From Green-Kubo to the full Boltzmann kinetic approach to heat transport in crystals and glasses

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We show that vertex corrections to the quasiharmonic Green-Kubo theory of heat transport in insulators naturally lead to a generalization of the expression for the conductivity that could be derived from the linearized Boltzmann equation, when the effects of the full scattering matrix are accounted for. Our results, which are obtained from the Mori-Zwanzig memory-function formalism, provide a fully *ab initio* derivation of the linearized Boltzmann transport equation and establish a connection between two recently proposed unified approaches to heat transport in insulating crystals and glasses.

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I. INTRODUCTION

The Green-Kubo (GK) theory of linear response [1,2] and the Boltzmann's kinetic approach (BKA), which leads to the transport equation with the same name (BTE) [3], are usually considered as independent and complementary methods to deal with charge and heat transport in condensed matter. By construction, the GK theory only applies to small perturbations, but it is otherwise general, for it applies to liquids as well as to solids, either crystalline or amorphous, both in the classical and fully quantum regimes. The BTE is not limited to the linear regime, but it is based on a (semi)classical treatment of charge and energy, which requires a proper definition of their carriers (e.g., electron and phonon quasiparticles) with well defined values of their positions, momenta, and energies [4]. These requirements make it problematic to apply the BKA to amorphous solids.

A couple of recent papers [5,6] have recently generalized these approaches, so as to encompass crystalline and disordered systems in the same theoretical and computational frameworks. The two papers differ conceptually in that the first is based on an elaborate generalization of the BKA, based on Wigner's dynamics (WD) [7], while the second is a straightforward specialization of the GK theory to solids in the quasiharmonic (QH) approximation, and dubbed therefore "QHGK." Notwithstanding, the two approaches give similar results for the heat conductivity, which coincide in the long-lifetime limit. Even when applied to crystals, these methods provide further insight into the limits of the quasiparticle picture of transport: The quasiparticle group velocities are replaced here with a anti-Hermitian matrix whose diagonal elements are indeed group velocities, and whose off-diagonal elements, which fully determine the transport mechanism in disordered systems, give rise to *interband* contributions to heat transport in crystals.

The conceptual content of these two approaches and the meaning of the physical approximations leading to them are best appreciated in a many-body framework [8], starting from the GK formula [2], which states that the heat conductivity is proportional to the integral of the time correlation function of the energy flux, $\langle \widehat{J}(t)\widehat{J}(0)\rangle$, where $\langle\cdot\rangle$ indicates an equilibrium thermal average and here and a caret, "$\widehat{\ }$", designates quantum mechanical operators. In the (quasi)harmonic approximation, the energy flux is quadratic in the phonon (or, more generally, normal-mode) creation and annihilation operators, $\hat{a}_p^\dagger$ and $\hat{a}_p$. The energy-flux correlation function is therefore a linear combination of products of four normal-mode operators of the form $\langle \hat{a}_p^\dagger(t)\hat{a}_q(t)\hat{a}_r^\dagger\hat{a}_s\rangle$ and $\langle \hat{a}_p^\dagger(t)\hat{a}_q^\dagger(t)\hat{a}_r\hat{a}_s\rangle$ [6]. The QHGK approach essentially results from the application of two related, but distinct, approximations. The first amounts to factorizing four-point correlation functions into linear combinations of products of two-point ones, such as, e.g.,

$$\langle \hat{a}_p^\dagger(t)\hat{a}_q(t)\hat{a}_r^\dagger\hat{a}_s\rangle \approx n_p n_r \delta_{pq}\delta_{rs} + \langle \hat{a}_p^\dagger(t)\hat{a}_p(0)\rangle\langle \hat{a}_q(t)\hat{a}_q^\dagger(0)\rangle\delta_{ps}\delta_{qr}, \quad (1)$$

where $n_p = \langle \hat{a}_p^\dagger\hat{a}_p\rangle = 1/(e^{\hbar\omega_p/k_bT} - 1)$ is a Bose-Einstein occupation number, ω_p being the normal-mode frequency, T the system's temperature, and k_B the Boltzmann's constant. In the parlance of many-body perturbation theory (MBPT), this factorization is described as the neglect of vertex corrections to the correlation function and referred to as the *dressed-bubble approximation* [8]. Physically, vertex corrections describe the correlation between the decay channels of different normal modes, and their neglect amounts to expressing the propagation and decay of each of them independently from all the others, as if determined by the interaction with a common, mean-field-like, heat bath. The second approximation consists in assuming that this heat bath is essentially a white noise, so that its interaction with the normal modes is Markovian, i.e., unaffected by any memory effects. The Markovian approximation essentially results in a damped exponential dependence of the single-mode *greater* Green's functions on

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time,

$$-i\langle\hat{a}_p(t)\hat{a}_p^\dagger\rangle \approx -i(n_p+1)e^{-i\omega_p t-\gamma_p|t|}, \tag{2}$$

which is to say that its spectral function (the imaginary part of its Laplace-Fourier transform) is Lorentzian. In a MBPT framework, this roughly corresponds to neglecting the frequency dependence of the phonon self-energies. The combination of these two approximations leads to a unified approach to heat transport that—while reducing in crystals to an enhanced version of the BKA in the so-called *relaxation-time approximation* (RTA), where interband effects are explicitly accounted for—equally applies to amorphous systems as well.

In this paper, we show how the two approximations that lead to the QHGK approach can be removed by treating the anharmonic decay of the vibrational normal modes through the Mori-Zwanzig (MZ) memory-function formalism [9,10]. Our main result is that a proper account of vertex corrections in the QHGK approach leads to an expression for the heat conductivity that, while applying to both lattice-periodic and disordered systems, in the former case naturally reduces to the *full* BTE beyond the RTA, i.e., properly accounting for the effects of the full scattering matrix. This result shows how the full linearized BTE can be derived entirely from first principles within the GK theory of linear response and sheds light onto the conceptual equivalence of the QHGK [6] and WD-BKA [5] approaches to heat transport. In Sec. II, we briefly present the Mori-Zwanzing approach to the Green-Kubo linear-response theory of heat transport; in Sec. II A, we derive the single-mode approximation to the GKMZ theory, which is closely related to the QHGK approach of Ref. [6]; in Sec. III, we derive the full Boltzmann equation from the GKMZ approach to heat transport; in Sec. IV, we draw a comparison with the WTE approach of Refs. [5,7]; in Sec. V, we present a numerical application to the Li_3ClO antiperovskite ionic conductor; and Sec. VI finally contains our conclusions.

II. GREEN-KUBO-MORI-ZWANZIG THEORY OF LATTICE HEAT CONDUCTIVITY

The quantum GK formula for the thermal conductivity, κ, reads

$$\kappa = \frac{1}{VT}\int_0^\infty dt \int_0^{\frac{1}{k_BT}} d\lambda \langle \widehat{J}(t-i\hbar\lambda)\widehat{J}(0)\rangle, \tag{3}$$

where V is the system's volume, $\widehat{J}$ is a generic Cartesian component, the energy-flux operator in the Heisenberg representation, and Cartesian indices have been suppressed to unclutter the notation. All the algebra that follows is considerably simplified by introducing the Kubo inner product [11,12] between quantum mechanical operators, defined as

$$(\widehat{A},\widehat{B}) \doteq \int_0^{\frac{1}{k_BT}} \langle \widehat{A}^\dagger(-i\hbar\lambda)\widehat{B}\rangle d\lambda, \tag{4}$$

where the time evolution of operators in the Heisenberg representation can be formally expressed in terms of the exponential of the Liouvillian superoperator [13], $\mathcal{L}$, defined as $\widehat{A}(t) = e^{i\widehat{H}t/\hbar}\widehat{A}e^{-i\widehat{H}t/\hbar} \doteq e^{i\mathcal{L}t}\widehat{A}$, and $\mathcal{L}\widehat{A} \doteq [\widehat{H},\widehat{A}]/\hbar = -i\dot{\widehat{A}}$. In terms of this scalar product, the quantum heat conductivity, Eq. (3), simply reads $\kappa = \frac{1}{VT}\int_0^\infty (\widehat{J}(t),\widehat{J}(0))dt$, in close formal analogy with its classical counterpart.

In the QH approximation, the energy flux can be cast into the form

$$\widehat{J} = -\frac{i\hbar}{2}\sum_{pq} v_{pq}\left(\frac{\omega_p+\omega_q}{2}\right)(\hat{a}_p^\dagger\hat{a}_q - \hat{a}_q^\dagger\hat{a}_p) + \frac{i\hbar}{2}\sum_{pq} v_{pq}\frac{\omega_p-\omega_q}{2}(\hat{a}_p^\dagger\hat{a}_q^\dagger - \hat{a}_p\hat{a}_q), \tag{5}$$

where v_{pq} is the real antisymmetric generalized group-velocity matrix [6,14]. The first, phonon-conserving term in Eq. (5) was dubbed *resonant* in Ref. [6], while the second, *antiresonant*; one was shown to give negligible contributions and will thus not be considered any further in the present work. By applying the GK formula, Eq. (3), and manipulating the indices on account of the antisymmetry of the group-velocity matrix—which makes the ordering of equal-time products of bosonic operators such as, e.g., $\hat{a}_p^\dagger(t)\hat{a}_q(t)$—irrelevant, one finally obtains

$$\kappa = \frac{\hbar^2}{VT}\sum_{IJ} v_I v_J \bar{\omega}_I\bar{\omega}_J\bar{C}_{IJ}(0), \tag{6}$$

where the indices $I=(pq)$ and $J=(rs)$ label pairs of normal modes, $\bar{\omega}_I = (\omega_p+\omega_q)/2$, $\widehat{A}_I = \hat{a}_p^\dagger\hat{a}_q$, and $\bar{C}_{IJ}(0)$ is the zero-frequency value of the Fourier-Laplace (FL) transform of the two-mode correlation function:

$$\bar{C}_{IJ}(z) = \int_0^\infty dt\, e^{izt}C_{IJ}(t), \text{ and}$$
$$C_{IJ}(t) = (\widehat{A}_I(t),\widehat{A}_J). \tag{7}$$

For the sake of clarity, we stress that velocity matrices appearing in the expression of vector quantities (such as a current) carry a Cartesian index, whereas products of two such matrices appearing in tensor quantities (such as the conductivity) carry two indices. Equation (6) shows that the computation of the heat conductivity reduces to that of two-phonon correlation functions. In the following, we show how this task can be effectively tackled by leveraging the MZ memory-function formalism.

In his celebrated 1965 paper [10], Mori showed that $\bar{C}_{IJ}(z)$ can be formally expressed as

$$\bar{C}_{IJ}(z) = i\sum_K \bar{\Lambda}^{-1}_{IK}(z)C_{KJ}, \text{ where} \tag{8}$$
$$C_{IJ} = C_{IJ}(0), \tag{9}$$
$$\bar{\Lambda}_{IK}(z) = z\delta_{IK} - \Omega_{IK} + i\bar{\Gamma}_{IK}(z), \tag{10}$$
$$\Omega_{IJ} = i\sum_K (\dot{\widehat{A}}_I,\widehat{A}_K)C^{-1}_{KJ}, \tag{11}$$
$$\bar{\Gamma}_{IJ}(z) = \sum_K (\dot{\widehat{A}}_I, \mathcal{Q}(z-\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\dot{\widehat{A}}_K)C^{-1}_{KJ}, \tag{12}$$

and $\mathcal{Q}$ is the projector over the operator manifold orthogonal to $\mathsf{span}(\{\widehat{A}_I\})$, defined by its action onto a generic operator, $\widehat{B}$, as

$$\mathcal{Q}\widehat{B} = \widehat{B} - \sum_{IJ}\widehat{A}_I(\widehat{A}_J,\widehat{B})C^{-1}_{IJ}. \tag{13}$$

Mind the difference between C_{IJ}, which is a function of time, and its FL transform $\bar{C}_{IJ}$, which is a function of frequency. More details on the Mori-Zwanzig formalism can be found, e.g., in Chapter 5 of Ref. [12].

The single-mode approximation

In order to proceed further, we seek to evaluate $\bar{C}_{IJ}(z)$, Eq. (8), to leading order in the strength of the anharmonic interactions, $\widehat{\mathcal{V}} = \widehat{H} - \widehat{H}^{\circ}$, $\widehat{H}^{\circ} = \sum_p \hbar\omega_p(\hat{a}_p^{\dagger}\hat{a}_p + 1/2)$ being the harmonic Hamiltonian. Let us start with C_{IJ}, Eq. (9), and Ω_{IJ}, Eq. (11), whose leading order in $\mathcal{V}$ is $O(1)$. In the harmonic approximation, one has

$$C_{IJ}^{\circ} = \int_0^{\frac{1}{k_b T}} d\lambda \langle \hat{a}_q^{\dagger}\hat{a}_s\rangle^{\circ}\langle \hat{a}_p\hat{a}_r^{\dagger}\rangle^{\circ} e^{\hbar\lambda(\omega_p-\omega_q)}\delta_{ps}\delta_{qr} = \frac{n_p - n_q}{\hbar(\omega_q - \omega_p)}\delta_{IJ}, \tag{14}$$

where $\langle\cdot\rangle^{\circ}$ indicates a thermal average in the canonical ensemble of the harmonic system, and

$$\Omega_{IJ} = (\omega_p - \omega_q)\delta_{IJ}. \tag{15}$$

In this approximation, the time evolution of $\widehat{A}_I$ is parallel to $\widehat{A}_I$: One concludes that $\mathcal{Q}\widehat{A}_I \sim O(\mathcal{V})$, and that $\bar{\Gamma}$ is $\sim O(\mathcal{V}^2)$ [Eq. (12)]. We notice that, to this order in $\mathcal{V}$, the thermal averages that implicitly appear in the Kubo inner product in Eq. (12) can be performed in the canonical ensemble of the harmonic Hamiltonian: We indicate this "harmonic" Kubo product by the symbol $(\widehat{A}, \widehat{B})^{\circ}$. The $\bar{\Lambda}$ matrix in Eq. (10) is singular at $z = 0$ for $\bar{\Gamma} = 0$: Its inverse in Eq. (8), is therefore $\bar{\Lambda}^{-1}(0) \sim O(\mathcal{V}^{-2})$, consistent with the divergence of the heat conductivity in the harmonic limit. By using Eq. (14), the heat conductivity, Eq. (6), can be cast into the form

$$\kappa = \frac{i\hbar^2}{VT}\sum_{IJ} v_I v_J \bar{\omega}_I\bar{\omega}_J \bar{\Lambda}_{IJ}^{-1}(0)C_{JJ}^{\circ} = \frac{i}{V}\sum_{IJ} c_J v_I v_J \frac{\omega_I}{\omega_J}\bar{\Lambda}_{IJ}^{-1}(0), \tag{16}$$

where $c_J = \hbar^2\bar{\omega}_J^2 C_{JJ}/T$ is the resonant generalized modal specific heat introduced in Ref. [6].

Equation (16) is completely general, though its implementation requires the computation and inversion of the $N^2 \times N^2$ matrix, $\bar{\Lambda}_{IJ}$, where N is the number of normal modes. This task is greatly facilitated when the off-diagonal elements of this matrix, i.e., of the $\bar{\Gamma}$ matrix in Eqs. (10) and (12), can be neglected. In this case, Eq. (16) can be shown to reduce to

$$\kappa = \frac{1}{V}\sum_{pq} c_{pq} v_{pq} v_{pq} \frac{\bar{\Gamma}'_{pq}}{(\omega_q - \omega_p - \bar{\Gamma}''_{pq})^2 + (\bar{\Gamma}'_{pq})^2}, \tag{17}$$

where $\bar{\Gamma}'_{pq} = \mathsf{Re}\,\bar{\Gamma}_{pq,pq}(0)$ and $\bar{\Gamma}''_{pq} = \mathsf{Im}\,\bar{\Gamma}_{pq,pq}(0)$, which is closely reminiscent of QHGK expression of Ref. [6]. The details of the derivation are reported in Appendix A.

The neglect of the off-diagonal elements of $\bar{\Gamma}$ is conceptually analogous to the single-mode (SM) approximation in the solution of the linearized BTE. This approximation has been shown to be particularly crude in the presence of strong hydrodynamic effects, especially (but not limited to) 2D materials [15], leading to an underestimate of the heat conductivity. In Sec. III, we will further elaborate on this analogy and show how the full BTE can be derived from the GKMZ theory. Some numerical evidence on the magnitude of the effects of nondiagonal terms in Γ will be provided in Sec. V.

Yet, no assumptions have been made on the time dependence of the single-mode Green's function or on the frequency dependence of its Fourier transform. Indeed, in Appendix B we show that for a cubic anharmonic potential Eq. (17) can be put into the *dressed-bubble* form of Refs. [8,16]:

$$\kappa = \frac{1}{V}\sum_{pq}\frac{\hbar^2(\omega_p+\omega_q)^2}{4} v_{pq}v_{pq}(I_{pq}+I_{qp}), \tag{18}$$

$$I_{pq} = \frac{1}{8\pi k_b T^2}\int d\omega \tilde{g}_p^{>}(\omega)\tilde{g}_q^{<}(\omega), \tag{19}$$

where

$$g_p^{>}(t) = -i\langle \hat{a}_p(t)\hat{a}_p^{\dagger}\rangle, \tag{20}$$

$$g_p^{<}(t) = \quad i\langle \hat{a}_p^{\dagger}\hat{a}_p(t)\rangle \tag{21}$$

are the so-called *greater* and *lesser* Green's functions, and $\tilde{g}_q^{\lessgtr}(\omega)$ indicate their Fourier transforms, whose line shape is not assumed *a priori*. In Eq. (18), we have omitted terms of order $O(N^{-1})$, which are negligible in the thermodynamic limit.

In the Markovian approximation, i.e., by further neglecting memory effects (which in the MBPT parlance amounts to neglecting the frequency dependence of the phonon self-energy), we arrive at the RTA approximation for the SM Green's function, $g_p^{>}(t) = -i(n_p+1)e^{-i\omega_p t-\gamma_p|t|}$ and $g_p^{<}(t) = i\,n_p e^{-i\omega_p t-\gamma_p|t|}$. By plugging these expressions into Eq. (19), one obtains

$$\kappa^M = \frac{1}{V}\sum_{pq} c_{pq}^M v_{pq}v_{pq}\tau_{pq}, \tag{22}$$

where

$$c_{pq}^M = \frac{n_p(n_q+1)+n_q(n_p+1)}{2k_B T^2}\frac{(\omega_p+\omega_q)^2}{4}, \tag{23}$$

$$\tau_{pq} = \frac{\gamma_p+\gamma_q}{(\omega_p-\omega_q)^2+(\gamma_p+\gamma_q)^2}, \tag{24}$$

and "M" stands for "Markovian," which coincides with the QHGK expression of Ref. [6], to within terms of order $O(\gamma^2)$, in agreement with the conclusions of Ref. [8]. Memory effects, defined in the MBPT formalism as the frequency dependence of the phonon self-energy function, i.e., as the non-Lorenzian features of the imaginary part of the Green's function, are likely important in the strongly anharmonic regime and have been shown to have a non-negligible impact on the thermal conductivity of a ferroelectric material near the critical temperature [16].

III. FROM GKMZ TO THE FULL BTE

Until now, no assumptions on the crystalline order of the system have been made. Lattice periodicity brings about a

great simplification that allows one to reduce the MZ approach to heat transport to the *full* (i.e., beyond the RTA) BTE. The crucial step permitting this reduction is the realization that lattice periodicity implies a Bloch block structure (no pun intended!) of the velocity matrices. In a periodic system, normal-mode indices split into a pair of Bloch-wave-vector and phonon-band indices: $q \to \{\boldsymbol{q}, \nu\}$ and the velocity matrices read

$$\begin{aligned} v_{\boldsymbol{q}\nu,\boldsymbol{k}\mu} &= v_{\boldsymbol{q},\nu\mu}\,\delta_{\boldsymbol{q}\boldsymbol{k}}, \text{ with} \\ v_{\boldsymbol{q},\nu\mu} &= v^*_{\boldsymbol{q},\mu\nu} = -v_{-\boldsymbol{q},\mu\nu}, \end{aligned} \tag{25}$$

where the diagonal term is the usual phonon group velocity: $v_{\boldsymbol{q},\nu\nu} = \nabla_{\boldsymbol{q}}\omega_{\boldsymbol{q}\nu}$. These relations allow us to to cast the energy current, Eq. (5) into the Hardy form [6,8,17]:

$$\begin{aligned} \widehat{J} = \hbar \sum_{\boldsymbol{q}\nu\nu'} \frac{\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{q}\nu'}}{2} v_{\boldsymbol{q}\nu\nu'} \hat{a}^\dagger_{\boldsymbol{q}\nu} \hat{a}_{\boldsymbol{q}\nu'} \\ + \hbar \sum_{\boldsymbol{q}\nu\nu'} \frac{\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}\nu'}}{4} v_{\boldsymbol{q}\nu\nu'} (\hat{a}_{-\boldsymbol{q}\nu} \hat{a}_{\boldsymbol{q}\nu'} - \hat{a}^\dagger_{\boldsymbol{q}\nu} \hat{a}^\dagger_{-\boldsymbol{q}\nu'}). \end{aligned} \tag{26}$$

Neglecting again the antiresonant (second-line) part of the flux, we find

$$\kappa = \frac{i}{VT} \sum_{\boldsymbol{q}\boldsymbol{k}\nu\nu'\mu\mu'} c_{\boldsymbol{k}\mu\mu'} v_{\boldsymbol{q}\nu\nu'} v_{\boldsymbol{k}\mu\mu'} \frac{\omega_{\boldsymbol{q}\nu\nu'}}{\omega_{\boldsymbol{k}\mu\mu'}} \bar{\Lambda}^{-1}_{\boldsymbol{q}\nu\nu',\boldsymbol{k}\mu\mu'}(0), \tag{27}$$

where $c_{\boldsymbol{k}\mu\mu'} = c_{\boldsymbol{k}\mu\boldsymbol{k}\mu'}$.

In Appendix C, it is shown that when the phonon line widths are small with respect interband separations, the $\bar{\Lambda}$ matrix in Eq. (27) is diagonal in the $\nu\nu'$ and $\mu\mu'$ indices. Assuming that this is the case, the matrix Ω_{IJ} in Eqs. (11) and (15) vanishes, and Eq. (27) becomes

$$\kappa = \frac{1}{V} \sum_{\boldsymbol{q}\nu\boldsymbol{k}\mu} c_{\boldsymbol{k}\mu} v_{\boldsymbol{q}\nu} v_{\boldsymbol{k}\mu} \frac{\omega_{\boldsymbol{q}\nu}}{\omega_{\boldsymbol{k}\mu}} \bar{\Gamma}^{-1}_{\boldsymbol{q}\nu\boldsymbol{k}\mu}(0), \tag{28}$$

where $c_{\boldsymbol{k}\mu} = c_{\boldsymbol{k}\mu\mu} = \frac{n_{\boldsymbol{k}\mu}(n_{\boldsymbol{k}\mu}+1)\hbar^2\omega^2}{k_B T^2}$ is the modal heat capacity. If we now define the scattering matrix S as

$$S_{\boldsymbol{q}\nu\boldsymbol{k}\mu} = \bar{\Gamma}_{\boldsymbol{k}\mu\boldsymbol{q}\nu} \frac{\omega_{\boldsymbol{k}\mu}}{\omega_{\boldsymbol{q}\nu}}, \tag{29}$$

then Eq. (28) can be written as

$$\kappa = \frac{1}{V} \sum_{\boldsymbol{q}\nu\boldsymbol{k}\mu} c_{\boldsymbol{q}\nu} v_{\boldsymbol{q}\nu} v_{\boldsymbol{k}\mu} S^{-1}_{\boldsymbol{q}\nu\boldsymbol{k}\mu}, \tag{30}$$

which has the same form as from the full BTE, provided S can be identified with the scattering matrix appearing therein [3,18]. In order to see that this is indeed the case, we compute the memory matrix, Eq. (12), to lowest (second) order in the cubic anharmonic interactions, K, taking into account lattice periodicity. The calculations are quite lengthy and are fully reported in Appendix D. The final, purely real, results read

$$\begin{aligned} \bar{\Gamma}_{\boldsymbol{q}\nu\boldsymbol{k}\mu}(z=0) = 2\gamma_{\boldsymbol{q}\nu}\delta_{\boldsymbol{q}\boldsymbol{k}}\delta_{\nu\mu} + \pi\hbar \sum_{\boldsymbol{q}'\nu'} |K_{\boldsymbol{q}\nu\boldsymbol{k}\mu\boldsymbol{q}'\nu'}|^2 n_{\boldsymbol{q}'\nu'} \Bigg[\frac{(n_{\boldsymbol{q}\nu}+1)}{n_{\boldsymbol{k}\mu}} \delta(\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{k}\mu} - \omega_{\boldsymbol{q}'\nu'}) - \frac{n_{\boldsymbol{q}\nu}}{n_{\boldsymbol{k}\mu}} \delta(\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{q}'\nu'} - \omega_{\boldsymbol{k}\mu}) \\ - \frac{n_{\boldsymbol{q}\nu}+1}{n_{\boldsymbol{k}\mu}+1} \delta(\omega_{\boldsymbol{k}\mu} + \omega_{\boldsymbol{q}'\nu'} - \omega_{\boldsymbol{q}\nu}) \Bigg], \end{aligned} \tag{31}$$

where $K_{\boldsymbol{q}\nu\boldsymbol{k}\mu\boldsymbol{q}'\nu'} = \frac{1}{\sqrt{8\omega_{\boldsymbol{q}\nu}\omega_{\boldsymbol{k}\mu}\omega_{\boldsymbol{q}'\nu'}}} \frac{\partial^3 V}{\partial X_{\boldsymbol{q}\nu}\partial X_{\boldsymbol{k}\mu}\partial X_{\boldsymbol{q}'\nu'}} \delta_{\boldsymbol{q}-\boldsymbol{k}-\boldsymbol{q}',\boldsymbol{G}}$, with $\frac{\partial^3 V}{\partial X_{\boldsymbol{q}\nu}\partial X_{\boldsymbol{k}\mu}\partial X_{\boldsymbol{q}'\nu'}}$ being the third derivative at the equilibrium of the potential with respect to the amplitude of the lattice distortion along the lattice normal modes $X_{\boldsymbol{q}\nu}$. The presence of $\delta_{\boldsymbol{q}-\boldsymbol{k}-\boldsymbol{q}',\boldsymbol{G}}$ ensures the conservation of the crystal momentum of the phonons involved, modulus a reciprocal lattice vector $\boldsymbol{G}$. For a cubic anharmonic potential, the phonon line width $\gamma_{\boldsymbol{q}\nu}$ is defined as [19]

$$\gamma_{\boldsymbol{q}\nu} = \pi\hbar \sum_{\boldsymbol{q}'\nu'\boldsymbol{k}\mu} |K_{\boldsymbol{q}\nu\boldsymbol{k}\mu\boldsymbol{q}'\nu'}|^2 \Bigg[\frac{1}{2}(n_{\boldsymbol{k}\mu} + n_{\boldsymbol{q}'\nu'} + 1)\delta(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{k}\mu} - \omega_{\boldsymbol{q}'\nu'}) + (n_{\boldsymbol{k}\mu} - n_{\boldsymbol{q}'\nu'})\delta(\omega_{\boldsymbol{q}\nu} + \omega_{\boldsymbol{q}'\nu'} - \omega_{\boldsymbol{k}\mu}) \Bigg]. \tag{32}$$

Equations (31) and (32) coincide with those appearing in the full BTE, computed to lowest order in the cubic anharmonic corrections to the lattice Hamiltonian [18], thus proving the equivalence of the treatments of thermal transport based on the Boltzmann's kinetic approach and the Green-Kubo theory of linear response.

IV. COMPARISON WITH THE WIGNER TRANSPORT EQUATION

As an alternative to the GK theory, the BTE for heat transport can be derived from MBPT, leveraging a Wigner-like lattice distribution obtained from phonon Green's functions [20]. Recently, this approach has been considerably refined by introducing a dependence of the Wigner distribution on band indices, which give rise to interband contributions to the heat conductivity when the distance between neighboring bands is comparable with the phonon linewidth [5,7,8]. The final expression for the heat conductivity in the WTE approach is given by Eq. (12) of Ref. [5]:

$$\begin{aligned} \kappa^{\mathrm{WTE}} = \kappa^{\mathrm{BTE}} + \frac{\hbar^2}{k_b T^2 V} \sum_{\boldsymbol{q}\nu\neq\nu'} \frac{\omega_{\boldsymbol{q}\nu'} + \omega_{\boldsymbol{q}\nu}}{4} [\omega_{\boldsymbol{q}\nu} n_{\boldsymbol{q}\nu}(n_{\boldsymbol{q}\nu}+1) \\ + \omega_{\boldsymbol{q}\nu'} n_{\boldsymbol{q}\nu'}(n_{\boldsymbol{q}\nu'}+1)] V_{\boldsymbol{q}\nu\nu'} V_{\boldsymbol{q}\nu'\nu} \\ \times \frac{\gamma_{\boldsymbol{q}\nu} + \gamma_{\boldsymbol{q}\nu'}}{(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}\nu'})^2 + (\gamma_{\boldsymbol{q}\nu} + \gamma_{\boldsymbol{q}\nu'})^2}, \end{aligned} \tag{33}$$

where κ^{BTE} is the BTE expression for the heat conductivity given by Eq. (30) and $V_{\boldsymbol{q}\nu\nu'} = \frac{2\sqrt{\omega_{\boldsymbol{q}\nu}\omega_{\boldsymbol{q}\nu'}}}{\omega_{\boldsymbol{q}\nu}+\omega_{\boldsymbol{q}\nu'}} v_{\boldsymbol{q}\nu'\nu}$ is the velocity

matrix defined in that work. By treating the difference between Eq. (27) and Eq. (30) in the RTA, the former can be cast into the form

$$\kappa = \kappa^{\mathrm{BTE}} + \frac{1}{V} \sum_{\boldsymbol{q}\nu \neq \nu'} c_{\boldsymbol{q}\nu\nu'} v_{\boldsymbol{q}\nu\nu'} v_{\boldsymbol{q}\nu'\nu} \times \frac{\gamma_{\boldsymbol{q}\nu} + \gamma_{\boldsymbol{q}\nu'}}{(\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}\nu'})^2 + (\gamma_{\boldsymbol{q}\nu} + \gamma_{\boldsymbol{q}\nu'})^2}, \tag{34}$$

which differs from Eq. (33) only by corrections of order $O(\gamma^2/\omega^2)$. These considerations show that, provided the same levels of approximation are adopted, the WTE and GKMZ give the same results, in line with the work of Ref. [8] and previous work for the electrical conductivity as reported, e.g., in Mahan's textbook [21]. Crucially, a proper account of interband contributions to heat conduction allows the WTE to be easily generalized to disordered systems, which, strictly speaking, do not display any dispersions, as they lack translational symmetry. This result emerges naturally from the GK approach, which does not presuppose any symmetry.

We conclude that crystals whose interband spacing is comparable with their phonons' linewidths cannot be described by full BTE alone. Among these crystals, we find materials such as (anti)perovskites with promising applications in various fields of electronics, which will be the subject of a numerical application in Sec. V.

V. APPLICATION TO Li_3ClO

The theory presented in this paper has been demonstrated on the lithium-rich antiperovskite Li_3ClO, which is a promising candidate for all solid-state lithium-metal batteries and whose transport properties have been recently studied with state-of-the-art methods [22]. We computed the heat conductivity of this material using the present theory and classical force fields, as described in Appendix E. In Fig. 1, we display our results obtained using different approximations. We identify two distinct regimes. At low temperatures, hydrodynamic effects [15]—which are accounted for in the full BTE but not in QHGK—may considerably enhance the heat conductivity, while interband contributions in Eqs. (33) and (34)—present in QHGK but not in the BTE—are negligible due to the vanishing of the vibrational linewidths as $T \to 0$; in this regime, the full BTE correctly describes the temperature dependence of the heat conductivity, while QHGK does not. At room temperature and above, instead, interband effects may be important, particularly in complex crystals as in the present case, while hydrodynamic effects are negligible; in this case, the QHGK approximation is applicable and the BTE is not. Equations (33) and (34) nicely and correctly interpolate between these two regimes.

VI. CONCLUSIONS

In this paper, we have critically analyzed the approximations that lead to the unified quasiharmonic Green-Kubo approach to heat transport in crystalline and disordered insulators [6] and shown how they can be dealt with by applying the Mori-Zwanzig memory-function formalism to one- and two-normal-mode correlation functions. In the first case, the MZ formalism allows one to account for vibrational memory (*self-energy*, in the MBPT parlance) effects on heat conduction, whereas in the second it permits one to dispose of the *dressed-bubble* approximation to the two-mode correlation functions and derive an expression for the heat conductivity that is equivalent to that provided by the full linearized Boltzmann's transport equation. Besides providing a fully *ab initio* derivation of the latter, we believe that our paper will pave the way to the study of systems where memory effects and vertex corrections to heat transport coefficients are both important. Moreover, we have clarified the interconnection and equivalence between the Wigner and quasiharmonic Green-Kubo approaches to heat transport in solids, provided the same levels of approximation are adopted—thus extending the work of Ref. [8].

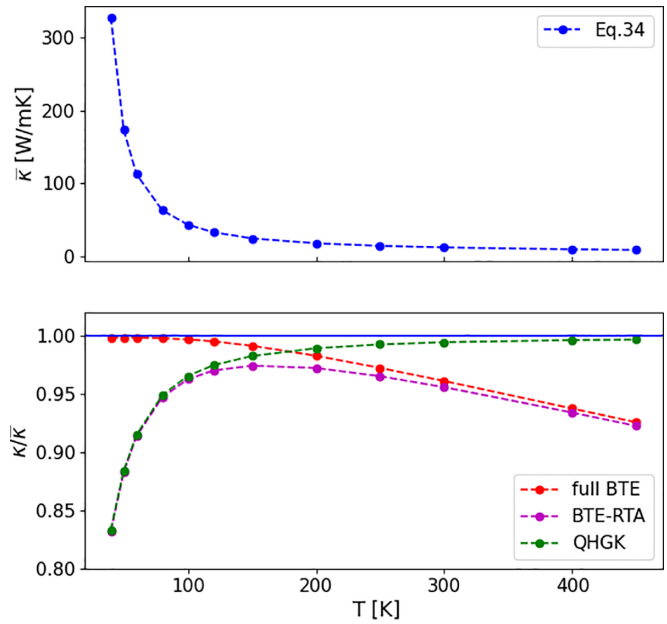

FIG. 1. Top: Thermal conductivity averaged over the three Cartesian coordinates as a function of temperature, computed with Eq. (34). Bottom: The ratio between the thermal conductivity computed with different methods and the one in the top panel.

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APPENDIX A: DERIVATION OF EQ. (17)

In order to prove Eq. (17), we first write Eqs. (6)–(9) in the diagonal ($I = J$) approximation:

$$\kappa \approx \frac{\hbar^2}{VT} \sum_{pq} v_{pq} v_{pq} \bar{\omega}_{pq}^2 \int_0^\infty (\widehat{A}_{pq}(t), \widehat{A}_{pq}). \tag{A1}$$

We now observe that $\widehat{A}_{pq} = \widehat{A}^{\dagger}_{qp}$ and that the Kubo inner product, Eq. (4), has the property $(\widehat{A}, \widehat{B}) = (\widehat{A}^{\dagger}, \widehat{B}^{\dagger})^*$. We conclude that

$$\int_0^\infty (\widehat{A}_{qp}(t), \widehat{A}_{qp}) = \left(\int_0^\infty (\widehat{A}_{pq}(t), \widehat{A}_{pq}) \right)^*, \tag{A2}$$

from which we deduce that the $\bar{C}_{pq,pq}(0)$ [Eq. (7)] matrix is Hermitian with respect to $p \leftrightarrow q$ exchange, whereas $\bar{\Gamma}_{pq,pq}$ and $\Omega_{pq,pq}$ [Eqs. (12)–(15)] are anti-Hermitian, and Eq, (17) follows immediately.

APPENDIX B: DERIVATION OF EQ. (18)

In order to compare Eqs. (17) and (18), we first compute the diagonal part ($II = (pq, pq)$) of the memory matrix, assuming that the anharmonic terms in the vibrational Hamiltonian can be truncated to third order in the atomic displacements:

$$\widehat{\mathcal{V}} \approx \frac{\hbar^{3/2}}{6} \sum_{pqr} K_{pqr} \widehat{X}_p \widehat{X}_q \widehat{X}_r, \tag{B1}$$

where $\widehat{X}_p = \hat{a}^{\dagger}_p + \hat{a}_p$ is a (rescaled) normal-mode coordinate. Using the method explained in Sec. D, we obtain

$$\bar{\Gamma}'_{pq,pq}(z=0) = \bar{\gamma}_p^{>'}(\omega_q) d_{pq} + \bar{\gamma}_q^{<'}(\omega_p) d_{qp} + O(N^{-1}), \tag{B2}$$

where N is the number of normal modes, $(\cdot)' = \mathsf{Re}(\cdot)$, $d_{pq} = \frac{\beta\hbar(\omega_p - \omega_q)}{e^{\beta\hbar(\omega_p-\omega_q)}-1}$, and $\bar{\gamma}_p^{\lessgtr}(\omega)$ are the FL transforms of the one-body greater and lesser Green's functions, whose expressions as obtained from Mori's formalism [10] are

$$\bar{g}_p^{>}(\omega) = -i\langle \hat{a}_p \hat{a}^{\dagger}_p \rangle \frac{1}{(\omega_p - \omega) - i\bar{\gamma}_p^{>}(\omega)},$$

$$\bar{g}_p^{<}(\omega) = i\langle \hat{a}^{\dagger}_p \hat{a}_p \rangle \frac{1}{(\omega_p - \omega) - i\bar{\gamma}_p^{<}(\omega)}. \tag{B3}$$

The corresponding Fourier transforms equal twice the imaginary part of Eqs. (B3), reading

$$\tilde{g}_p^{>}(\omega) = -i\langle \hat{a}_p \hat{a}^{\dagger}_p \rangle \frac{2\bar{\gamma}_p^{>'}(\omega)}{|(\omega_p - \omega) - i\bar{\gamma}_p^{>}(\omega)|^2}, \tag{B4}$$

$$\tilde{g}_p^{<}(\omega) = \quad i\langle \hat{a}^{\dagger}_p \hat{a}_p \rangle \frac{2\bar{\gamma}_p^{<'}(\omega)}{|(\omega_p - \omega) - i\bar{\gamma}_p^{<}(\omega)|^2}. \tag{B5}$$

To lowest order in the cubic anharmonic correction to the lattice potential energy, Eq. (B4) reads

$$\tilde{\gamma}_p^{<'}(\omega) = \frac{\pi\hbar}{16 n_p} \sum_{qr} |K_{pqr}|^2 [n_q n_r \delta(\omega - \omega_q - \omega_r) + (n_q + 1) n_r \delta(\omega + \omega_q - \omega_r)$$
$$+ n_q (n_r + 1)\delta(\omega - \omega_q + \omega_r) + (n_q + 1)(n_r + 1)\delta(\omega + \omega_q + \omega_r)] + O(K^3). \tag{B6}$$

Neglecting corrections of order $O(N^{-1})$, we obtain

$$\kappa = \frac{1}{V} \sum_{pq} \frac{\hbar^2 (\omega_p + \omega_q)^2}{4} v_{pq} v_{pq} (I_{pq} + I_{qp}), \text{ where} \tag{B7}$$

$$I_{pq} = \frac{n_p (n_q + 1)}{2 k_b T^2} \frac{\bar{\gamma}_p^{>'}(\omega_q) + \bar{\gamma}_q^{<'}(\omega_p)}{|(\omega_p - \omega_q) - i(\bar{\gamma}_p^{>}(\omega_q) d_{pq} + \bar{\gamma}_q^{<}(\omega_p) d_{qp})|^2}. \tag{B8}$$

Let us compare this expression with Eq. (18), which gives the QHGK approximation within the full dressed-bubble approximation, including memory (non-Markovian) effects. The integral in Eq. (18) can be computed using Cauchy's residue theorem. For instance, in the $\omega_q \neq \omega_p$ case, substituting Eq. (B4) into Eq. (19), we obtain an integrand with four distinct poles, whose positions in the QH approximation are

$$\omega_p^{\pm} = \omega_p + \bar{\gamma}''_p(\omega_p) \pm i\bar{\gamma}'_p(\omega_p) + O\big(\gamma_p^2\big)$$
$$\omega_q^{\pm} = \omega_q + \bar{\gamma}''_q(\omega_q) \pm i\bar{\gamma}'_q(\omega_q) + O\big(\gamma_q^2\big), \tag{B9}$$

where $\bar{\gamma}''_q = \mathsf{Im}\bar{\gamma}_q$. Closing the path in the upper complex half-plane, we get

$$I_{pq} = 2\pi i \sum_{\mathrm{Im}\bar{z}>0} \mathsf{Res}(f(\bar{z})) = \frac{(n_p + 1) n_q}{2 k_b T^2} \left(\frac{\bar{\gamma}_p^{>'}(\omega_q^+)}{|(\omega_p - \omega_q^+) - i\bar{\gamma}_p^{>}(\omega_q^+)|^2} + \frac{\bar{\gamma}_q^{<'}(\omega_p^+)}{|(\omega_q - \omega_p^+) - i\bar{\gamma}_q^{>}(\omega_p^+)|^2} \right), \tag{B10}$$

where we used $\langle \hat{a}_p \hat{a}^{\dagger}_p \rangle \approx n_p + 1$. We observe that Eqs. (B10) and (B8) have the same numerator but a slightly different denominator. Their difference is negligible if $|\frac{\bar{\gamma}_p(\omega_q) - \bar{\gamma}_p(\omega_p)}{\omega_p - \omega_q}| \ll 1$, which happens in the quasiharmonic limit ($\bar{\gamma}, \frac{\partial\bar{\gamma}}{\partial\omega} \sim O(K^2) \to 0$) if the memory function is regular enough. If $\bar{\gamma}(\omega) = \gamma$, independent of ω, both Eqs. (B10) and (B8) return the Markovian approximation, Eq. (22), to order $O(\gamma^2)$.

In these calculations we have neglected terms of order $O(N^{-1})$, which can be identified with the diagonal part of the

vertex corrections. We notice that similar $O(N^{-1})$ corrections are also neglected when comparing BTE-RTA, $\tau_{\boldsymbol{q}\nu} = 1/2\gamma_{\boldsymbol{q}\nu}$, with the diagonal of the full BTE scattering matrix: $S_{\boldsymbol{q}\nu\boldsymbol{q}\nu} = 2\gamma_{\boldsymbol{q}\nu} + O(N^{-1})$.

APPENDIX C: DERIVATION EQ. (28) FOR WELL SEPARATED BANDS

Equation (28) is derived under the assumption that the interband ($\nu \neq \nu'$ and $\mu \neq \mu'$) elements of the $\bar{\Gamma}^{-1}_{\boldsymbol{q}\nu\nu',\boldsymbol{q}'\mu\mu'}$ matrix can be neglected. This is indeed the case when the phonon bands are well separated, in the sense that $|\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}\nu'}| \gg \Gamma_{\boldsymbol{q}\nu\nu',\boldsymbol{k}\mu\mu'}\ \forall\,(\boldsymbol{k}\mu\mu')$. We say in this case that *interband contributions* are negligible and we call the corresponding approximation the *intraband approximation*. Let us decompose the $\bar{\Lambda}$ matrix into a diagonal part, $D_{IJ} = (-\Omega_{II} + i\bar{\Gamma}_{II})\delta_{IJ}$, and an off-diagonal part $O = \bar{\Lambda} - D$ and apply the identity

$$\bar{\Lambda}^{-1} = (D+O)^{-1} = D^{-1} - D^{-1}O(D+O)^{-1}. \tag{C1}$$

The last term can be rewritten as

$$\begin{aligned}(D^{-1}O(D+O)^{-1}))_{IJ} &= \sum_K D^{-1}_{IK}(O(D+O)^{-1})_{KJ} \\ &= D^{-1}_{II}(O(D+O)^{-1})_{IJ}.\end{aligned} \tag{C2}$$

The O matrix does not diverge when $|\omega_{\boldsymbol{q}\nu} - \omega_{\boldsymbol{q}\nu'}| \to \infty$. Therefore,

$$\lim_{|\omega_{\boldsymbol{q}\nu}-\omega_{\boldsymbol{q}\nu'}|\to\infty}\left[\frac{1}{\omega_{\boldsymbol{q}\nu'} - \omega_{\boldsymbol{q}\nu} + i\bar{\Gamma}_{\boldsymbol{q}\nu\nu',\boldsymbol{q}\nu\nu'}} - \frac{1}{\omega_{\boldsymbol{q}\nu'} - \omega_{\boldsymbol{q}\nu} + i\bar{\Gamma}_{\boldsymbol{q}\nu\nu',\boldsymbol{q}\nu\nu'}}(O(D+O)^{-1})_{\boldsymbol{q}\nu\nu',\boldsymbol{k}\mu\mu'}\right] = 0. \tag{C3}$$

Therefore, only the $\nu = \nu'$ elements survive in this limit. Due to the relation between $\bar{\Lambda}_{IJ}$ and $\bar{\Lambda}_{JI}$, the argument can be repeated for the second pair of band indices μ, μ'. Thus, for well-separated bands

$$(\bar{\Lambda})^{-1}_{\boldsymbol{q}\nu\nu',\boldsymbol{k}\mu\mu'} \approx \delta_{\nu\nu'}\delta_{\mu\mu'}(\bar{\Lambda})^{-1}_{\boldsymbol{q}\nu\nu,\boldsymbol{k}\mu\mu}, \tag{C4}$$

which motivates the *intraband approximation*.

APPENDIX D: COMPUTATION OF THE MEMORY MATRIX IN THE CUBIC APPROXIMATION [Eq. (31)]

In order to compute the memory matrix leading to the BTE, Eq. (31), we express the $\bar{\Gamma}_{IJ}$ matrix in Eq. (12) as the FL transform of the time-correlation function of the projected time derivatives of the $\widehat{A}_I$ and $\widehat{A}_J$ operators:

$$\bar{\Gamma}_{IJ}(0) = \frac{1}{C^{\circ}_{JJ}}\int_0^{\infty}(\boldsymbol{\mathcal{Q}}\dot{\widehat{A}}_I, \mathrm{e}^{-i\boldsymbol{\mathcal{Q}}\mathcal{L}\boldsymbol{\mathcal{Q}}t}\boldsymbol{\mathcal{Q}}\dot{\widehat{A}}_J)dt, \tag{D1}$$

where we used the harmonic approximation of C_{IJ} and

$$\begin{aligned}\boldsymbol{\mathcal{Q}}\dot{\widehat{A}}_I &\doteq \frac{i}{\hbar}\boldsymbol{\mathcal{Q}}[\hat{a}^{\dagger}a_p\hat{a}_q, \widehat{H}] \\ &= -\frac{i\hbar^{1/2}}{2}\sum_{rs}K_{prs}\widehat{X}_r\widehat{X}_s\hat{a}_q + \hat{a}^{\dagger}_p\frac{i\hbar^{1/2}}{2}\sum_{rs}K_{qrs}\widehat{X}_r\widehat{X}_s,\end{aligned} \tag{D2}$$

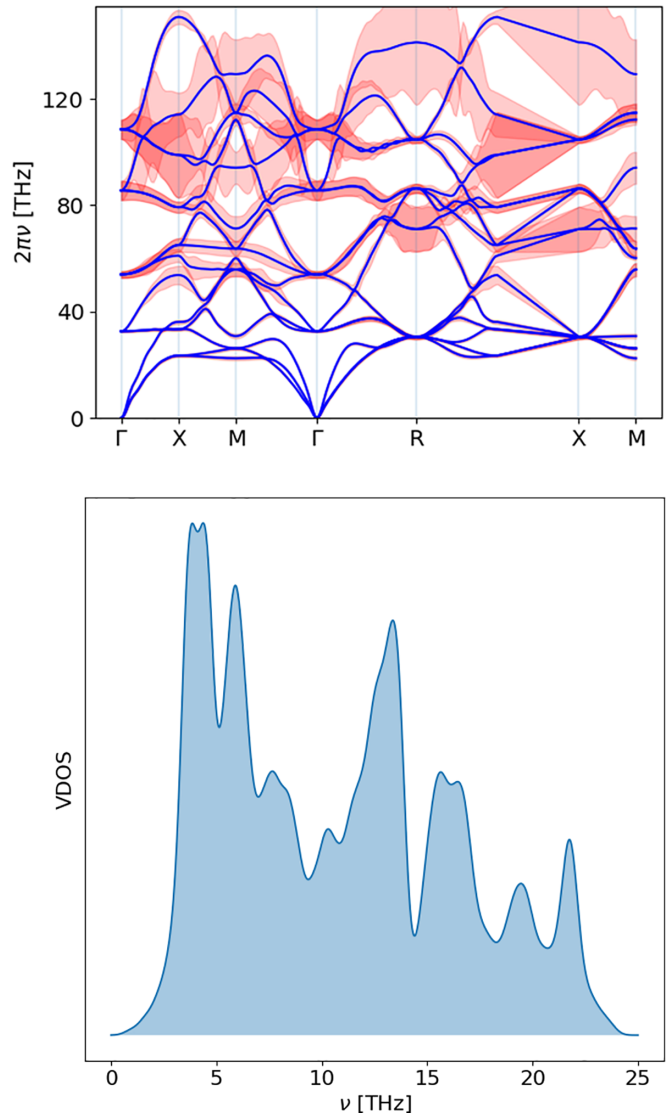

FIG. 2. Phonon dispersions and linewidths (upper panel) and VDOS (lower panel) of Li_3ClO (see text).

where we use a cubic anharmonic potential as in Eq. (B1). As explained in the main text, at our desired order of approximation, $\bar{\Gamma} \sim O(K^2)$, both the average and the Liouvillian operator can be evaluated in the harmonic approximation.

Regarding the FL transforms (LFT) ($\bar{f}(\omega)$), it is computed through the Fourier transform (FT) ($\tilde{f}(\omega)$), using the relation

$$\bar{f}(\omega) = \int_0^{\infty} e^{i\omega t}f(t) \tag{D3}$$

$$= \frac{1}{2}\tilde{f}(\omega) + \frac{i}{2\pi}\int_{-\infty}^{\infty}d\omega\,\frac{1}{\omega-\omega'}\tilde{f}(\omega'). \tag{D4}$$

Assuming that the FT is real, half of it is the real part of the LFT (the dissipative part), while the imaginary part would be given by the second term in the relation, the convolution one.

Combining Eq. (12) and Eq. (D2) we obtain

$$\begin{aligned}\bar{\Gamma}'_{pq,rs}(0) = \frac{\hbar}{8C_{rs,rs}} \sum_{tuvz} \int_{-\infty}^{\infty} dt \int_0^{\frac{1}{k_b T}} d\lambda \\ \times [K_{ptu}K_{rvz}\langle \widehat{X}_t(\tau)\widehat{X}_u(\tau)\hat{a}_q(\tau)\hat{a}_s^\dagger \widehat{X}_v\widehat{X}_z\rangle^\circ \\ + K_{qtu}K_{rvz}\langle \hat{a}_p^\dagger(\tau)\widehat{X}_t(\tau)\widehat{X}_u(\tau)\widehat{X}_v\widehat{X}_z\hat{a}_r\rangle^\circ \\ - K_{ptu}K_{rvz}\langle \widehat{X}_t(\tau)\widehat{X}_u(\tau)\hat{a}_q(\tau)\widehat{X}_v\widehat{X}_z\hat{a}_r\rangle^\circ \\ - K_{qtu}K_{rvz}\langle \hat{a}_p^\dagger(\tau)\widehat{X}_t(\tau)\widehat{X}_u(\tau)\hat{a}_s^\dagger\widehat{X}_v\widehat{X}_z\rangle^\circ]. \quad \text{(D5)}\end{aligned}$$

This expression contains a great number of combinations of annihilation and creation operators. Let us compute one of them. For instance,

$$\begin{aligned}&\int_{-\infty}^{\infty} dt \int_0^{\beta} d\lambda\, K_{ptu}K_{rvz}\langle \hat{a}_t^\dagger(\tau)\hat{a}_u^\dagger(\tau)\hat{a}_q(\tau)\hat{a}_s^\dagger\hat{a}_v\hat{a}_z\rangle^\circ \\ &= 2\pi K_{ptu}K_{rvz}\frac{e^{\beta\hbar(\omega_t+\omega_u-\omega_q)}-1}{\hbar(\omega_t+\omega_u-\omega_q)}\delta(\omega_t+\omega_u-\omega_q) \\ &\quad\times \langle \hat{a}_t^\dagger\hat{a}_u^\dagger\hat{a}_q\hat{a}_s^\dagger\hat{a}_v\hat{a}_z\rangle^\circ \\ &= 2\pi\beta K_{ptu}K_{rvz}\delta(\omega_t+\omega_u-\omega_q)\langle \hat{a}_t^\dagger\hat{a}_u^\dagger\hat{a}_q\hat{a}_s^\dagger\hat{a}_v\hat{a}_z\rangle^\circ. \quad \text{(D6)}\end{aligned}$$

Now we should apply Wick's theorem on the thermal average; however, several of the resulting terms vanish because they are proportional to a delta function of a finite argument. For instance, coupling $\hat{a}_u^\dagger\hat{a}_q$ would lead to $\sim\delta(\omega_t)$. Thus, keeping only the nonvanishing combinations, one gets

$$\begin{aligned}&2\pi\beta K_{ptu}K_{rvz}(n_t n_u(n_q+1) \\ &\quad\times\delta(\omega_t+\omega_u-\omega_q)(\delta_{tv}\delta_{uz}\delta_{qs}+\delta_{tz}\delta_{uv}\delta_{qs})). \quad \text{(D7)}\end{aligned}$$

All the other elements of $\bar{\Gamma}$ can be computed by performing analogous calculations. We note that by applying the same argument as in Sec. A, we can conclude that $\bar{\Gamma}_{pq,rs}(0)$ is real when $\widehat{A}_{pq}$ and $\widehat{A}_{rs}$ are Hermitian.

APPENDIX E: TECHNICAL DETAILS AND INTERMEDIATE RESULTS OF THE NUMERICAL APPLICATION

The Li_3ClO compound is simulated in a cubic cell with edge $a_0 = 3.875$ Å, using the Buckingham potential [23], and the PPPM [24] method to treat the Coulomb interaction. Second- and third-order interatomic force constants were computed with LAMMPS [25] using a finite-difference method in a [5,5,5] supercell, while the κALDO code [18] was used to evaluate vibrational frequencies, anharmonic linewidths, and thermal conductivities. Lattice-dynamical calculations were performed on a [16,16,16]k-point mesh. In Fig. 2, we display the phonon dispersions of the material and the vibrational density of states (VDOS), computed with a Gaussian broadening function with a standard deviation of 0.3 THz. The pink area surrounding the phonon dispersion represents twice the line widths—computed at 250 K on a coarse grid and Fourier-interpolated on a finer one—highlighting the regions in reciprocal space where the separation between phonon bands is comparable with the vibrational broadening, and interband contributions to the heat conductivity are expected to be important; see Eqs. (33) and (34).

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