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 quasi-harmonic Green-Kubo theory of heat transport in insulators naturally lead to a generalisation of the expression for the conductivity that could be derived from the linearized Boltzmann equation, when the effects of the Green-Kubo theory are accounted for. Our results, which are obtained from the Mori-Zwanzig memory-function formalism, provide a fully \textit{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.

\section{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 quasi-particles) 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 elaborated 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 quasi-harmonic (QH) approximation, and dubbed therefore “QHGK”. Notwithstanding, the two approaches give similar results for the heat conductivity, which coincides in the long-life-time limit. Even when applied to crystals, these methods provide further insight into the limits of the quasi-particle picture of transport: the quasi-particle 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 \textit{inter-band} 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, \( \langle \hat{J}(t)\hat{J}(0) \rangle \), where \( \langle \cdot \rangle \) indicates an equilibrium thermal average and here and a caret, \( \hat{\cdot} \), 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 \( \langle \hat{a}_{p_1}^\dagger(t)\hat{a}_{q_1}(t)\hat{a}_{r_1}^\dagger\hat{a}_{s_1} \rangle \) and \( \langle \hat{a}_{p_2}^\dagger(t)\hat{a}_{q_2}(t)\hat{a}_{r_2}^\dagger\hat{a}_{s_2} \rangle \) [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.,

\begin{equation}
\langle \hat{a}_{p_1}^\dagger(t)\hat{a}_{q}(t)\hat{a}_{r_1}^\dagger\hat{a}_{s} \rangle \approx n_p n_r \delta_{pq} \delta_{rs} + \langle \hat{a}_{p_2}^\dagger(t)\hat{a}_{p}(0) \rangle \langle \hat{a}_{q_2}(t)\hat{a}_{q}(0) \rangle \delta_{ps} \delta_{qr},
\end{equation}

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, \( \omega_p \) being the normal-mode frequency, \( T \) the system’s temperature, and \( k_B \) the Boltzmann’s constant. In the many-body parlance, this factorization is described as the neglect of vertex corrections to the correlation function and referred to as the \textit{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, \textit{i.e.} unaffected by any memory effects. The Markovian approximation essentially results in a damped exponential dependence

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of the single-mode greater Green’s function on time,
\[ -i\langle \hat{a}_p(t)\hat{a}_p^\dagger \rangle \approx -i (n_p + 1)e^{-i\omega_p t - \gamma_p |t|}, \]  
which is to say that its spectral function (the imaginary part of its Laplace-Fourier transform) is Lorentzian. In a many-body 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 inter-band 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-Zwanzig approach to the Green-Kubo linear-response theory of heat transport; in Sec. III we derive the single-mode approximation to the GKMZ theory, which is closely related to the QHGK approach of Ref. [6]; 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$_3$ClO anti-perovskite ionic conductor; Sec. VI finally contains our conclusions.

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

The quantum GK formula for the thermal conductivity, \( \kappa \), reads:
\[ \kappa = \frac{1}{VT} \int_0^{\infty} dt \int \frac{d\omega}{2\pi} \frac{d\lambda}{2\pi} \langle \hat{J}(t) - i\hbar \lambda \hat{J}(0) \rangle, \]  
where the time evolution of operators in the Heisenberg representation can be formally expressed in terms of the exponential of the Liouvillian super-operator [13], \( \mathcal{L} \), defined as \( \hat{A}(t) = e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} = e^{i\mathcal{L}t/\hbar} \), and \( \mathcal{L} \hat{A} \equiv [\hat{H}, \hat{A}]/\hbar = -i\dot{\hat{A}} \). In terms of this scalar product, the quantum heat conductivity, Eq. (3), simply reads
\[ \kappa = \frac{1}{VT} \int_0^{\infty} \langle \hat{J}(t), \hat{J}(0) \rangle dt, \]  
in close formal analogy with its classical counterpart.

In the QH approximation, the energy flux can be cast into the form:
\[ \hat{J} = -\frac{i\hbar}{2} \sum_{pq} v_{pq} \left( \frac{\omega_p + \omega_q}{2} \right) (\hat{a}_q^\dagger \hat{a}_p - \hat{a}_p^\dagger \hat{a}_q) + \frac{i\hbar}{2} \sum_{pq} v_{pq} \left( \frac{\omega_p - \omega_q}{2} \right) (\hat{a}_q^\dagger \hat{a}_q - \hat{a}_p \hat{a}_q^\dagger), \]  
where \( v_{pq} \) is the real anti-symmetric generalized group-velocity matrix [6, 14]. The first, phonon-conserving, term in Eq. (5) was dubbed resonant in Ref. [6], while the second, anti-resonant, 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, i.e., \( \hat{a}^\dagger_p(t)\hat{a}_q(t) \)—irrelevant, one finally obtains:
\[ \kappa = \frac{\hbar^2}{VT} \sum_{IJ} v_{I} v_{J} \tilde{\omega}_I \tilde{\omega}_J \tilde{C}_{IJ}(0), \]  
where the indices \( I = (pq) \) and \( J = (rs) \) label pairs of normal modes, \( \tilde{\omega}_I = (\omega_p + \omega_q)/2, \) \( \tilde{\omega}_J = (\omega_r + \omega_s)/2, \) \( \tilde{\omega}_I = \hat{a}_q^\dagger \hat{a}_q, \) and \( \tilde{C}_{IJ}(0) \) is the zero-frequency value of the Fourier-Laplace (FL) transform of the two-mode correlation function:
\[ \tilde{C}_{IJ}(z) = \int_0^{\infty} dt e^{izt} C_{IJ}(t), \]  
\[ C_{IJ}(t) = \langle \hat{A}_{I}(t), \hat{A}_{J} \rangle. \]  
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. Eq. (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 \( \tilde{C}_{IJ}(z) \) can be formally expressed as:
\[ \tilde{C}_{IJ}(z) = i \sum_K \tilde{A}_{IK}^{-1}(z) C_{KJ}, \]  
where
\[ C_{IJ} = C_{IJ}(0), \]  
where
\[ \tilde{A}_{IK}(z) = z\delta_{IK} - \Omega_{IK} + i\Gamma_{IK}(z), \]

\[ \Omega_{IJ} = i\sum_K (\hat{A}_I, \hat{A}_J) C_{KJ}^{-1}, \]

\[ \tilde{\Gamma}_{IJ}(z) = \sum_K (\hat{A}_I, \mathcal{Q}(z - \mathcal{Q}\mathcal{Q})^{-1} \mathcal{Q}\hat{A}_K) C_{KJ}^{-1}, \]

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

\[ \mathcal{Q}\hat{B} = \hat{B} - \sum_{IJ} \hat{A}_I(\hat{A}_J, \hat{B}) C_{IJ}^{-1}. \]

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

A. The single-mode approximation

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

\[ C_{IJ}^0 = \int_0^{\frac{1}{\hbar\omega}} d\lambda \langle \hat{a}_p^\dagger\hat{a}_q^\dagger \rangle^o e^{\delta\lambda(\omega_p - \omega_q)} \delta_{ps} \delta_{qr}, \]

\[ = \frac{n_p - n_q}{\hbar(\omega_q - \omega_p)} \delta_{IJ}, \]

where \( \langle . \rangle^o \) indicates a thermal average in the canonical ensemble of the harmonic system, and

\[ \Omega_{IJ} = (\omega_p - \omega_q) \delta_{IJ}. \]

In this approximation the time evolution of \( \hat{A}_I \) is parallel to \( \hat{A}_J \); one concludes that \( \mathcal{Q}\hat{A}_I \sim \mathcal{O}(\mathcal{V}) \), and that \( \tilde{\Gamma} \) is \( \sim \mathcal{O}(\mathcal{V}^2) \) (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 \( \langle \hat{A}, \hat{B} \rangle^\delta \). The \( \tilde{\Lambda} \) matrix in Eq. (10) is singular at \( z = 0 \) for \( \tilde{\Gamma} = 0 \); its inverse in Eq. (8), is therefore \( \tilde{\Lambda}^{-1}(0) \sim \mathcal{O}(\mathcal{V}^{-2}) \), consistently 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:

\[ \kappa = \frac{i\hbar^2}{VT} \sum_{IJ} v_I v_J \omega_I \omega_J \tilde{\Lambda}_{IJ}^{-1}(0) C_{IJ}^0, \]

\[ = \frac{i}{V} \sum_{IJ} c_J v_I v_J \omega_I \omega_J \tilde{\Lambda}_{IJ}^{-1}(0), \]

where \( c_J = \hbar^2\omega_J^2 C_{JJ}/T \) is the resonant generalized modal specific heat introduced in Ref. [6].

Eq. (16) is completely general, though its implementation requires the computation and inversion of the \( N^2 \times N^2 \) matrix, \( \tilde{\Lambda}_{IJ} \), 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 \( \tilde{\Gamma} \) matrix in Eqs. (10) and (12), can be neglected. In this case, Eq. (16) can be shown to reduce to:

\[ \kappa = \frac{1}{V} \sum_{pq} C_{pq} v_p v_q \frac{\tilde{\Gamma}_{pq}'(0)}{\hbar^2(\omega_p + \omega_q)^2 + (\Gamma_{pq})^2}, \]

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

The neglect of the off-diagonal elements of \( \tilde{\Gamma} \) 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 non-diagonal terms in \( \tilde{\Gamma} \) 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 A we show that for a cubic anharmonic potential Eq. (17) can be put into the dressed-bubble form of Refs. [8, 16]:

\[ \kappa = \frac{1}{V} \sum_{pq} \frac{\hbar^2(\omega_p + \omega_q)^2}{4} v_p v_q (I_{pq} + I'_{pq}), \]

\[ I_{pq} = \frac{1}{8\pi k_B T^2} \int d\omega \bar{g}_p^>(\omega) \bar{g}_q^<(-\omega), \]

where

\[ g_p^>(t) = -i\langle \hat{a}_p(t)\hat{a}_p^\dagger \rangle, \]

\[ g_p^<(-t) = i\langle \hat{a}_p^\dagger \hat{a}_p(t) \rangle \]

are the so-called greater and lesser Green’s function, and \( \bar{g}_p^>(\omega) \) indicate their Fourier transforms, whose lineshape is not assumed \text{a priori}. In Eq. (18) we have omitted terms of order \( \mathcal{O}(N^{-1}) \), which are negligible in the thermodynamic limit.

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

\[ \kappa^M = \frac{1}{V} \sum_{pq} C_{pq}^M v_p v_q \tilde{\Gamma}_{pq}, \]

\[ \tilde{\Gamma}_{pq} = \text{Re} \tilde{\Gamma}_{pq}(0) \]
where

\[ v_{pq}^M = \frac{n_p(n_q + 1) + n_q(n_p + 1)}{2k_BT^2} \left( \frac{\omega_p + \omega_q}{4} \right)^2, \]

\[ \tau_{pq} = \frac{\gamma_p + \gamma_q}{(\omega_p - \omega_q)^2 + (\gamma_p + \gamma_q)^2}, \]

and “\( M \)” stands for “Markovian”, which coincides with the QH GK expression of Ref. [6], to within terms of order \( \mathcal{O}(\gamma^2) \), in agreement with the conclusions of Ref. [8]. Memory effects, defined in the MZ formalism as the difference between the exact Green’s function and the Markovian ansatz, have been shown to have a non-negligible impact on the lattice 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- wavevector and phonon-band indices: \( q \rightarrow \{ q, \nu \} \) and the velocity matrices read:

\[ v_{q,\nu,\mu} = \overline{v}_{q,\nu,\mu} \delta_{\mu\nu}, \text{ with } \overline{v}_{q,\nu,\mu} = \overline{v}_{q,\mu,\nu} = -v_{-q,\nu,\mu}, \]

(25)

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

\[
j = \hbar \sum_{\nu\nu'} \frac{\omega_{q,\nu} + \omega_{q,\nu'}}{2} v_{q,\nu,\nu'} \hat{a}_{q,\nu}^\dagger \hat{a}_{q,\nu'}
+ \hbar \sum_{\nu\nu'} \frac{\omega_{q,\nu} - \omega_{q,\nu'}}{4} v_{q,\nu,\nu'} \left( \hat{a}_{-q,\nu} \hat{a}_{q,\nu'} - \hat{a}_{q,\nu} \hat{a}_{-q,\nu'} \right). \tag{26}\]

Neglecting again the anti-resonant (second-line) part of the flux, we find:

\[
\kappa = \frac{i}{VT} \sum_{qk\nu \nu'} c_{k\mu \nu} v_{q,\nu,\nu'} v_{k\mu \nu} \times \left[ \frac{\omega_{q,\nu} - \omega_{q,\nu'}}{\omega_{k,\mu}} \Lambda^{-1}_{q,\nu', k,\mu} (0), \right. \tag{27}\]

where \( c_{k\mu \nu} = c_{k\mu \nu}^* \).

In Appendix C it is shown that when the phonon linewidths are small with respect inter-band separations, the \( \Lambda \) matrix in Eq. (27) is diagonal in the \( \nu \nu' \) and \( \mu \mu' \) indices. Assuming that this is the case, the matrix \( \Omega_{IJ} \) in Eqs. (11) and (15) vanishes, and Eq. (27) becomes:

\[
\kappa = \frac{1}{VT} \sum_{qk\mu} c_{k\mu} v_{q,\nu,\nu'} v_{k\mu \nu} \omega_{q,\nu} \omega_{k,\mu} \Lambda^{-1}_{q,\nu', k,\mu} (0), \tag{28}\]

where \( c_{k\mu} = c_{k\mu \nu} = n_{k\mu} (n_{k\mu} + 1) \hbar^2 \omega^2 \). The modal heat capacity. If we now define the scattering matrix \( S \) as

\[
S_{q,\nu,\nu'} = \Gamma_{k,\mu \nu} \omega_{k,\mu} \omega_{q,\nu}, \tag{29}\]

then Eq. (28) can be written as:

\[
\kappa = \frac{1}{VT} \sum_{qk\mu} c_{q,\nu,\nu'} v_{q,\nu,\nu'} S_{q,\nu,\nu'}^{-1} S_{q,\nu,\nu'}^{\dagger}, \tag{30}\]

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, \( K \), and taking into account lattice periodicity. The calculations are quite lengthy and are fully reported in Appendix D. The final, purely real, results reads:

\[
\hat{\Gamma}_{q,\nu,\nu'} (z = 0) = 2\gamma_{q,\nu} \delta_{q,\nu} \delta_{\nu,\nu'} + \pi \hbar \sum_{q',\nu'} |K_{q,\nu,\mu,\nu'}|^2 n_{q',\nu'} \left[ \frac{n_{q,\nu} + 1}{n_{k,\mu}} \delta (\omega_{q,\nu} + \omega_{k,\mu} - \omega_{q',\nu'}) \right.
- \frac{n_{q,\nu}}{n_{k,\mu}} \delta (\omega_{q,\nu'} + \omega_{q,\nu'} - \omega_{k,\mu}) - \frac{n_{q,\nu} + 1}{n_{k,\mu} + 1} \delta (\omega_{k,\mu} + \omega_{q',\nu'} - \omega_{q,\nu})), \tag{31}\]

where \( K_{q,\nu,\mu,\nu'} \) is non-zero only for momentum-conserving triplets and \( \gamma_{q,\nu} \) is the anharmonic phonon linewidth [19]:

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

Eqs. (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 many-body perturbation theory, 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 inter-band contributions to the heat conductivity when the distance between neighbouring 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], reading:

\[
\kappa_{WTE} = \kappa_{BTE} + \frac{\hbar^2}{k_b T^2 V} \sum_{q\nu \neq q\nu'} \frac{\omega_{q\nu} + \omega_{q\nu'}}{4} \left( \omega_{q\nu} n_{q\nu} (n_{q\nu} + 1) + \omega_{q\nu'} n_{q\nu'} (n_{q\nu'} + 1) \right) V_{q\nu\nu'} V_{q\nu'\nu'} \frac{\gamma_{q\nu} + \gamma_{q\nu'}}{(\omega_{q\nu} - \omega_{q\nu'})^2 + (\gamma_{q\nu} + \gamma_{q\nu'})^2},
\]

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

\[
\kappa = \kappa_{BTE} + \frac{1}{V} \sum_{q\nu \neq q\nu'} c_{q\nu\nu'} v_{q\nu\nu'} v_{q\nu'\nu'} \frac{\gamma_{q\nu} + \gamma_{q\nu'}}{(\omega_{q\nu} - \omega_{q\nu'})^2 + (\gamma_{q\nu} + \gamma_{q\nu'})^2},
\]

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 inter-band 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 can not 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 Li₃ClO

The theory presented in this paper has been demonstrated on the lithium-rich anti-perovskite Li₃ClO, 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 the technical details reported in Appendix E. In Fig. 1 we display our results obtained using different approximations. We identify two distinct regimes. At low temperature, 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. (33-34)—present in QHGK but not in the BTE—are negligible due to the vanishing of the vibrational linewidths as \(T \rightarrow 0\); in this regime, the full BTE correctly describes the temperature dependence of the heat conductivity, while QHGK...
VI. CONCLUSIONS

In this paper we have critically analyzed the approximations that lead to the unified quasi-harmonic 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 many-body parlance) effects on heat conduction, whereas in the second it permits to dispose of the parallane) effects on heat conduction, whereas in the second it permits 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 quasi-harmonic Green-Kubo approaches to heat transport in solids, provided the same levels of approximation are adopted—thus extending the work of Ref. [8].

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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:

\[ \kappa \approx \frac{\hbar^2}{VT} \sum_{pq} v_{pq} v_{pq} \omega_{pq}^2 \int_0^\infty \langle \hat{A}_{pq}(t), \hat{A}_{pq} \rangle. \]  

(A1)

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

\[ \int_0^\infty \langle \hat{A}_{qp}(t), \hat{A}_{qp} \rangle = \left( \int_0^\infty \langle \hat{A}_{pq}(t), \hat{A}_{pq} \rangle \right)^*, \]  

(A2)

from which we deduce that the \( C_{pq,pq}(0) \) (Eq. 7) matrix is Hermitian with respect to \( p \leftrightarrow q \) exchange, whereas \( \Gamma_{pq,pq} \) 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 the anharmonic terms in the vibrational Hamiltonian can be truncated to third order in the atomic displacements:

\[ \hat{V} \approx \frac{\hbar^3/2}{6} \sum_{pqr} K_{pqr} \hat{X}_p \hat{X}_q \hat{X}_r, \]  

(B1)

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

\[ \hat{R}_{pq,pq}^{\dagger}(z = 0) = \]  

(B2)

where \( N \) is the number of normal modes, \( \langle \cdot \rangle' = \text{Re} \langle \cdot \rangle \), \( d_{pq} = \frac{\hbar}{2\pi \hbar (\omega_p - \omega_q)} \), and \( \tilde{\gamma}_p^{\dagger}(\omega) \) are the FL transforms of the one-body greater/lesser Green’s functions, whose expressions as obtained from Mori’s formalism [10] is

\[ g_p^\dagger(\omega) = \frac{1}{(\omega + i \delta)} (\omega + i \delta)^{-1}, \]  

(B3)

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

\[ \tilde{g}_p^\dagger(\omega) = -i \langle \hat{a}_p \hat{a}_p^\dagger \rangle \frac{2 \tilde{\gamma}_p^{\dagger}(\omega)}{[\langle \omega_p - \omega \rangle - i \tilde{\gamma}_p^{\dagger}(\omega)]^2}, \]  

(B4)

\[ \tilde{g}_p^\dagger(\omega) = i \langle \hat{a}_p \hat{a}_p^\dagger \rangle \frac{2 \tilde{\gamma}_p^{\dagger}(\omega)}{[\langle \omega_p - \omega \rangle - i \tilde{\gamma}_p^{\dagger}(\omega)]^2}. \]  

(B5)

To lowest order in the cubic anharmonic correction to the lattice potential energy, Eq. (B4) reads:
Neglecting corrections of order $O(N^{-1})$, we obtain:

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

where

$$I_{pq} = \frac{n_p (n_q + 1)}{2k_B T^2} \left( \frac{\tilde{\gamma}^\omega_p (\omega_q) + \tilde{\gamma}^\omega_q (\omega_p)}{|(\omega_p - \omega_q) - i \gamma_p^\tau (\omega_q) d_{pq} + \gamma_q^\tau (\omega_p) d_{qp}|^2} \right).$$

Let us compare this expression with Eq. (18), which gives the QHGGK 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 4 distinct poles, whose positions in the QH approximation are:

$$\omega_p^\pm = \omega_p + \tilde{\gamma}^\omega_p (\omega_p) \pm i \gamma_p^\tau (\omega_p) + O(\gamma_p^2)$$

$$\omega_q^\pm = \omega_q + \tilde{\gamma}^\omega_q (\omega_q) \pm i \gamma_q^\tau (\omega_q) + O(\gamma_q^2),$$

where $\tilde{\gamma}_q^\tau = \text{Im} \gamma_q$. Closing the path in the upper complex half-plane, we get:

$$I_{pq} = 2\pi i \sum_{\text{Im} z > 0} \text{Res}(f(z)) = \frac{(n_p + 1) n_q}{2k_B T^2} \left( \frac{\tilde{\gamma}^\omega_p (\omega_q^+)}{|(\omega_p - \omega_q^+) - i \gamma_p^\tau (\omega_q^+)|^2} + \frac{\tilde{\gamma}^\omega_q (\omega_p^+)}{|(\omega_q - \omega_p^+) - i \gamma_q^\tau (\omega_p^+)|^2} \right),$$

where we used $\langle \hat{a}_p \hat{a}_p^\dagger \rangle \approx n_p + 1$. We observe that Eq. (B10) and Eq. (B8) have the same numerator but a slightly different denominator. Their difference is negligible if $|\gamma_p^\tau (\omega_p) - \gamma_q^\tau (\omega_q)| \ll 1$, which happens in the quasi-harmonic limit ($\tilde{\gamma}, \frac{\partial \tilde{\gamma}}{\partial \omega} \sim O(K^2) \rightarrow 0$) if the memory function is regular enough. If $\tilde{\gamma}(\omega) = \gamma$, independent of $\omega$, 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, $\tau_{qv} = 1/2 \gamma_{qv}$, with the diagonal of the full BTE scattering matrix: $S_{qvqv} = 2\gamma_{qv} + O(N^{-1})$.

### Appendix C: Derivation Eq. (28) for well separated bands

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

$$\tilde{\Lambda}^{-1} = (D + O)^{-1} = D^{-1} - D^{-1} O (D + O)^{-1}.$$  \hspace{1cm} (C1)

The last term can be rewritten as:

$$(D^{-1} O (D + O)^{-1})_{II} = \sum_{K} D_{II}^{-1} (O (D + O)^{-1})_{II} K_J D_{II}^{-1} (O (D + O)^{-1})_{IJ}.$$  \hspace{1cm} (C2)

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

$$\lim_{|\omega_{q\nu'} - \omega_{q\nu}| \rightarrow \infty} \left[ \frac{1}{\omega_{q\nu'} - \omega_{q\nu} + i\Gamma_{q\nu', q\nu'}} - \frac{1}{\omega_{q\nu'} - \omega_{q\nu} + i\Gamma_{q\nu', q\nu}(O (D + O)^{-1})_{q\nu' \mu \mu'}} \right] = 0.$$  \hspace{1cm} (C3)

Therefore, only the $\nu = \nu'$ elements survive in this limit. Due to the relation between $\tilde{\Lambda}_{II}$ and $\tilde{\Lambda}_{IJ}$, the argument can be repeated for the second pair of band indices $\mu, \mu'$. 

$$\hat{\gamma}_p^\omega (\omega) = \frac{\hbar}{2 \pi} \int_{-\infty}^{\infty} d\omega' \frac{\tilde{\gamma} (\omega)}{\omega^2 - \omega'^2}.$$
Thus, for well separated bands:

\[ (\tilde{\Lambda})^{-1}_{q\nu, r \mu'} \approx \delta_{q \nu, \nu'} \delta_{r \mu', \mu} (\tilde{\Lambda})^{-1}_{q\nu, r \mu} \]  

(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 \( \hat{\Gamma}_{IJ} \) matrix in Eq. (12) as

\[
\hat{\Gamma}_{IJ}(0) = \frac{1}{C_{IJ}} \int_0^\infty \left( \mathcal{Q} \hat{A}_I, e^{-i\mathcal{Q} \mathcal{Q}^\dagger} \mathcal{Q} \hat{A}_J \right) dt, \tag{D1}
\]

where we used the harmonic approximation of \( C_{IJ} \) and the FL transform of the time-correlation function of the projected time-derivatives of the \( \hat{A}_I \) and \( \hat{A}_J \) operators:

\[
\hat{\Gamma}_{IJ}(0) = \frac{1}{C_{IJ}} \int_0^\infty \left( \mathcal{Q} \hat{A}_I, e^{-i\mathcal{Q} \mathcal{Q}^\dagger} \mathcal{Q} \hat{A}_J \right) dt, \tag{D1}
\]

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

Regarding the FL transforms (LFT) \( \left( \tilde{\mathcal{F}}(\omega) \right) \) it is computated through the Fourier Transform (FT) \( \left( \tilde{\mathcal{F}}(\omega) \right) \), using the relation:

\[
\tilde{\mathcal{F}}(\omega) = \int_0^\infty e^{i\omega t} f(t) dt = \frac{1}{2} \tilde{f}(\omega) + \frac{i}{2\pi} \int_{-\infty}^\infty d\omega' \frac{1}{\omega - \omega'} \tilde{f}(\omega'). \tag{D4}
\]

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:

\[
\Gamma'_{pq, rs}(0) = \frac{\hbar}{8C_{rs, rs}} \sum_{tuvz} \int_{-\infty}^\infty dt \int_0^{\pi_T} d\lambda \times \[ K_{ptu} K_{rsv} \left\langle \hat{X}_t(\tau) \hat{X}_u(\tau) a_q(\tau) a_q^\dagger \hat{X}_v(\tau) \right\rangle + K_{qtu} K_{rsv} \left\langle a_q^\dagger(\tau) \hat{X}_t(\tau) \hat{X}_u(\tau) \hat{X}_v \right\rangle + K_{qtu} K_{rsv} \left\langle \hat{X}_t(\tau) \hat{X}_u(\tau) a_q(\tau) \hat{X}_v \right\rangle - K_{ptu} K_{rsv} \left\langle a_q^\dagger(\tau) \hat{X}_t(\tau) \hat{X}_u(\tau) a_q^\dagger \hat{X}_v \right\rangle \right] . \tag{D5}
\]

This expression contains a great number of combinations of annihilation/creation operator. Let us compute one of them. For instance:

\[
\int_{-\infty}^\infty dt \int_0^\beta d\lambda K_{ptu} K_{rsv} \left\langle a_q^\dagger(\tau) a_q^\dagger(\tau) a_q^\dagger \right\rangle = 2\pi \beta K_{ptu} K_{rsv} e^{\beta \hbar(\omega_t + \omega_u - \omega_q)} \frac{1}{\hbar(\omega_t + \omega_u - \omega_q)} \delta(\omega_t + \omega_u - \omega_q) \left\langle a_q^\dagger a_q^\dagger a_q^\dagger \right\rangle = 2\pi \beta K_{ptu} K_{rsv} \delta(\omega_t + \omega_u - \omega_q) \left\langle a_q^\dagger a_q^\dagger a_q^\dagger \right\rangle . \tag{D6}
\]

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 \( a_q^\dagger a_q^\dagger \) would lead to \( \sim \delta(\omega_t) \). Thus, keeping only the non-vanishing com-
binations, one gets:

\[
2\pi \beta K_{ptu} K_{rvz} (n_t n_u (n_q + 1) \\
\times \delta (\omega_t + \omega_u - \omega_q) (\delta_{tu}\delta_{uz}\delta_{qs} + \delta_{tq}\delta_{uv}\delta_{qs})).
\]

(D7)

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

Appendix E: Technical details and intermediate results of the numerical application

The Li\(_3\)ClO 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 where computed with LAMMPS [25] using a finite-difference method in a \([5,5,5]\) supercell, while the saldo 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 linewidths—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. (33-34).

FIG. 2. Phonon dispersions and linewidths (upper panel) and VDOS (lower panel) of Li\(_3\)ClO (see text).

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The velocity matrix can always be assumed to be real, because so can be chosen the vibrational normal modes. When normal modes are degenerate, as it is the case, e.g., in periodic crystals, the matrix is not necessarily real, but can be made so by considering real linear combinations of vibrational modes with opposite crystal momentum.

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