbf{q}_0(t)$ [6,7]:

$$q(\omega) = \frac{V}{3k_B T^2}\int_0^\infty \langle q_0(0)q_0(t)\rangle e^{i\omega t}\,dt\,\|\overrightarrow{\mathrm{grad}}T\|\,. \tag{3}$$

Here, $\langle \mathbf{q}_0(0)\mathbf{q}_0(t)\rangle = \frac{1}{V}\int_V \mathbf{q}_0(0,\mathbf{r})\mathbf{q}_0(t,\mathbf{r})\rho_0\,dV$ is the heat flux autocorrelation function, and T_0 is the equilibrium temperature. Equation (1) directly leads to $\langle q_0(0)q_0(t)\rangle = \langle q_0(0)^2\rangle e^{-(t/\tau)}$, but this relation also relies on a deeper physical basis, proving that the autocorrelation of the phonon occupation number follows the same exponential law [8]. Inserting the time explicit autocorrelation function in Eq. (3) allows one to identify the heat flux as follows:

$$\begin{aligned}\frac{q(\omega)}{\|\overrightarrow{\mathrm{grad}}T\|} &= \frac{V}{3k_B T^2}\int_0^\infty \langle q_0(0)q_0(t)\rangle e^{e\omega t}\,dt \\ &= \frac{V\langle q_0(0)^2\rangle}{3k_B T^2}\int_0^\infty e^{i\omega t-(t/\tau)}\,dt\,.\end{aligned} \tag{4}$$

We distinguish two cases knowing that the phonon mean relaxation time τ is of the order of 10–100 ps in solid crystals at room temperature.

(i) When $\omega \ll 1/\tau = 0.1-0.01$ GHz, the exponential term $e^{i\omega t}$ can be factorized since it varies very slowly in the interval $[0-3\tau]$ where the heat flux autocorrelation contribution remains non-negligible. This is the most general case leading to Fourier's law $|q(\omega)|/\|\overrightarrow{\mathrm{grad}}T\| = \lambda$, where the bulk thermal conductivity is defined by the Green Kubo formula:

$$\lambda = \frac{V}{3k_B T^2} \int_0^\infty \langle q_0(0) q_0(t) \rangle \, dt = \frac{V \langle q_0(0)^2 \rangle \tau}{3k_B T^2}, \quad (5)$$

Note that, in this situation, the assumption of local equilibrium is required.

(ii) When $\omega \approx > 1/\tau = 10-100$ GHz, Eq. (4) leads to the following definition of the effective thermal conductivity λ_e [8]:

$$\lambda_e = \frac{|q(\omega)|}{\|\overrightarrow{\mathrm{grad}} T\|} = \frac{V}{3k_B T^2} \frac{\langle q_0(0)^2 \rangle}{\sqrt{1/\tau^2 + \omega^2}}. \quad (6)$$

Equation (6) shows that the heat flux amplitude will decrease as the reverse of the frequency ω starting from about 10 GHz until the lowest eigenfrequencies of the heat carriers ≈ 1 THz leading to a 2 orders of magnitude diminution for the dissipated heat flux. The same equation was also found in previous works [1,8] but to obtain a frequency decomposition of the thermal conductivity.

We now prove the validity of the predicted behavior based on molecular dynamics simulations. In MD computations, all the particle trajectories for a given system with a reasonably small number of atoms are calculated, which allows the derivation of the thermodynamic quantities of the system. Using the MD technique and the Stillinger-Weber interatomic potential model for Si [9], the atomic trajectories, i.e., the time-dependent positions $\mathbf{r}_i(t)$ and velocities $\mathbf{v}_i(t)$, are computed. The temperature T can be readily calculated from the velocity $\mathbf{v}_i$ of the atoms in the simulation domain since the Boltzmann distribution function allows the straightforward derivation of the mean kinetic energy $\langle E_c \rangle$:

$$\langle E_c \rangle = \frac{1}{2} M \sum_{i=1}^{N} v_i^2 = \frac{3}{2} N k_B T, \quad (7)$$

where k_B is the Boltzmann constant, N the number of particles in the system, and M the atomic mass. However, Eq. (7) holds only if the specific heat is not temperature dependent, which is true for temperatures above the Debye temperature. For temperatures lower than the Debye temperature, a quantum correction to the MD temperature must be carried out as described in previous publications [3]. The heat flux expression is derived from the integration of the energy balance equation combined with the definition of the total instantaneous heat flux in a statistical ensemble of constant energy [10]. For the computed two- and three-body potentials, the heat flux can be calculated from [8]

$$\mathbf{q}(t) = \frac{1}{V} \left[\sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \left(\frac{1}{2} \mathbf{r}_{ij} \cdot (\mathbf{F}_{ij} \cdot \mathbf{v}_i) + \frac{1}{6} \sum_{k=1, k \neq i,j}^{N} (\mathbf{r}_{ij} + \mathbf{r}_{ik})(\mathbf{F}_{ijk} \cdot \mathbf{v}_i) \right) \right], \quad (8)$$

where $\mathbf{F}_{ij}$ and $\mathbf{F}_{ijk}$ are the two- and three-body forces, and V is the system volume. The second term on the right-hand side represents the contributions of the three-body potential. Equation (8) includes only positions, velocities, and forces that are directly computed in basic MD simulations. The ratio in Eq. (4) is estimated by computing the Fourier transform of the heat flux expression (8) since the property of the Fourier transform F, $F[\langle q_0(0) q_0(t) \rangle] = |F[q_0(t)]|^2$ allows one to write

$$\lambda_e = \frac{V}{3k_B T^2} \int_0^\infty \langle q_0(0) q_0(t) \rangle e^{i\omega t} \, dt = \frac{V}{3k_B T^2} |F[q_0(t)]|^2. \quad (9)$$

To perform MD computations of crystals, we construct the simulation domain from unit cells forming a face-centered cubic lattice with two atoms as the basis. Systems with 10 × 10 × 10 unit cells are studied. These simulations include 8000 atoms since a diamondlike cell includes eight atoms. The density is imposed by setting the lattice constant to 0.543 nm, and periodic boundary conditions are applied in all directions. Computations of five thousand of MD reference times $t_u = 7.663 \cdot 10^{-2}$ ps are performed; this also represents a physical experiment duration of 0.35 ns. For a 10 × 10 × 10 unit cells box simulation with 8000 Si atoms, a computation time of eight days on an ORIGIN 200 calculator is observed.

A Gauss thermostat [10] is used to fix the temperature, and the final results are checked to ensure that they are not modified by a change in the thermostat parameters. The techniques consist in imposing the kinetic energy corresponding to the thermostat temperature on randomly selected atoms. This selection allows one to get rid of side effects as slow decaying bulk motions in the crystal. When the temperature reaches the required value, the thermostat is removed and the heat flux calculation executed. We also check that the total energy is well conserved throughout the computation. To take low-temperature quantum effects into account, the thermal conductivity λ_e has to be corrected by the following scaling factors [8]: 0.628 at 200 K and 0.933 at 500 K.

Figure 1 reports the MD results for the frequency evolution of the effective thermal conductivity λ_e at 200 and 500 K from 10 GHz to 1 THz. A satisfying fitting can be achieved with a ω^{-1} power law in this frequency range which clearly confirms the predictions of Eq. (6). The thermal conductivity values are decreasing from 60 to 1 W/mK which corresponds to a reduction of 2 orders of magnitude when compared to the reference bulk data of 150 W/mK. The proof of the ω^{-1} behavior is strengthened by Fig. 2, where the product of the effective thermal conductivity by the frequency is represented for the two equilibrium temperatures. It clearly appears that data are fluctuating around constant values: 1.69×10^{12} W/mK s (500 K) and 1.11×10^{12} W/mK s (200 K). The root mean square data (2% at 500 K and 0.6% at 200 K) show that a good accuracy is obtained with our MD computations, and an expected higher value is also retrieved at higher temperatures where thermal fluctuations have

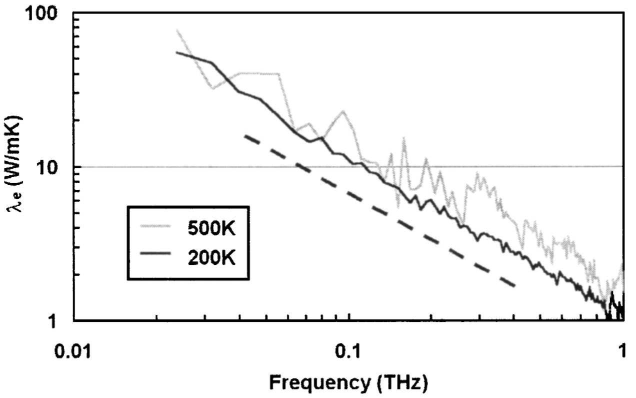

FIG. 1. Effective thermal conductivity λ_e at 200 K (black solid line) and 500 K (grey line) as a function of frequency in a log-log representation showing the ω^{-1} dependence. The dashed line has a slope of -1.

larger amplitudes. The temperature dependence in the high frequency range is mostly governed by the heat capacity temperature dependence, i.e., low temperature quantum effects. Indeed, the predominance of the ballistic transfer of phonons leads to a relaxation time independent response as proven by Eq. (6) when $\omega \gg 1/\tau$. Besides, the $\langle q(0)^2 \rangle / T^2$ term can be estimated as proportional to the heat capacity and the square of the sound velocity in the kinetic formulation. The sound velocity is only weakly temperature dependent, therefore the heat capacity variations only remain.

Figure 2 shows a frequency delay between the starts of the divergence to the power law in the low frequency regime. This effect signals the temperature dependence of τ, and we therefore presume that the relaxation time value at 500 K is between 10–100 ps, while it is larger than 100 ps at 200 K. This effect signals the temperature dependence of τ, and we therefore presume that the relaxation time value at 500 K is between 10–100 ps, while it is larger than 100 ps at 200 K. Our deduction is corroborated by Fig. 3, where the time evolutions of the heat flux autocorrelation functions are plotted. The relaxation times characterize the exponential decay and can be approximated to 30–40 ps at 500 K and 120–140 ps at 200 K. This information added to the observation of the ω^{-1} law indicates that size effects due to periodic boundary conditions do not affect the studied frequency range as pointed out in the literature [8].

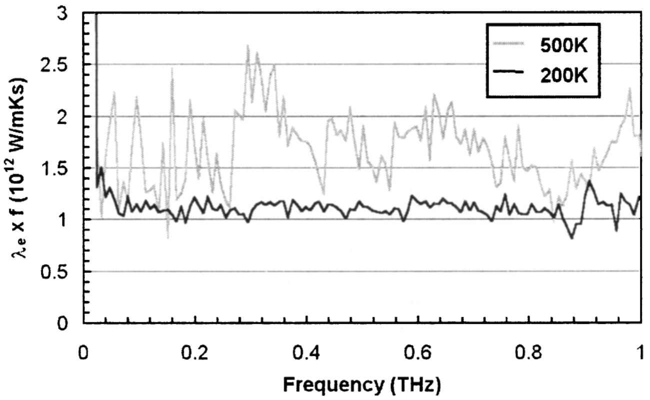

FIG. 2. Effective thermal conductivity λ_e multiplied by the frequency ω including the low-temperature quantum effects correction. The data are scattered around the mean value of $V\langle q(0)^2 \rangle / (3k_B T^2)$.

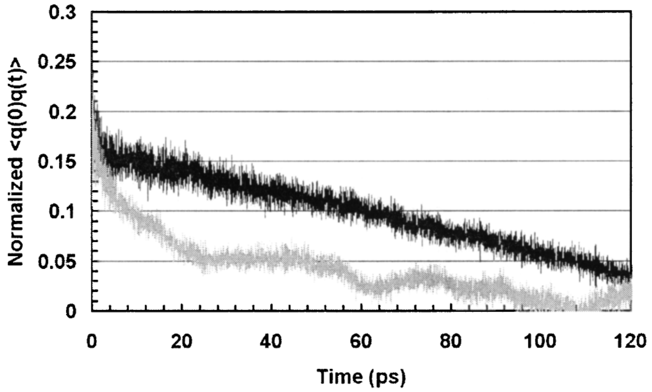

FIG. 3. Normalized autocorrelation functions $\langle q(0)q(t) \rangle$ at 200 K (black line) and 500 K (grey line). The lower temperature results exhibit a longer relaxation time.

In conclusion, we have used molecular dynamics experiments to obtain quantitative estimations of the effective thermal conductivity of Si crystals submitted to high frequency perturbations. We found out that the law governing the effective thermal conductivity implies considerable disagreements with classical predictions and a behavior of highly insulating material. Depending on the excitation period, the ability of the medium to conduct heat can be reduced by 2 orders of magnitude. We also showed that this behavior is in accordance with the predictions of the fluctuation-dissipation theorem. We pointed out that the temperature dependence of this particular phenomena is mainly related to low temperature quantum effects on the heat capacity. We emphasize that the studied effect is significant at gigahertz frequencies in crystals or in media where the phonon mean relaxation time is large. Consequently, this special behavior is rejected to higher frequencies when temperature increases or in amorphous solids and in liquids. The presented phenomena, however, remains of interest for the thermal design of microsystems and nanosystems, where fabrication is based on silicon technology.

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