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Theoretical analysis of oscillatory terms in lattice heat-current time correlation functions and their contributions to thermal conductivity

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Abstract

Lattice heat-current time correlation functions for insulators and semiconductors obtained using molecular dynamics (MD) simulations exhibit features of both pure exponential decay and oscillatory-exponential decay. For some materials the oscillatory terms contribute significantly to the lattice heat conductivity calculated from the correlation functions. However, the origin of the oscillatory terms is not well understood and their contribution to the heat conductivity is accounted for by fitting them to empirical functions. Here, a translationally invariant expression for the heat current in terms of creation and annihilation operators is derived. By using this full phonon-picture definition of the heat current and applying the relaxation-time approximation, we explain, at least in part, the origin of the oscillatory terms in the lattice heat-current correlation function. We discuss the relationship between the crystal Hamiltonian and the magnitude of the oscillatory terms. A solvable one-dimensional model is used to illustrate the potential importance of terms that are omitted in the commonly used phonon-picture expression for the heat current. While the derivations are fully quantum mechanical, classical-limit expressions are provided that enable direct contact with classical quantities obtainable from MD.

I. INTRODUCTION

The heat conductivity tensor $\kappa_{\alpha\alpha'}$ in the Green-Kubo (GK) framework is given by^{1,2}

$$\kappa_{\alpha\alpha'} = \frac{1}{k_B T^2 V} \int_0^\infty dt \langle J_\alpha(0) J_{\alpha'}(t) \rangle_q, \quad (1)$$

where J_α is the α th component of the heat-current operator, T is temperature, V is the system volume, and the integrand is the quantum correlation function, defined as

$$\langle J_\alpha(0) J_{\alpha'}(t) \rangle_q = \frac{1}{\beta} \int_0^\beta d\zeta \text{Tr}(\rho e^{\zeta H} J_\alpha(0) e^{-\zeta H} J_{\alpha'}(t)), \quad (2)$$

where H is the system Hamiltonian, ρ is the corresponding canonical equilibrium density matrix, and $\beta = (k_B T)^{-1}$. Direct numerical application of Eq. (1) to crystalline materials is problematic due to the enormous cost of quantum calculations even for small systems. For this reason simulations of crystal heat conductivity are usually performed using molecular dynamics (MD) simulations based on the classical analog of Eq. (1) in which the quantum correlation function is replaced by the classical one. The classical GK approach has become a powerful tool for obtaining heat conductivities of various materials due, in part, to the simplicity of its implementation, which only involves equilibrium MD simulations.³⁻¹⁰ (This stands in contrast to *ad hoc* non-equilibrium methods,¹¹⁻¹⁵ for which several empirical choices in simulation protocol must be determined or guessed.) While the brute-force GK approach is attractive insofar as it provides access to the full heat conductivity tensor from a single equilibrium simulation, it is intellectually unsatisfying in that it yields little insight into the underlying physics of the heat transport: The primary fundamental energy carriers in crystalline dielectrics and semiconductors below the gap are phonons, and the GK approach as implemented in MD (*i.e.*, using particle Cartesian coordinates and momenta) gives no direct information about the phonon picture of heat transport. This limitation also makes it difficult to apply physically justified quantum corrections to the MD results. These corrections can be quite important in materials that have substantial numbers of high-frequency modes, as such modes are effectively in the quantum ground state at room temperature and therefore are not accurately described by classical mechanics.

Theoretical analysis of the heat-current correlation function in Eq. (2) in the phonon picture typically relies on a definition of heat current, $\mathbf{J}_P = \sum_{\mathbf{k},s} \mathbf{v}_s(\mathbf{k}) E_s(\mathbf{k})$, introduced by Peierls.¹⁶ Here, $E_s(\mathbf{k})$, which is an operator in the quantum case and a dynamical variable in the classical case, is the energy of a phonon mode and $\mathbf{v}_s(\mathbf{k})$ is the corresponding

mode group velocity. Each mode is specified by wave vector \mathbf{k} and branch s . Dynamics of the mode energy in anharmonic crystals is usually described by the Boltzmann phonon equation.¹⁶ Due to the difficulty of solving this equation^{17,18} the full mode dynamics is often treated using the relaxation-time approximation,^{17,19,20} wherein the deviation of the average energy of each mode from the corresponding equilibrium value is assumed to decay exponentially with time. Under the relaxation-time approximation, use of the Peierls expression to evaluate the heat-current correlation function given by Eq. (2) leads to a superposition of monotonically decaying exponentials. Whereas there are crystalline materials for which this picture works fairly well,^{3–5} there are other ones for which it fails.^{6,7,10} For the latter materials the exponential terms in the correlation function are superposed with decaying oscillatory terms with various frequencies. Even crystalline argon, which has an fcc lattice and for which the exponential decay terms are dominant, exhibits weak oscillations in its heat-current correlation function.^{3,5}

The contribution of the oscillatory terms to the total heat conductivity depends on the particular material studied and can be substantial for technologically relevant substances. For example, in the case of silica the contributions from oscillatory terms are estimated to be approximately 20% for certain zeolites and 8% for quartz.⁶ In an MD-based study of the high-explosive crystal α -RDX (α -hexahydro-1,3,5-trinitro-*s*-triazine) it was estimated empirically that the oscillatory terms contribute approximately 30% to the overall heat conductivity values.⁷ It is widely accepted^{4,6,7} that these terms arise due to the presence of optical modes in the materials studied. Nonetheless, despite their importance, rigorous theoretical understanding of the origin and relative magnitude of these oscillations in the heat-current correlation function is lacking. Practically, MD simulation results, which almost always are obtained within the Cartesian picture that captures all oscillations and effects of anharmonicity—albeit without an obvious path to fundamental understanding—are fitted to empirical oscillatory functions to account for such modes.^{6,7} In this work we show that this unfortunate level of empiricism can be remedied, at least in part, *via* more detailed theoretical analysis.

II. TRANSLATIONALLY INVARIANT HEAT-CURRENT OPERATOR IN THE PHONON PICTURE

Here we outline the derivation of the phonon-picture lattice heat-current operator used in our analysis of the heat conductivity that introduces an important correction to the original derivation by Hardy²¹ and derivations due to other authors.^{22,23} Consider the crystal Hamiltonian of the form

$$H = \sum_{\mathbf{n}, i, \alpha} \frac{p_{i\alpha}^2(\mathbf{n})}{2m_i} + \frac{1}{2} \sum_{\substack{\mathbf{n}, \mathbf{n}' \\ i, j, \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) q_{i\alpha}(\mathbf{n}) q_{j\beta}(\mathbf{n}') + \text{anharmonic terms.} \quad (3)$$

Here, $p_{i\alpha}(\mathbf{n})$ and $q_{i\alpha}(\mathbf{n})$ are, respectively, operators of linear momentum and displacement from the minimum-energy position, for the α th Cartesian component for atom i located in a unit cell specified by lattice vector \mathbf{n} ; m_i is the mass of atom i ; and $U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n})$ is the matrix of second derivatives of the potential energy. Anharmonic potential-energy terms in Eq. (3) include cubic and higher-order terms in the displacement operators. For the Hamiltonian (3) to be translationally invariant the following necessary and sufficient condition has to be satisfied:²⁴

$$\sum_{\mathbf{n}', j} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) = \sum_{\mathbf{n}, i} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) = 0. \quad (4)$$

The total heat current corresponding to this Hamiltonian can be written as^{3,9,25,26}

$$\mathbf{J} = \frac{d}{dt} \sum_{\mathbf{n}, i} \frac{\mathbf{x}_i(\mathbf{n}) e_i(\mathbf{n}) + e_i(\mathbf{n}) \mathbf{x}_i(\mathbf{n})}{2}, \quad (5)$$

where $\mathbf{x}_i(\mathbf{n})$ is the vector specifying the position of atom i in unit cell \mathbf{n} and $e_i(\mathbf{n})$ is the local energy of that atom. The total heat current for the Hamiltonian (3) consists of terms that are quadratic in operators $p_{i\alpha}(\mathbf{n})$ and $q_{i\alpha}(\mathbf{n})$, along with the higher-order terms. The quadratic part of the heat current is expected to be dominant for temperatures well below the crystal melting point,^{21,23} in which case the total current can be approximated by

$$\mathbf{J} = \sum_{\mathbf{n}, i} (\mathbf{n} + \mathbf{r}_i) \frac{d(\epsilon_i^k(\mathbf{n}) + \epsilon_i^p(\mathbf{n}))}{dt}. \quad (6)$$

Here, \mathbf{r}_i is the vector specifying the equilibrium position of atom i in the unit cell and $\epsilon_i^k(\mathbf{n})$ and $\epsilon_i^p(\mathbf{n})$ are, respectively, the local kinetic energy and the quadratic part of the local potential energy. (Note that Eq. (6) does not include so-called convective terms.

These are of cubic or higher degree in the displacement and/or momentum operators and are generally expected to be small for solids.) The local kinetic energy is defined as $\epsilon_i^k(\mathbf{n}) = \sum_{\alpha} p_{i,\alpha}^2(\mathbf{n})/2m_i$. However, it is well known that there is an ambiguity in defining the local potential-energy operator.^{21,23,26} The seemingly obvious choice for the quadratic part of the local potential energy $\epsilon_i^p(\mathbf{n})$, used in Refs. 21 and 23 and given by

$$\epsilon_i^p(\mathbf{n}) = \frac{1}{2} \sum_{\mathbf{n}', j, \alpha, \beta} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) q_{i\alpha}(\mathbf{n}) q_{j\beta}(\mathbf{n}'), \quad (7)$$

has the disadvantage of not being invariant with respect to translations and, as a result, leads to a heat-current expression that has the same property. We will demonstrate in Sec. IV using a model system that application of Eq. (7) can lead to unphysical results for the heat conductivity. Defining an unambiguous, translationally invariant local energy for the most general translationally invariant quadratic Hamiltonian (given by the first line of Eq. (3)) appears to be impossible. Indeed, quadratic Hamiltonians are obtained as the second-order terms of a Taylor expansion of the full Hamiltonians that, in general, are composed of terms involving two-body, three-body, and higher-order n -body interactions. The ambiguity of splitting the potential energy among the n particles in an n -body potential term^{21,23,26} is transferred to the quadratic part of full local potential energy as well. (It is interesting to note that the quadratic Hamiltonian can be viewed as a sum of translationally non-invariant two-body terms.) Here we provide a physically reasonable translationally invariant definition of the local energy that is valid when the matrices of second derivatives satisfy $U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) = U_{ij\beta\alpha}(\mathbf{n}' - \mathbf{n})$. This includes the important case of pairwise central potentials.²⁴ Using the expression just above along with the condition (4), the quadratic part of the potential energy (denoted here by V) can be re-written as a sum of explicitly translationally invariant terms; that is,

$$V = -\frac{1}{4} \sum_{\substack{\mathbf{n}, \mathbf{n}' \\ i, j, \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) (q_{i\alpha}(\mathbf{n}) - q_{j\alpha}(\mathbf{n}')) \times (q_{i\beta}(\mathbf{n}) - q_{j\beta}(\mathbf{n}')). \quad (8)$$

This form of V leads naturally to the following translationally invariant definition of the local potential energy

$$\epsilon_i^p(\mathbf{n}) = -\frac{1}{4} \sum_{\substack{\mathbf{n}', j \\ \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) (q_{i\alpha}(\mathbf{n}) - q_{j\alpha}(\mathbf{n}'))$$

$$\begin{aligned}
& \times (q_{i\beta}(\mathbf{n}) - q_{j\beta}(\mathbf{n}')) \\
& = \frac{1}{2} \sum_{\substack{\mathbf{n}', j \\ \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) [q_{i\alpha}(\mathbf{n}) - \frac{1}{2} q_{j\alpha}(\mathbf{n}')] q_{j\beta}(\mathbf{n}'),
\end{aligned} \tag{9}$$

where the last line was obtained by applying Eq. (4). Note that this last expression differs from the definition (7) introduced by Hardy by the presence of the second term in the square brackets. It can be shown²⁷ that in the case of pairwise central potentials the definition (9) reduces to dividing the pair potential energy equally between the two particles and expanding it through quadratic terms in atomic displacement. Such splitting of the interaction energy for pair potentials is generally accepted to be unambiguous.²⁶ We assume here that the definition of the local potential energy given by Eq. (7) is also unambiguous.

Inserting (9) into Eq. (6), using the Heisenberg equation of motion for $\epsilon_i(\mathbf{n})$ and keeping only the quadratic terms, we obtain

$$\begin{aligned}
\mathbf{J} = & \frac{1}{4} \sum_{\substack{\mathbf{n}, \mathbf{n}' \\ i, j, \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}' - \mathbf{n}) \left[(q_{i\alpha}(\mathbf{n}) - q_{j\alpha}(\mathbf{n}')) \frac{p_{j\beta}(\mathbf{n}')}{m_j} \right. \\
& \left. + \frac{p_{j\beta}(\mathbf{n}')}{m_j} (q_{i\alpha}(\mathbf{n}) - q_{j\alpha}(\mathbf{n}')) \right] (\mathbf{n} - \mathbf{n}' + \mathbf{r}_i - \mathbf{r}_j).
\end{aligned} \tag{10}$$

This expression is explicitly translationally invariant as it depends on the differences of atomic displacements for the same Cartesian components. Using eigenstates $\xi_{i\alpha}^s(\mathbf{k})$ and eigenvalues $\omega_s^2(\mathbf{k})$ of the dynamical matrix $D_{ij\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{n}} U_{ij\alpha\beta}(\mathbf{n}) \exp(i\mathbf{k} \cdot \mathbf{n}) / \sqrt{m_i m_j}$ of the Hamiltonian in Eq. (3), we can introduce the normal coordinates $Q_s(\mathbf{k})$ and momenta $P_s(\mathbf{k})$ for the system of N unit cells as

$$\begin{aligned}
Q_s(\mathbf{k}) &= \sum_{\mathbf{n}, i, \alpha} \sqrt{\frac{m_i}{N}} q_{i\alpha}(\mathbf{n}) \xi_{i\alpha}^{s*}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{n}}, \\
P_s(\mathbf{k}) &= \sum_{\mathbf{n}, i, \alpha} \frac{1}{\sqrt{N m_i}} p_{i\alpha}(\mathbf{n}) \xi_{i\alpha}^s(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{n}},
\end{aligned} \tag{11}$$

and creation and annihilation operators $a_s^\dagger(\mathbf{k})$ and $a_s(\mathbf{k})$ through

$$\begin{aligned}
a_s^\dagger(\mathbf{k}) &= \sqrt{\frac{\omega_s(\mathbf{k})}{2\hbar}} Q_s(-\mathbf{k}) - i \frac{1}{\sqrt{2\hbar\omega_s(\mathbf{k})}} P_s(\mathbf{k}), \\
a_s(\mathbf{k}) &= \sqrt{\frac{\omega_s(\mathbf{k})}{2\hbar}} Q_s(\mathbf{k}) + i \frac{1}{\sqrt{2\hbar\omega_s(\mathbf{k})}} P_s(-\mathbf{k}).
\end{aligned} \tag{12}$$

With these, we can re-write the heat current as

$$\mathbf{J} = \frac{\hbar}{2} \sum_{\mathbf{k}, s, s'} \left[(\mathbf{v}_{ss'}(\mathbf{k}) \omega_s(\mathbf{k}) + \mathbf{v}_{s's}^*(\mathbf{k}) \omega_{s'}(\mathbf{k})) a_s^\dagger(\mathbf{k}) a_{s'}(\mathbf{k}) \right]$$

$$\begin{aligned}
& +\mathbf{v}_{ss'}(\mathbf{k})\omega_s(\mathbf{k})a_s^\dagger(\mathbf{k})a_{s'}^\dagger(-\mathbf{k}) \\
& +\mathbf{v}_{s's}^*(\mathbf{k})\omega_{s'}(\mathbf{k})a_s(-\mathbf{k})a_{s'}(\mathbf{k})\Big],
\end{aligned} \tag{13}$$

where vector coefficients $\mathbf{v}_{ss'}(\mathbf{k})$ (with components $v_{ss'}^\alpha(\mathbf{k})$) couple modes with the same absolute value of \mathbf{k} but different branches in general. These coefficients are given by

$$\mathbf{v}_{ss'}(\mathbf{k}) = \mathbf{v}'_{ss'}(\mathbf{k}) + \mathbf{v}''_{ss'}(\mathbf{k}), \tag{14}$$

where

$$\begin{aligned}
\mathbf{v}'_{ss'}(\mathbf{k}) &= \frac{i}{2\sqrt{\omega_s(\mathbf{k})\omega_{s'}(\mathbf{k})}} \sum_{\substack{\mathbf{n}, i, j \\ \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}) \\
&\times \frac{\xi_{i\alpha}^{s*}(\mathbf{k})\xi_{j\beta}^{s'}(\mathbf{k})}{\sqrt{m_i m_j}} e^{i\mathbf{k}\cdot\mathbf{n}} (\mathbf{n} + \mathbf{r}_j - \mathbf{r}_i),
\end{aligned} \tag{15}$$

$$\begin{aligned}
\mathbf{v}''_{ss'}(\mathbf{k}) &= \frac{-i}{2\sqrt{\omega_s(\mathbf{k})\omega_{s'}(\mathbf{k})}} \sum_{\substack{\mathbf{n}, i, j \\ \alpha, \beta}} U_{ij\alpha\beta}(\mathbf{n}) \\
&\times \frac{\xi_{i\alpha}^{s*}(\mathbf{k})\xi_{i\beta}^{s'}(\mathbf{k})}{m_i} (\mathbf{n} + \mathbf{r}_j - \mathbf{r}_i).
\end{aligned} \tag{16}$$

Coefficients $\mathbf{v}'_{ss'}(\mathbf{k})$ are the ones used by Hardy²¹ in his definition of the heat current. These coefficients satisfy the equality $\mathbf{v}'_{ss'}(\mathbf{k}) = \mathbf{v}'_{s's}^*(\mathbf{k})$ and, thus, for a fixed \mathbf{k} their Cartesian components can be viewed as Hermitian matrices. These coefficients also satisfy $\mathbf{v}'_{ss'}(\mathbf{k}) = -\mathbf{v}'_{s's}(-\mathbf{k})$. It can also be shown²¹ that they are equal to zero for modes with $\omega_s(\mathbf{k}) = \omega_{s'}(\mathbf{k})$ when $s \neq s'$. The coefficients $\mathbf{v}'_{ss'}(\mathbf{k})$ reduce to group velocities when $s = s'$.^{21,23} Coefficients $\mathbf{v}''_{ss'}(\mathbf{k})$ ensure the translational invariance of the heat-current expression (13) but do not appear in the original derivation by Hardy²¹ and other authors.²³ In contrast to $\mathbf{v}'_{ss'}(\mathbf{k})$, coefficients $\mathbf{v}''_{ss'}(\mathbf{k})$ are antihermitian, that is, $\mathbf{v}''_{ss'}(\mathbf{k}) = -\mathbf{v}''_{s's}^*(\mathbf{k})$. They also satisfy $\mathbf{v}''_{ss'}(\mathbf{k}) = \mathbf{v}''_{s's}(-\mathbf{k})$. In general, they are *not* equal to zero for modes with $\omega_s(\mathbf{k}) = \omega_{s'}(\mathbf{k})$ when $s \neq s'$. It is also worth mentioning that the expressions for the generalized group velocities are identical in both the quantum and classical pictures. (Planck's constant does not appear in Eqs. (15) and (16).)

III. HEAT-CURRENT CORRELATION FUNCTION AND THERMAL CONDUCTIVITY TENSOR

The terms with $s = s'$ in the first line of Eq. (13) correspond to the Peierls¹⁶ definition of the heat current, that is, $\mathbf{J}_P = \sum_{\mathbf{k}, s} \mathbf{v}'_s(\mathbf{k})\omega_s(\mathbf{k})a_s^\dagger(\mathbf{k})a_s(\mathbf{k})$ (where the second identical

subscript in $\mathbf{v}'_{ss'}(\mathbf{k})$ is omitted). In most phonon-picture treatments of crystal heat conductivity only this part of the full summation in Eq. (13) is considered. In the present analysis of the heat-current correlation function and the associated heat conductivity tensor, we use the full expression for the heat current given by Eq. (13). We apply the *ad hoc* relaxation-time approximation,^{17,19,20} wherein the effect of anharmonic mode coupling on the mode dynamics is approximated by using effective decay rates $\gamma_s(\mathbf{k})$ for each mode, that is, $a_s^\dagger(\mathbf{k}, t) = a_s^\dagger(\mathbf{k}, 0) \exp(i\omega_s(\mathbf{k})t - \gamma_s(\mathbf{k})t)$ and $a_s(\mathbf{k}, t) = a_s(\mathbf{k}, 0) \exp(-i\omega_s(\mathbf{k})t - \gamma_s(\mathbf{k})t)$. The relaxation-time approximation has been widely applied to approximate exact lattice-mode dynamics; see, for example, Refs. 17–20, 28–31. Despite its simplicity, the relaxation-time approximation generally provides a qualitatively correct picture of the mode dynamics. It was shown in several numerical studies that heat conductivities calculated using this approximation agree quite well with those obtained from MD simulations or more rigorous theoretical approaches.^{18,28–31} With all the time dependence appearing in the exponential factors, evaluation of the correlation function in Eq. (2) using the full heat current (13) reduces to the calculation of the expectation values of products of two creation and two annihilation operators over the harmonic equilibrium ensemble. This calculation yields the following expression for the heat-current correlation function:

$$\begin{aligned} \langle J_\alpha(0) J_{\alpha'}(t) \rangle_q &= \frac{1}{4\beta^2} \sum_{\mathbf{k}, s, s'} e^{-(\gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k}))t} \\ &\times \left(G_{ss'\alpha\alpha'}^-(\mathbf{k}) \cos(\omega_s(\mathbf{k}) - \omega_{s'}(\mathbf{k}))t \right. \\ &\left. + G_{ss'\alpha\alpha'}^+(\mathbf{k}) \cos(\omega_s(\mathbf{k}) + \omega_{s'}(\mathbf{k}))t \right), \end{aligned} \quad (17)$$

with

$$\begin{aligned} G_{ss'\alpha\alpha'}^\pm(\mathbf{k}) &= \frac{\hbar\beta(n_{s'}(\mathbf{k}) \pm n_s(\mathbf{k}) + (1 \pm 1)/2)}{\omega_s(\mathbf{k}) \pm \omega_{s'}(\mathbf{k})} \\ &\times (v_{ss'}^\alpha(\mathbf{k})\omega_s(\mathbf{k}) \mp v_{s's}^{\alpha*}(\mathbf{k})\omega_{s'}(\mathbf{k})) \\ &\times (v_{ss'}^{\alpha'*}(\mathbf{k})\omega_s(\mathbf{k}) \mp v_{s's}^{\alpha'}(\mathbf{k})\omega_{s'}(\mathbf{k})), \end{aligned} \quad (18)$$

where $n_s(\mathbf{k}) = (\exp(\beta\hbar\omega_s(\mathbf{k})) - 1)^{-1}$ is the Bose-Einstein distribution. The classical analog of Eq. (17), which is relevant for interpreting MD results, is obtained by taking the limit $\hbar \rightarrow 0$ and has the same form as Eq. (17) but with coefficients $G_{ss'\alpha\alpha'}^\pm(\mathbf{k})$ replaced by their classical limits

$$\lim_{\hbar \rightarrow 0} G_{ss'\alpha\alpha'}^\pm(\mathbf{k}) = \frac{1}{\omega_s(\mathbf{k})\omega_{s'}(\mathbf{k})}$$

$$\begin{aligned}
&= \times (v_{ss'}^\alpha(\mathbf{k})\omega_s(\mathbf{k}) \mp v_{s's}^{\alpha*}(\mathbf{k})\omega_{s'}(\mathbf{k})) \\
&\times (v_{ss'}^{\alpha'*}(\mathbf{k})\omega_s(\mathbf{k}) \mp v_{s's}^{\alpha'}(\mathbf{k})\omega_{s'}(\mathbf{k})).
\end{aligned} \tag{19}$$

It is understood that in the classical case the effective relaxation rates in Eq. (17) are also replaced by their classical values. It is evident from Eq. (17) that both classically and quantum mechanically the heat-current correlation function is a superposition of exponentially decaying oscillatory terms, with frequencies of the oscillations given by sums and differences of the crystal normal-mode frequencies; terms with $s = s'$ correspond to pure exponential decay. Thus, the oscillations appear naturally as a consequence of using the full definition of the heat current (13), and the magnitudes of individual terms are given by the functions $G_{ss'\alpha\alpha'}^\pm(\mathbf{k})$.

Integrating the correlation function in Eq. (17) over time leads to the following expression for the quantum mechanical heat conductivity tensor:

$$\begin{aligned}
\kappa_{\alpha\alpha'} = \frac{k_B}{4V} \sum_{\mathbf{k}, s, s'} &\left[\frac{G_{ss'\alpha\alpha'}^-(\mathbf{k})(\gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k}))}{(\omega_s(\mathbf{k}) - \omega_{s'}(\mathbf{k}))^2 + (\gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k}))^2} \right. \\
&\left. + \frac{G_{ss'\alpha\alpha'}^+(\mathbf{k})(\gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k}))}{(\omega_s(\mathbf{k}) + \omega_{s'}(\mathbf{k}))^2 + (\gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k}))^2} \right].
\end{aligned} \tag{20}$$

The classical heat conductivity tensor has the same form but with coefficients $G_{ss'\alpha\alpha'}^\pm(\mathbf{k})$ taken in their classical limit, that is, Eq. (19). To the best of our knowledge, Eq. (20) is a new expression although related expressions that consider the so-called off-diagonal contributions to heat conductivity were derived in Refs. 23, 32–34. Note, however, that these published related expressions include only coefficients $\mathbf{v}_{ss'}'(\mathbf{k})$ (15) and not the full coefficients $\mathbf{v}_{ss'}(\mathbf{k})$ (14); and, therefore, may lead to incorrect results when heat conductivity is calculated explicitly. The terms with $s = s'$ in the first line of Eq. (20) correspond to the Peierls¹⁶ result for the heat conductivity whereas the $s \neq s'$ terms give the contribution from the oscillatory terms in the heat-current correlation function. Simple analysis of the functional form of Lorentzians and functions $G_{ss'\alpha\alpha'}^\pm(\mathbf{k})$ in Eq. (20) shows that the second term in the square brackets is always smaller than the first. In general, however, application of Eq. (20) to calculate overall heat conductivity as well as contributions from the specific terms requires knowledge of the generalized group velocities, mode frequencies, and relaxation rates. Whereas frequencies and relaxation rates for various crystalline materials have been routinely calculated numerically,^{6,8–10} to our knowledge the generalized group velocities were never thoroughly investigated. Our preliminary calculations²⁷ of the generalized group velocities for α -RDX show that, for some mode pairs, their magnitude can be much larger

than the typical group velocities. This is consistent with the large contribution from the oscillatory terms reported for α -RDX in Ref. 7.

The contribution from the oscillatory terms in Eq. (20) can be expected to be small (of order γ) when $\omega_s(\mathbf{k}) \pm \omega_{s'}(\mathbf{k}) \gg \gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k})$. However, crystals with unit cells that contain many degrees of freedom generally have a large number of optical modes that are often nearly or completely degenerate for a given \mathbf{k} value. For pairs of such modes the frequency difference $\omega_s(\mathbf{k}) - \omega_{s'}(\mathbf{k})$ is small or zero. Thus, for such pairs of modes $\omega_s(\mathbf{k}) - \omega_{s'}(\mathbf{k}) \lesssim \gamma_s(\mathbf{k}) + \gamma_{s'}(\mathbf{k})$ and the contribution of the corresponding terms to the heat conductivity is of order $1/\gamma$; that is, of the same order as the diagonal terms. Specific magnitudes of contributions from particular such pairs depend on the relative values of the relaxation rates and the generalized group velocities and can, in principle, be substantial. Depending on the crystal type and the \mathbf{k} -space direction, the difference $\omega_s(\mathbf{k}) - \omega_{s'}(\mathbf{k})$ can also be small or zero for acoustic mode pairs and, thus, contributions from such pairs of acoustic modes also can be important in principle.

We emphasize that the formalism developed in Sections II and III is general. In principle, it is equally applicable to crystalline systems of any non-fractal dimensionality—1-D, 2-D, and 3-D—and of arbitrary symmetry class. In the next section, we apply key results from Sections II and III to an exactly solvable, one-dimensional system. It is widely understood that 1-D and 2-D systems can exhibit pathologies for various properties and processes (*e.g.*, heat transport and diffusion among others); and in this regard, such systems are often thought of as edge cases, the results for which much be regarded with caution. However, for the present purpose of demonstrating the application and potential utility of the new theoretical expressions derived in Sections II and III, we view concerns with these potential pitfalls as outweighed by considerations of closed-form analytic tractability and the ability to determine precisely and unambiguously the contributions of oscillatory and non-oscillatory terms to both the heat current and the thermal conductivity.

IV. AN EXACTLY SOLVABLE 1-D MODEL

To emphasize the importance of using the full definition of the heat current (13), we consider an exactly solvable model, namely a one-dimensional harmonic chain of particles of equal mass with alternating coupling constants and interatomic distances.^{35,36} This model yields an analytic expression for the generalized group velocities given by Eq. (14). On one

hand, we use this model to show that, even in crystals with just two degrees of freedom per unit cell, the generalized group velocities can be similar in magnitude to the conventional group velocities. On the other hand, despite the simplicity of the model, it can be used to approximate the longitudinal modes in linear chains of identical atoms or atomic groups separated by bonds of alternating type, such as acetylenic carbon atoms (*i.e.*, carbyne) or polyacetylene. The Hamiltonian of the model is given by

$$H = \sum_{n,i} \frac{p_i^2(n)}{2m} + c_1 \sum_n (q_1(n) - q_2(n))^2 + c_2 \sum_n (q_2(n) - q_1(n+a))^2. \quad (21)$$

There are two degrees of freedom per unit cell, thus index i takes values of 1 and 2. The lattice spacing a is the sum of distances a_1 and a_2 , which are the alternating spacings between particles connected by springs with constants c_1 and c_2 , respectively. Note that the individual distances a_1 and a_2 do not appear separately in the Hamiltonian and for this reason frequencies and group velocities depend only on their sum a . The values of a_1 and a_2 do, however, affect the value of the generalized group velocity. Diagonalization of the Hamiltonian in Eq. (21) yields two phonon branches, acoustic and optical, with frequencies $\omega_s(k)$ given by

$$\omega_s(k) = \sqrt{\frac{2(c_1 + c_2 + (-1)^s f(k))}{m}}, \quad (22)$$

with s taking values of 1 and 2 and $f(k) = \sqrt{c_1^2 + c_2^2 + 2c_1c_2 \cos ka}$. Coefficients $v'_{ss'}(k)$ and $v''_{ss'}(k)$ are obtained by application of Eqs. (15) and (16):

$$v'_{ss}(k) = \frac{(-1)^{s-1} ac_1 c_2 \sin ka}{\sqrt{2m(c_1 + c_2 + (-1)^s f(k))} f(k)}, \quad (23)$$

$$v'_{21}(k) = i \frac{a(c_1^2 - c_2^2) + (a_1 - a_2)f^2(k)}{4f(k)\sqrt{m\sqrt{c_1c_2}|\sin \frac{ka}{2}|}}, \quad (24)$$

$$v''_{ss}(k) = 0, \quad (25)$$

$$v''_{21}(k) = -i \frac{a_1 c_1 - a_2 c_2}{2\sqrt{m\sqrt{c_1c_2}|\sin \frac{ka}{2}|}}. \quad (26)$$

As discussed in Sec. II, coefficients $v'_{ss}(k)$ are the group velocities corresponding to frequencies (22); and $v'_{12}(k) = v'_{21}^*(k)$ and $v''_{12}(k) = -v''_{21}^*(k)$. These coefficients as functions of k are shown in Fig. 1, for the parameters $c_1 = 804.1 \text{ J m}^{-2}$ and $c_2 = 481.2 \text{ J m}^{-2}$. These parameters were fitted using Eqs. (22) and (23) to match the carbyne chain longitudinal acoustic group velocity at $k = 0$ (31835 m s^{-1}) and the acoustic mode frequency at $k = \pi/a$

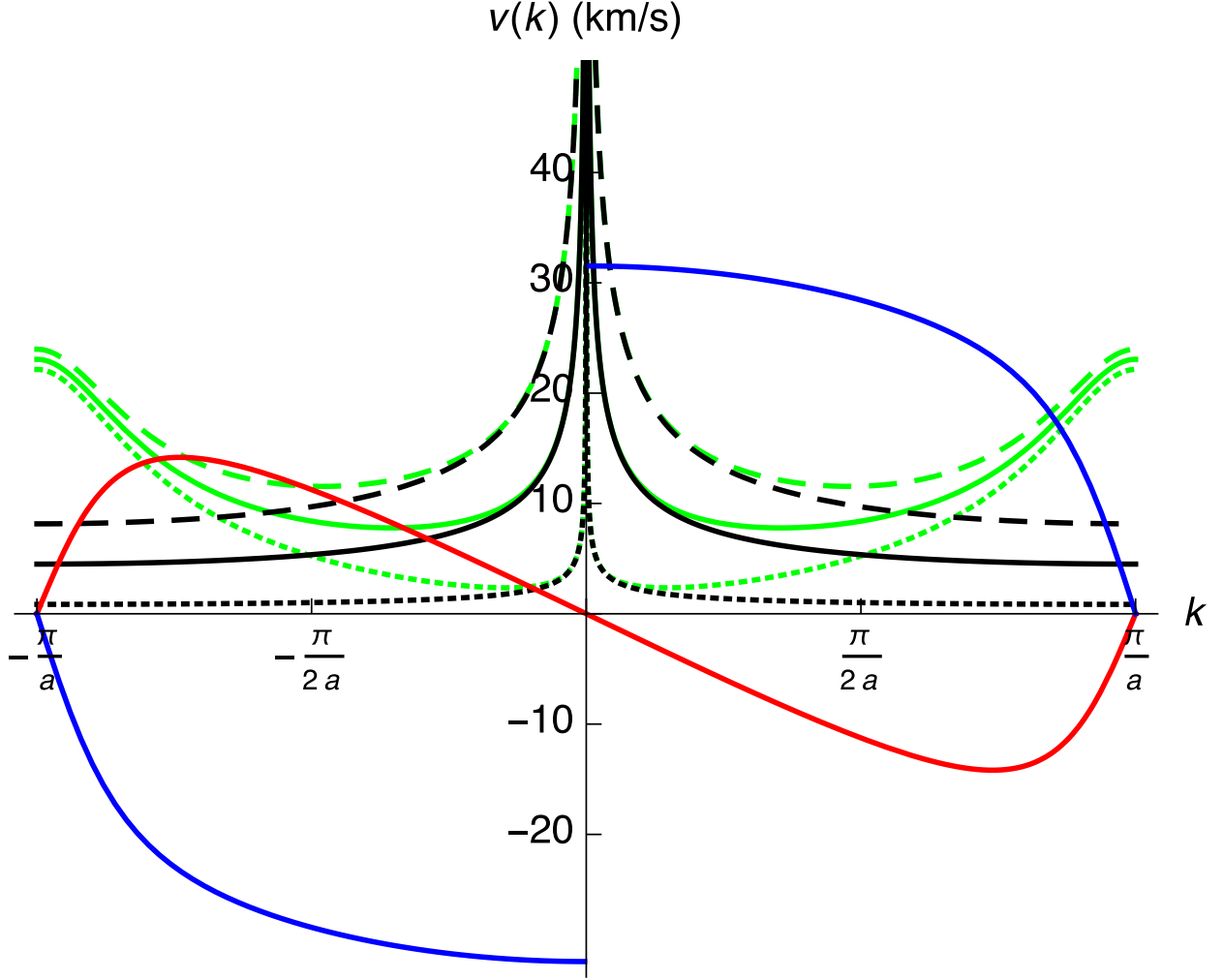


FIG. 1. Acoustic mode group velocity $v'_{11}(k)$ (blue), optical mode group velocity $v'_{22}(k)$ (red), and the imaginary parts of coefficients $v'_{21}(k)$ (solid green) and $-v''_{21}(k)$ (solid black), for parameters fitted to approximate longitudinal lattice-mode frequencies in a carbyne chain. (The dashed green and black curves are discussed in the text.) As noted in Sec. II, the results in this figure are identical for both the quantum and classical pictures.

(1650 cm^{-1}) evaluated from the experimental data given in Ref. 37. The interatomic distances $a_1 = 1.207 \text{ \AA}$ and $a_2 = 1.358 \text{ \AA}$ were taken from Ref. 38 where they were obtained using high-level electronic structure calculations. The mass was set to 12 amu. Coefficients $v'_{21}(k)$ (green solid curve) and $-v''_{21}(k)$ (black solid curve) behave as $k^{-1/2}$ for small values of k and remain finite at the zone boundary where the group velocities are equal to zero. The singularities at $k = 0$ for both of these coefficients cancel out exactly when heat currents and corresponding correlation functions and heat conductivities are calculated using Eqs. (17) and (20), respectively. By contrast, if the coefficient $v''_{21}(k)$ is omitted (which corresponds

to the translationally non-invariant local energy definition (7)), the $k^{-1/2}$ singularity of coefficient $v'_{21}(k)$ leads to divergence of the average value of the squared heat-current per unit cell for this 1-D model. (The average squared heat-current per unit cell remains finite if the full translationally invariant definition of the current is used.)

To demonstrate the sensitivity of the generalized group velocity to the geometry of the unit cell, we also show in Fig. 1 the imaginary parts of $v'_{21}(k)$ (dashed green curves) and $-v''_{21}(k)$ (dashed black curves) for a_1 equal to 1.007 Å (short dashes) and 1.407 Å (long dashes), with lattice constant $a = a_1 + a_2 = 2.565$ Å and all other parameters the same as in carbyne. Note that, as discussed above, such changes in a_1 and a_2 do not affect the mode frequencies and group velocities. By contrast, both coefficient $v'_{21}(k)$ and $v''_{21}(k)$ are affected by the unit-cell geometry.

To show the typical behavior of the heat-current correlation function, we augment our model by introducing phenomenological mode decay rates $\gamma_s(k)$ to mimic anharmonic mode-mode couplings. We choose *ad hoc* rates of the form $\gamma_s(k) = \eta\sqrt{\omega_s(k)}$. Note that one-dimensional lattices typically have size-dependent heat conductivity that diverges when the chain becomes infinitely long; see, for example, Refs. 39–41 and references therein. However, while understanding the limitations of the present model, for the purpose of demonstrating the main result of this work, we specifically employ decay rates that ensure a finite value of the coefficient of heat conductivity given by Eq. (20). Figure 2 shows the behavior of the heat-current correlation function given by Eq. (17) in the classical limit for a choice of parameters typically found in molecular crystals. Specifically, coefficient c_1 is set to be large, the same as in the carbyne example above to model a stiff covalently bonded molecule, while coefficient c_2 is taken to be much smaller (200.0 J m⁻²) to represent weak van der Waals interaction between molecules. The interatomic distances a_1 and a_2 are chosen as 1.2 Å and 2.4 Å, respectively, and the atomic mass once again is 12 amu. Decay rates were chosen to be a few times lower than the frequencies for the corresponding mode branch for most k values (see inset in Fig. 2) and the parameter η was set to 9.216 cm^{-1/2}. Relative contributions of the constituent terms shown in Fig. 2 to the total heat conductivity given by Eq. (20) are as follows: acoustic, 91.4%; optical, 1.7%; and oscillatory, 6.9%. Thus, the contribution from the oscillatory terms for our model, although small, is larger than the one from the optical modes. Note that, independent of the specific mode dynamics, the heat-current correlation function at time $t = 0$ corresponds to the average squared heat-current in equilibrium. As can be seen from Fig. 2, the contribution to this average value from the off-diagonal terms of

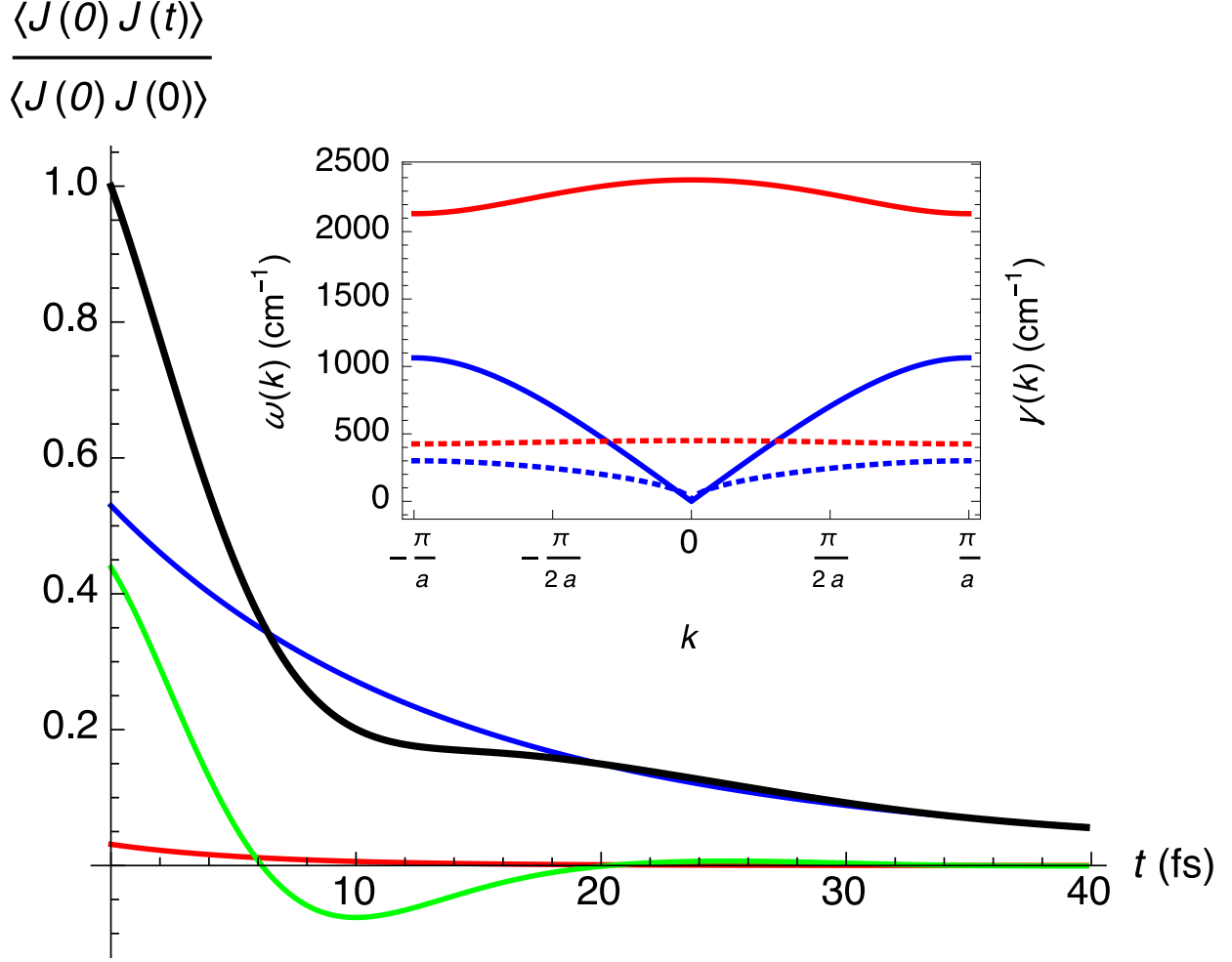


FIG. 2. Main panel: Total scaled heat-current correlation function (black, heavy) and its contributions from the acoustic modes (blue), optical modes (red), and oscillatory terms dependent on coefficient $v_{21}(k)$ (green) for molecular-crystal-like choice of parameters in the classical limit. Inset: Frequencies (solid curves, left ordinate) and decay rates (dashed curves, right ordinate) for the acoustic (blue) and optical (red) branches used to construct the plots in the main panel.

the total heat current (the green curve at the time $t = 0$) is approximately 43% of the total heat current (the black curve at $t = 0$). We reiterate that this observation is independent of the *ad hoc* nature of the time evolution that we used. Based on the form of Eq. (20), one can anticipate that the contribution of the oscillatory terms to the total heat conductivity in realistic crystals will become more significant in materials with a large number of mode branches s , as the total number of the coupling terms grows as s^2 for large s .

V. CONCLUSIONS

We showed that the oscillatory behavior of the heat-current correlation function observed in molecular dynamics simulations can be at least partially explained by considering the full definition of the heat-current operator that includes the off-diagonal terms in the phonon representation. We emphasized the necessity to use a translationally invariant phonon-picture definition of the heat current. Using the relaxation-time approximation, we obtained expressions for both the correlation function and the thermal conductivity tensor that include the off-diagonal terms and applied them to an analytically solvable 1-D Hamiltonian that approximates longitudinal lattice modes in carbyne. Using *ad hoc* mode-relaxation rates that ensure a finite conductivity for the model, we estimated contributions to the heat conductivity from diagonal and off-diagonal parts of the heat current. Further validation of these results requires applying them to real crystalline materials either in the framework of molecular dynamics or quantum mechanics.

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