Hydrodynamic heat transport in dielectric crystals in the collective limit and the drifting/driftless velocity conundrum

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We apply a recently developed method for solving the linearized phonon Boltzmann equation to study the hydrodynamic thermal transport in dielectrics in the collective limit, i.e., when normal collisions dominate resistive ones. The method recovers Guyer and Krumhansl results for a single Debye branch and extends them to general dispersion relations and branches. Specifically, we obtain explicit microscopic expressions for the phonon distribution and for the transport coefficients in this limit. We find that the phonon distribution differs from the commonly used displaced distribution in two terms: one accounting for viscous flow and another one which allows us to solve a long-standing issue on drifting and driftless second-sound velocities. Thus, the new method allows us to generalize previous results and fill some gaps on fundamental aspects of the collective limit through a simple mathematical formalism. We compare the hydrodynamic framework with previous models and discuss its limitations.

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I. INTRODUCTION

Hydrodynamic heat transport consists of thermal transport displaying features similar to mass transport in fluids, such as viscosity and inertia. In dielectric crystals, it was first experimentally found in the 1960s for solid helium, where Poiseuille-like flow [1] and second sound [2] were detected, and in the 1970s the observation of second sound extended to a handful of materials at cryogenics temperatures [3–5]. Since the mid-2010s it has received renewed interest because theoretical models based in first-principles calculations predicted hydrodynamic phenomena for low-dimensional materials at higher temperatures, such as graphene and other two-dimensional (2D) materials [6–8], carbon nanotubes [9], and in graphite [10,11]. Quite remarkably, hydrodynamic effects like Poiseuille flow have been observed recently in black phosphorous and graphite [12,13] and second sound have been recently measured in graphite at temperatures below 200 K [11,14].

Hydrodynamic transport cannot be described by Fourier's law, which predicts heat to propagate diffusively. Then, theoretical studies of hydrodynamic heat transport in insulating crystals are generally addressed by directly solving the linearized Boltzmann transport equation (BTE) for phonons [15,16]. However, the complexity of the BTE and the difficulty of implementing boundary conditions only allows solutions for simple geometries and/or simplifying assumptions at a high computational cost [10,17,18].

Hydrodynamic behavior is expected to occur in the limit when momentum-conserving normal collisions are much more frequent than resistive ones (the so-called collective or Ziman limit). Until recently this was considered a necessary condition for hydrodynamic heat transport to exist, to the point that when phonon normal collisions are also much more frequent than collisions with boundaries the system is said to be in the hydrodynamic regime. In the collective limit, Guyer and Krumhansl [19] deduced from the BTE an equation for the heat flux (GKE) that resembles the Navier-Stokes equation for fluids and recovers Fourier's law when time and space variations are small. The GKE thus nicely generalizes Fourier's law while predicting hydrodynamic behavior such as Poiseuille flow and second sound. Interestingly, it provides a unified picture of the heat propagation phenomenology and, with proper boundary conditions, can be applied to complex geometries, in contrast to direct BTE solutions.

The improvement of experimental techniques since the early 2010s has allowed us to observe thermal responses at small sizes and timescales which differ from Fourier's law in situations when resistive collisions dominate (kinetic limit) [20–23]. Remarkably enough, the GKE, originally derived in the collective limit, has been shown to capture such non-Fourier effects at the nanoscale for several kinetic materials, including InGaAs [23], silicon [24–31], and germanium [32]. These experimental observations asked for a theoretical foundation and, recently, a hydrodynamic equation of the GKE type has been derived for general dielectrics by solving the BTE using a new method for small but finite Knudsen numbers (the quotient between phonon mean free paths and a macroscopic scale) [31]. The derivation considered general linearized collision operators, and general dispersion relations and number of branches, thus generalizing previous results [24,33,34]. The method, which from now on we will call flux derivatives formalism (FDF), allows us to obtain the phonon distribution and the transport coefficients of the hydrodynamic equation from first principles. In Ref. [31] the kinetic limit was analyzed using the relaxation time approximation (RTA),

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finding good agreement with experiments in silicon in a wide range of temperatures and with second-sound experiments in germanium from 100 to 300 K [32].

The aim of the present work is to apply the FDF to the collective limit, i.e., the opposite limit from the one studied in Ref. [31]. This study will allow us to check the validity of the formalism by comparison with previous literature and study hydrodynamic behavior from the perspective given by the new method. We will see that it generalizes previous results and improves our understanding on fundamental issues through a simpler mathematical formalism. For the sake of simplicity, throughout the paper we will consider isotropic systems.

The paper is organized as follows. We first summarize the FDF method in Sec. II for the paper to be self-contained. Next we apply the FDF to the collective limit and recover Guyer and Krumhansl results [19] for a single branch in the Debye aproximation and generalize them to general dispersion relations. We also obtain the nonequilibrium phonon distribution function, which generalizes the classical expression and will allow us to clarify in Sec. IV a longstanding conundrum related to drifting and driftless second-sound velocities. Finally, Sec. V is devoted to concluding remarks.

II. FLUX DERIVATIVES FORMALISM

In classical kinetic theory, two well-known methods are used to obtain macroscopic equations from the Boltzmann transport equation: the Chapman-Enskog's method [35] and the Grad's moment method [36]. They provide microscopic expressions for the transport coefficients appearing therein and the nonequilibrium distribution function. The Chapman-Enskog method uses as independent variables the first moments of the distribution, which for heat transport reduces to the temperature T. As a result, the phonon distribution and the macroscopic equations depend on the temperature and its gradients. It is based on an expansion in the Knudsen number and produces Fourier's law to first order and Burnett and super-Burnett equations at higher orders [37]. On the other hand, Grad's method assumes as independent variables the moments of the distribution, which include the temperature, as in Chapman-Enskog, but also the heat flux and eventually higher-order fluxes. The distribution function depends on these variables but not on their derivatives. Beyond Fourier, the macroscopic equations produced by both methods display some shortcomings, such as the instability of transient solutions in Burnett and super-Burnett equations or the discontinuity of some properties in Grad's equations due to their hyperbolic character, added to the difficulty of posing proper boundary conditions for higher derivatives or higher moments, respectively [37].

The FDF introduced in Ref. [31] uses a mixed approach of Chapman-Enskog and Grad methods. The key point is to extend the set of independent variables to include the heat flux and its first derivatives in space and time. For moderate Knudsen numbers, it generally yields an equation for the heat flux of the GKE type which overcomes the shortcomings found in Chapman-Enskog and Grad methods. We summarize below the main results of the Flux derivatives method [31] and present them in the form more appropriate for the developments in the rest of the paper.

The linearized BTE for phonons writes:

$$\frac{\partial f_\lambda}{\partial t} + \vec{v}_\lambda \cdot \vec{\nabla} f_\lambda = C(f_\lambda), \tag{1}$$

where f_λ is the phonon distribution function of the λ-phonon mode (wave vector $\vec{k}$ and polarization s), $\vec{v}_\lambda$ the phonon group velocity, and $C(f_\lambda)$ is the linearized collision operator acting on the distribution function. In terms of the scattering matrix, $\mathbf{\Omega}$, it writes $C(f_\lambda) = -\Sigma_{\lambda'} \Omega_{\lambda\lambda'} n_{\lambda'}$, with $n_\lambda = f_\lambda - f_\lambda^{\rm eq}$ and $f_\lambda^{\rm eq}$ the Bose-Einstein distribution. By projecting the BTE to the energy and to the crystal momentum, one obtains the transport equations:

$$\frac{\partial e}{\partial t} + \vec{\nabla} \cdot \vec{q} = 0, \tag{2}$$

$$\frac{\partial \vec{p}}{\partial t} + \vec{\nabla} \cdot \overline{\overline{\Pi}} = \int \hbar \vec{k}_\lambda C(f_\lambda) d\lambda, \tag{3}$$

where $e = \int \hbar\omega_\lambda f_\lambda d\lambda$ is the energy density, $\vec{q} = \int \hbar\omega \vec{v}_\lambda f_\lambda d\lambda$ the heat flux, $\vec{p} = \int \hbar \vec{k}_\lambda f_\lambda d\lambda$ the momentum density, and $\overline{\overline{\Pi}} = \int \hbar \vec{k}_\lambda \vec{v}_\lambda f_\lambda d\lambda$ the flux of crystal-momentum. In order to close the system, one needs to relate $\vec{p}$ and $\overline{\overline{\Pi}}$ to the energy density and the heat flux, so that a solution of the BTE is required. In most previous methods, the solution of the BTE is set as an expansion on the basis of eigenvectors of the collision operator and the unknowns are the macroscopic prefactors [19,38–41]. Instead, we proposed that for moderate Knudsen numbers the perturbed distribution function is an expansion on the heat flux $\vec{q}$ and its first derivatives in time and space, considered as independent variables (i.e., at a given point in space they can take independent values), and the unknowns are the microscopic prefactors:

$$f_\lambda = f_\lambda^{\rm eq} + \vec{\beta}_\lambda \cdot \vec{q} + \vec{\gamma}_\lambda \cdot \frac{\partial \vec{q}}{\partial t} + \overline{\overline{G}}_\lambda : \vec{\nabla}\vec{q}, \tag{4}$$

where $\vec{\beta}_\lambda$, $\vec{\gamma}_\lambda$, and $\overline{\overline{G}}_\lambda$ are weight functions dependent on the phonon mode to be determined. In an isotropic material, the case we focus on for simplicity, one has $\overline{\overline{G}}_\lambda \equiv \overline{\overline{G}}_{1,\lambda} + \overline{\overline{G}}_{2,\lambda}$, with $\overline{\overline{G}}_{1,\lambda} \equiv g_{1,\lambda} \hat{k}\hat{k}$ and $\overline{\overline{G}}_{2,\lambda} \equiv g_{2,\lambda} \mathbb{I}$, where $\hat{k}$ denotes the unitary vector in the direction of $\vec{k}$, $\mathbb{I}$ is the identity tensor, and $g_{1,\lambda}$ and $g_{2,\lambda}$ are scalar quantities; symbol ":" indicates the double contraction of tensor indexes. The combination of Eqs. (1)–(4) provides the equations for the weight functions. They are obtained by neglecting second-order derivatives as compared to first-order ones, i.e., for small-enough spatial and time variations, and equating the prefactors of the macroscopic variables, considered as independent [31]:

$$C(\vec{\beta}_\lambda) = -\frac{1}{\kappa} \frac{\partial f_\lambda^{\rm eq}}{\partial T} \vec{v}_\lambda, \tag{5a}$$

$$C(\vec{\gamma}_\lambda) = \vec{\beta}_\lambda - \frac{\tau}{\kappa} \frac{\partial f_\lambda^{\rm eq}}{\partial T} \vec{v}_\lambda, \tag{5b}$$

$$C(\overline{\overline{G}}_{1,\lambda}) = \vec{\beta}_\lambda \vec{v}_\lambda, \tag{5c}$$

$$C(g_{2,\lambda}) = -\frac{1}{C_V} \frac{\partial f_\lambda^{\rm eq}}{\partial T}, \tag{5d}$$

where C_V is the heat capacity per unit volume and κ and τ are, respectively, the thermal conductivity and flux

relaxation time [see Eq. (7b) below]. The left-hand side terms in the latter equations use a compact notation; for instance, in Eq. (5a), $C(\vec{\beta}_\lambda)$ is a vector with i Cartesian component $C(\beta^i_\lambda) = -\Sigma_{\lambda'}\Omega_{\lambda\lambda'}\beta^i_{\lambda'}$. The values of κ and τ can be obtained with the help of two consistency relations arising from imposing the definition of heat flux in Eq. (4):

$$\int \hbar\omega_\lambda \vec{\beta}_\lambda \vec{v}_\lambda d\lambda = \mathbb{I}, \tag{6a}$$

$$\int \hbar\omega_\lambda \vec{\gamma}_\lambda \vec{v}_\lambda d\lambda = 0. \tag{6b}$$

Interestingly, the nonequilibrium distribution (4) with the weight functions obeying Eqs. (5a)–(5d) satisfies the conservation of energy for general collision operators, i.e., $\int \hbar\omega_\lambda C(f_\lambda) d\lambda = 0$. This allows us to apply the formalism to approximate collision operators, like in RTA and Callaway models, while guaranteeing energy conservation. This contrasts to the direct application of these approaches, where energy conservation requires additional constraints [18,42].

Finally, by introducing Eq. (4) in the expressions for the energy, the momentum density $\vec{p}$ and $\overline{\overline{\Pi}}$, the transport equations (2) and (3) read

$$C_V \frac{\partial T'}{\partial t} + \vec{\nabla}\cdot\vec{q} = 0, \tag{7a}$$

$$\vec{q} = -\tau\frac{\partial \vec{q}}{\partial t} - \kappa\vec{\nabla}T' + \ell^2[\nabla^2\vec{q} + \alpha\vec{\nabla}(\vec{\nabla}\cdot\vec{q})], \tag{7b}$$

with T' the local-equilibrium temperature, ℓ the nonlocal length, and α a nonlocal coefficient; as κ and τ, all these parameters are intrinsic size-independent coefficients determined by the weights [indeed there is an extra term that can be typically neglected, see Appendix (B)]. Equation (7b) is the GKE [19], which generalizes Fourier's law by including memory and nonlocal effects. The second derivatives of the heat flux characterized by parameter ℓ resemble the viscous terms in the Navier-Stokes equation, and for this reason heat transport obeying this equation was addressed as phonon hydrodynamics. If spatial variations are much larger than the nonlocal length ℓ, then the viscous terms can be neglected, and if time variations are much slower than the relaxation time τ, then the time derivative term is negligible, thus recovering Fourier's law. Let us note in passing that this equation is consistent with our assumption of $\vec{q}$, $\partial\vec{q}/\partial t$, and $\nabla\vec{q}$ as independent variables since, at a given point in space, they can take arbitrary values by choosing the appropriate value of ∇T.

The local-equilibrium temperature T' is defined as $e = e_{\rm eq}(T')$, with $e_{\rm eq}$ the equilibrium expression for the energy [19,40,41,43], and it is related to the temperature T in $f^{\rm eq}$ through $T' - T = \tau_e \partial T'/\partial t$, with τ_e a time constant [31]. In order to use the linearized BTE, temperature differences must be small, i.e., $(T' - T)/T << 1$, which sets a limit to time variations that the model can describe. If ω is the frequency of the thermal perturbation and ΔT its amplitude, then the latter inequality leads to $\omega\tau_e\Delta T/T << 1$.

The microscopic expressions for the transport coefficients give:

$$\kappa = -\frac{\int \hbar k_x v_x \partial_T f^{\rm eq}_\lambda d\lambda}{\int \hbar k_x C(\beta_x) d\lambda}, \tag{8a}$$

$$\tau = \frac{\int \hbar k_x C(\gamma_x) d\lambda - \int \hbar k_x \beta_x d\lambda}{\int \hbar k_x C(\beta_x) d\lambda}, \tag{8b}$$

$$\ell^2 = \frac{\int \hbar k_x v_y G_{1,xy} d\lambda}{\int \hbar k_x C(\beta_x) d\lambda}, \tag{8c}$$

$$\alpha = 2 + \frac{\int \hbar k_x v_x g_2 d\lambda}{\int \hbar k_x v_y G_{1,xy} d\lambda} - \frac{\kappa\tau_e}{C_V \ell^2}, \tag{8d}$$

$$\tau_e = -\int \hbar\omega_\lambda (G_{1,xx} + g_2) d\lambda. \tag{8e}$$

These coefficients can be expressed in other ways, but the expressions listed above are in the form more appropriate for the discussions in the present work. In particular, they can be applied to systems of any dimension.

In summary, given a collision operator, the solution of Eqs. (5a)–(5d) provides the weights that specify the nonequilibrium phonon distribution and the transport parameters from first principles through the above equations. These could be solved in principle for the full collision operator through iterative or variational methods, for instance, though this must be studied with care because the solution for $\vec{\beta}$ are the inputs for the solutions of $\vec{\gamma}$ and $\overline{\overline{G}}_1$. This is beyond the scope of the present paper. In the next section, we apply this framework to the collective limit, where some simplifications allow for an analytical treatment.

III. COLLECTIVE LIMIT

When normal scattering dominates over resistive collisions, the former strongly correlate the evolution of the populations of different phonon modes so that they are not independent and RTA does not apply. A precise study of this limit requires to include the off-diagonal terms in the linear collision operator C [19,39]. The latter can be separated into the momentum-preserving normal collisions operator N and the resistive collisions operator R, $C = N + R$. The GKE equation was originally derived by Guyer and Krumhansl in the collective limit, i.e., when $N \gg R$, assuming a single branch and Debye approximation [19,44]. In this section, we analyze this limit through the Flux derivatives formalism. This will allow us to compare to Guyer and Krumhansl results under their assumptions and, interestingly, generalize them to several branches and general dispersion relations. The recovery of GK results through this completely different method not only supports the FDF but also clarifies some doubts raised on the validity of the GK derivation [45]. In addition, we will obtain an explicit expression for the phonon nonequilibrium distribution which goes beyond the displaced Bose-Einstein distribution often considered in this limit. This generalized distribution function helps shed light on a long-standing issue about the velocity of second sound in this limit in Sec. IV. We first evaluate this distribution and later use it to calculate the transport coefficients.

A. Nonequilibrium distribution function

According to the FDF, the distribution function depends on the heat flux and its derivatives as given by Eq. (4) with the weight functions the solutions of Eqs. (5a)–(5d).

In the limit where resistive collisions are absent, in stationary and homogeneous situations, the solution of the BTE is the displaced (or drifting) Bose-Einstein distribution [16,46]:

$$f_\lambda^{\rm disp} = \frac{1}{\exp\left[\hbar(\omega_\lambda - \vec{k}\cdot\vec{u})/k_B T\right] - 1}, \tag{9}$$

where k_B is Boltzmann constant and $\vec{u}$ is the drift velocity, which is uniform across the system as it is T. It can be shown that $f_\lambda^{\rm disp}$ maximizes the entropy and that, in these conditions, phonon distributions relax to it [47]. This distribution describes a collective motion of phonons which seem to move at the same drift velocity, as molecules in a moving fluid. Not far from equilibrium it writes

$$f_\lambda^{\rm disp} = f_\lambda^{\rm eq} + \frac{T}{\omega_\lambda}\frac{\partial f_\lambda^{\rm eq}}{\partial T}\vec{k}\cdot\vec{u}. \tag{10}$$

On the other hand, under stationary and homogeneous conditions, ansatz (4) simplifies to $f_\lambda = f_\lambda^{\rm eq} + \vec{\beta}_\lambda\cdot\vec{q}$. Notice that this has the same form of (10), since this yields for the heat flux $\vec{q}\propto\vec{u}$, which allows us to identify $\vec{\beta}_\lambda$ in the collective limit as

$$\vec{\beta}_\lambda^{\rm col} = \frac{\frac{\vec{k}_\lambda}{\omega_\lambda}\partial_T f_\lambda^{\rm eq}}{\int \hbar k_x v_x \partial_T f_\lambda^{\rm eq}}. \tag{11}$$

The other weight functions can be evaluated by taking into account that in the limit $N \gg R$ one can approximate the collision operator acting on function x_λ as $C(x_\lambda)\simeq N(x_\lambda)\simeq -\frac{x_\lambda}{\tau_{N,\lambda}}$, with $\tau_{N,\lambda}$ the relaxation time for normal scattering of the λ mode and x_λ is any of the components of $\vec{\gamma}_\lambda$, $\overline{\overline{G}}_{1,\lambda}$, or $g_{2,\lambda}$. Let us note, however, that this does not apply to $\vec{\beta}_\lambda^{\rm col}$, since N conserves momentum and then $N(\vec{\beta}_\lambda^{\rm col}) = N(f_\lambda^{\rm disp}) = 0$. By using Eqs. (5b)–(5d) one has

$$\vec{\gamma}_\lambda = \tau_{N,\lambda}\left(\frac{\tau}{\kappa}\frac{\partial f_\lambda^{\rm eq}}{\partial T}\vec{v}_\lambda - \vec{\beta}_\lambda^{\rm col}\right) + D\vec{\beta}_\lambda^{\rm col} \tag{12}$$

$$\overline{\overline{G}}_{1,\lambda} = -\tau_{N,\lambda}\vec{\beta}_\lambda^{\rm col}\vec{v}, \tag{13}$$

$$g_{2,\lambda} = \frac{\tau_{N,\lambda}}{C_V}\frac{\partial f_\lambda^{\rm eq}}{\partial T}. \tag{14}$$

The last term in Eq. (12) is introduced because the integration of $\vec{\gamma}_\lambda$ in this limit is determined aside from a function proportional to $\vec{\beta}_\lambda^{\rm col}$ because $N(\vec{\beta}_\lambda^{\rm col}) = 0$. Transport coefficients τ and κ are determined below, and coefficient D is subsequently obtained by constraint (6b). All weights in the distribution function (4) are thus specified.

We now compare these results to Guyer and Krumhansl's [19]. In their derivation, the authors expressed the distribution function in terms of the eigenvectors of the symmetrized normal scattering operator. Since only two of these eigenvectors are known, they could only find explicit expressions for the first two terms of the expansion. This gives the displaced distribution (10) or, equivalently, $f_\lambda^{\rm eq} + \vec{\beta}_\lambda\cdot\vec{q}$, but not the higher-order terms. Our formalism, instead, provides higher-order corrections in terms of the flux derivatives, Eq. (4), with explicit expressions for the weights. One might think that these corrections, which are of order τ_N, are small and could be neglected. Instead, let us stress that they are necessary for a consistent and complete description of the collective limit, like the inclusion of thermal viscosity through the term in $\vec{\nabla}\vec{q}$ or, as will be shown in Sec. IV, the proper expression for second-sound velocity.

B. Transport coefficients

We now evaluate the transport coefficients by introducing the weights calculated above in the general expressions of the formalism, Eqs. (8a)–(8e), and compare to previous work. Since crystal momentum is conserved in normal collisions, i.e., $\int \hbar k_x N(f_\lambda) d\lambda = 0$, below we use that $\int \hbar k_x C(x_\lambda) d\lambda = \int \hbar k_x R(x_\lambda) d\lambda$ for any weight function component x_λ.

1. Relaxation time τ

The general expression for τ, Eq. (8b), gives in the collective limit

$$\tau = \frac{\int \hbar k_x R(\gamma_x^{\rm col}) d\lambda - \int \hbar k_x \beta_x^{\rm col} d\lambda}{\int \hbar k_x R\left(\beta_x^{\rm col}\right) d\lambda}.$$

Since in this limit $R\to 0$, one has $\int \hbar k_x R(\gamma_x) d\lambda \ll \int \hbar k_x \beta_x d\lambda$, and the heat flux relaxation time is

$$\tau = -\frac{\int \hbar k_x \beta_x^{\rm col} d\lambda}{\int \hbar k_x R\left(\beta_x^{\rm col}\right) d\lambda} \equiv -R_{11}^{*-1}, \tag{15}$$

which is the inverse of an average resistive scattering rate. The notation R_{11}^* follows the original one by Guyer and Krumhansl [19], since it can be seen that the quotient in Eq. (15) can be written as $R_{11}^* \equiv <\phi_x^1|\mathbf{R}^*|\phi_x^1>$, i.e., the component of the symmetrized resistive collision operator $\mathbf{R}^*$ projected to the normalized eigenvector $|\phi_x^1>$ of the symmetrized normal scattering operator $\mathbf{N}^*$ [see Appendix (A) for the definitions of symmetrized operators and eigenvectors of $\mathbf{N}^*$]. This is also the result found by Guyer and Krumhansl. When one approximates $R\simeq -\frac{1}{\tau_{R,\lambda}}$, with $\tau_{R,\lambda}$ the λ-mode resistive relaxation time, then $\tau = <\phi_x^1|\frac{1}{\tau_{R,\lambda}}|\phi_x^1>^{-1}$, which is the most common expression used for the relaxation time in the collective limit [7,19,44].

2. Thermal conductivity κ

The general expression for the thermal conductivity (8a) yields

$$\kappa = -\frac{\int \hbar k_x v_x \partial_T f_\lambda^{\rm eq} d\lambda}{\int \hbar k_x R\left(\beta_x^{\rm col}\right) d\lambda},$$

and using expressions (15) for τ, and (11) for $\beta_x^{\rm col}$, it can be rewritten as

$$\kappa = \frac{\left(\int \hbar k_x v_x \partial_T f_\lambda^{\rm eq} d\lambda\right)^2}{\int \hbar k_x^2/\omega\, \partial_T f_\lambda^{\rm eq} d\lambda}\tau = C_V \langle\phi^0|v_x|\phi_x^1\rangle^2 \tau. \tag{16}$$

By defining the average $\langle x_\lambda\rangle \equiv \int \hbar\omega_\lambda \partial_T f_\lambda^{\rm eq} x_\lambda d\lambda / C_v$ and the phase velocity $v_{p,\lambda}\equiv\omega_\lambda/k_\lambda$, the latter expression can be rewritten in d dimensions as

$$\kappa = \frac{1}{d}C_V\left\langle\frac{v}{v_p}\right\rangle^2\left\langle v_p^{-2}\right\rangle^{-1}\tau. \tag{17}$$

And if one considers the Debye approximation and a single phonon branch with velocity v in 3D, as assumed in the

original work by Guyer and Krumhansl, one has $\kappa = \frac{1}{3} C_V v^2 \tau$, which is the result obtained in Ref. [19].

3. Nonlocal length ℓ

Introducing Eq. (13) into (8c) yields

$$\ell^2 = -\frac{\int \hbar k_x v_y^2 \beta_x^{\rm col} \tau_{N,\lambda} d\lambda}{\int \hbar k_x R\big(\beta_x^{\rm col}\big) d\lambda}.$$

By using Eq. (15), it can be written in terms of eigenvector $|\phi_x^1>$ as

$$\ell^2 = \langle \phi_x^1 | v_y^2 \tau_N | \phi_x^1 \rangle \tau. \tag{18}$$

This result agrees with Ref. [48] obtained using Callaway model. According to the GKE, Eq. (7b), the thermal viscous diffusivity is given by $\nu = \ell^2/\tau$, so that it is simply given by an average on $v_y^2 \tau_N$, which reflects the physical origin of the diffusion of heat flux and crystal momentum in this limit, namely normal scattering. In contrast to fluids, where momentum is conserved, resistive collisions destroy momentum, so that it diffuses only a finite time of order τ. As a result, the transport equation for phonons is characterized by the length diffused by momentum before being destroyed, which approximately is $\nu\tau = \ell^2$.

In term of averages, Eq. (18) writes in d dimensions as

$$\ell^2 = \frac{1}{d+2} \left\langle \frac{v^2}{v_p^2} \tau_N \right\rangle \langle v_p^{-2} \rangle^{-1} \tau. \tag{19}$$

For a single Debye branch in 3D it yields $\ell^2 = \frac{1}{5} v^2 \langle \tau_N \rangle \tau$, as obtained by Guyer and Krumhansl [19,44].

4. Time parameter τ_e

Substituting Eqs. (13) and (14) into (8e) gives

$$\tau_e = \left\langle \frac{v}{v_p} \tau_N \right\rangle \left\langle \frac{v}{v_p} \right\rangle - \langle \tau_N \rangle. \tag{20}$$

One finds that in the Debye approximation $\tau_e = 0$ and, in general, it is of order $\langle \tau_N \rangle$. In consequence, condition $(T - T')/T = \omega \tau_e \Delta T/T \ll 1$ is safely satisfied for $\omega \langle \tau_N \rangle < 1$, which is already a condition for the collective regime, namely the timescale of experiments must be larger than normal scattering times [39,40,44]. For larger frequencies one enters the ballistic regime.

5. Nonlocal coefficient α

One finds from (8e)

$$\alpha = 2 - \frac{d+2}{d} \frac{\left\langle \frac{v}{v_p} \tau_N \right\rangle}{\left\langle \frac{v^2}{v_p^2} \tau_N \right\rangle} \left\langle \frac{v}{v_p} \right\rangle - \frac{\kappa \tau_e}{C_V \ell^2}. \tag{21}$$

In three dimensions and Debye approximation, one thus gets $\alpha = 1/3$. This value contrasts to $\alpha = 2$ obtained by Guyer and Krumhansl [19], but it is in agreement with Refs. [34,40]. Hardy and Albers explained that this discrepancy is due to an approximation in the normal collision operator made in Ref. [19].

We end this section by comparing our results with the work by Hardy and Albers [40]. They derived a macroscopic equation in the collective limit similar to the GKE for general dispersion relations in terms of eigenvenvectors of the normal scattering operator N^*, thus generalizing GK results. In the ideal collective limit ($\tau_N/\tau_R \to 0$), their expressions for the thermal conductivity and the relaxation time coincide with those found in this section. The other coefficients, however, are expressed in terms of the spectrum of N^* eigenvenvectors, ϕ^i, which being unknown for $i > 1$, prevents their calculation. For instance, ℓ^2 in isotropic systems can be expressed as $\Sigma'_\sigma < \phi_x^1 | v_y | \phi^\sigma > < \phi^\sigma | v_y | \phi_x^1 > \tau_N^\sigma \tau$, where $1/\tau_N^\sigma$ is the eigenvalue of ϕ^σ and the prime indicates that the sum extends only to $\sigma > 1$. Let us note that this expression is formally very similar to our Eq. (18). Assuming a constant τ_N^σ and different Debye branches, Hardy and Albers yield $\ell^2 = \frac{1}{5} \tau_N \langle v_p^{-2} \rangle^{-1} \tau$ and $\alpha = 1/3$, in agreement with the results of Eqs. (19) and (21), respectively, for these conditions.

IV. VELOCITY OF SECOND SOUND IN THE COLLECTIVE LIMIT

Second sound (SS) is the propagation of heat in the form of waves, as first sound is the wave propagation of momentum or density disturbances. These waves have been experimentally observed in some solids at cryogenic temperatures [3–5] and more recently in graphite below 200 K [11,14]. In these cases, normal collisions dominate, which is the expected regime for second sound to be detected [39,44]. Recently, however, second sound has also been observed in germanium at room temperature [32], where resistive collisions are very important. Here we focus on second sound in the collective limit. Quite surprisingly, in this limit two expressions for the velocity of second sound have been used in the literature [6,7,9,39] coming from different approximations of the BTE, the so-called drifting and driftless approximations. Remarkably, they lead to different results, and the differences are especially important in low-dimensional materials. For example, for (20,20) single-wall carbon nanotubes at 300 K the predicted speeds are some 4000 m/s for the drifting expression and 8000 m/s for the driftless one [9]. In the study of second sound in unstrained graphene and other 2D materials, Ref. [6] uses the driftless expression because the drifting one was expected to diverge, whereas Ref. [7] calculates graphene SS velocity using the drifting expression considering renormalization of the dispersion relation due to coupling of bending and stretching modes. We are thus faced to two different predictions for the same experimental situation, i.e., the speed of second sound in the collective limit. It is thus both theoretically and experimentally relevant to solve this conflict.

In this section we show that a proper analysis of the BTE predicts just a single velocity for second sound in the collective limit, thus solving the conundrum. In the following, we first present the derivations leading to the drifting and driftless expressions for the SS speed and then show how the FDF solves the paradox.

Drifting and driftless approximations use the energy conservation equation and assume that, in the limit of negligible resistive scattering, the phonon distribution function tends to the displaced distribution. The conflict comes from two possibilities of projecting the BTE to obtain macroscopic equations: either on the crystal momentum (drifting approximation) or on the heat flux (driftless approximation) [9,39].

A. Drifting approximation

In this limit, crystal momentum is conserved so that the BTE leads to the following balance for energy and momentum:

$$\frac{\partial e}{\partial t} + \vec{\nabla}\cdot\vec{q} = 0, \tag{22}$$

$$\frac{\partial \vec{p}}{\partial t} + \vec{\nabla}\cdot\overline{\overline{\Pi}} = 0. \tag{23}$$

Introducing the displaced distribution (10) in the expressions for e, $\vec{q}$, $\vec{p}$, and $\overline{\overline{\Pi}}$ yields

$$C_V\frac{\partial T}{\partial t} + \left(\int k_i v_{i,\lambda} T \frac{\partial f^{\rm eq}_\lambda}{\partial T} d\lambda\right)\vec{\nabla}\cdot\vec{u} = 0 \tag{24}$$

$$\left(\int \frac{k_i^2}{\omega} T \frac{\partial f^{\rm eq}_\lambda}{\partial T} d\lambda\right)\frac{\partial \vec{u}}{\partial t} + \left(\int \hbar k_i v_{i,\lambda} T \frac{\partial f^{\rm eq}_\lambda}{\partial T} d\lambda\right)\vec{\nabla}T = 0, \tag{25}$$

where subindex i refers to a Cartesian component. The combination of these equations supply a wave equation for temperature (and for the drift velocity) with propagation speed

$$v^2_{\rm drift} = \frac{\left(\int \hbar k_i v_i \partial_T f^{\rm eq}_\lambda d\lambda\right)^2}{C_V \int \hbar k_i^2/\omega\, \partial_T f^{\rm eq}_\lambda d\lambda} = \langle \phi^0 | v_i | \phi^1_i \rangle^2. \tag{26}$$

In the Debye approximation in three dimensions it yields

$$v^2_{\rm drift} = \frac{1}{3}\left\langle \frac{1}{v_p^2}\right\rangle^{-1} = \frac{1}{3}\frac{C_V}{\Sigma_j C_j/v_j^2}, \tag{27}$$

with C_j and v_j the heat capacity and velocity of the j branch, respectively. For identical branches it gives $v^2_{\rm drift} = v^2/3$, with v the first-sound velocity [19,39].

B. Driftless approximation

If instead projecting the BTE on the quasimomentum one projects it on the heat flux, then one gets a balance for the heat flux

$$\frac{\partial \vec{q}}{\partial t} + \vec{\nabla}\cdot\overline{\overline{Q}} = \int \hbar\omega \vec{v}_\lambda N(f_\lambda) d\lambda, \tag{28}$$

with $\overline{\overline{Q}} = \int \hbar\omega \vec{v}_\lambda \vec{v}_\lambda f_\lambda d\lambda$ the flux of the heat flux. For the displaced distribution, the right-hand side of Eq. (28) vanishes, since $N(f^{\rm disp}_\lambda)$ is identically null. And combining this equation with the conservation of energy yields a wave equation for temperature but now with a different velocity

$$v^2_{\rm dless} = \frac{1}{C_V}\int \hbar\omega v_i^2 \partial_T f^{\rm eq}_\lambda d\lambda = \langle v_i^2\rangle. \tag{29}$$

In the Debye approximation, it yields in three dimensions

$$v^2_{\rm dless} = \frac{1}{3}\langle v_p^2\rangle = \frac{1}{3}\frac{\Sigma_j C_j v_j^2}{C_V}, \tag{30}$$

which is different from (27) except for identical branches [39].

In Ref. [39], expression (29) for the SS velocity was obtained without assuming that the distribution function is the drifting one, thus the name of driftless velocity. This is also the expression derived in Ref. [6] using Callaway approximation and projecting on the energy flux. This contrasts to Ref. [7], where the authors project on momentum and obtain Eq. (26). Therefore, one is lead to the puzzling result that the drifting distribution leads to two different SS velocities depending on which projection one chooses. Figure 1 highlights the differences between drifting and driftless SS velocities for graphene obtained from expressions (26) and (29) both for our calculations (solid lines) and from Refs. [7] and [6] (dashed lines). It shows that drifting and driftless velocities differ in a factor around 2 as found for carbon nanotubes [9]. We have not found any divergence in expression (26), though some deviations are observed with respect to the values obtained in Ref. [7], which employs phonon stiffening.

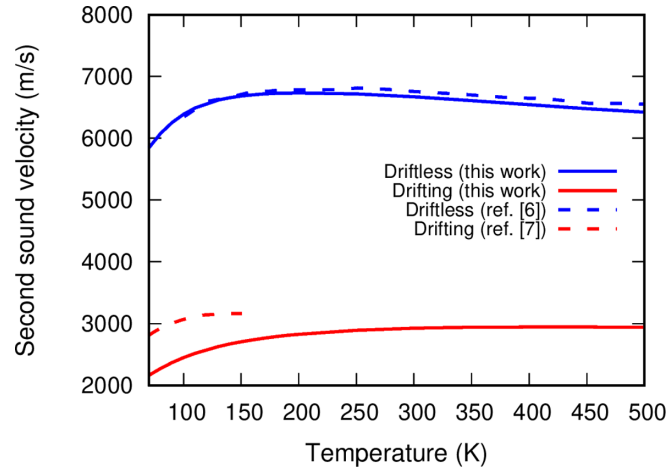

FIG. 1. Second-sound drifting and driftless velocities for graphene at different temperatures from expressions (26) and (29), respectively, calculated in this work (solid lines) and from Lee *et al.* [7] (drifting) and Cepellotti *et al.* [6] (driftless) (dashed lines).

Let us finally note that in Ref. [9] the vanishing of the right-hand side of (28) is assumed as a hypothesis of conservation of heat flux under normal scattering. Here we show that it directly vanishes from the drifting distribution assumption. In the next section we will see that the puzzle clarifies if one uses the distribution function (4) instead of the drifting distribution.

C. Flux derivatives formalism

In our framework, the heat flux obeys the GK equation (7b). In the ideal collective limit, where R scattering can be neglected ($\tau \to \infty$) and $\tau_N \to 0$, it reduces to

$$\tau\frac{\partial \vec{q}}{\partial t} + \kappa\vec{\nabla}T' = 0, \tag{31}$$

which combined with energy conservation yields a thermal wave equation with a SS velocity given by

$$v^2_{\rm SS} = \frac{\kappa}{C_V\tau}. \tag{32}$$

Using the expression for κ in the previous section, Eq. (16), one finds

$$v_{\rm SS} = v_{\rm drift}. \tag{33}$$

Then the FDF supplies the drifting SS velocity in the collective limit.

This result can also be obtained in a faster way by projecting Eq. (5b) on the crystal momentum $\hbar k_x$. Since normal collisions conserve momentum, $\int \hbar k_x N(\gamma_\lambda) d\lambda = 0$, and (5b) directly yields the quotient κ/τ without requiring the expressions for κ and τ,

$$\frac{\kappa}{\tau} = \frac{\int \hbar k_x v_x \partial_T f_\lambda^{\rm eq} d\lambda}{\int \hbar k_x \beta_x^{\rm col} d\lambda}. \tag{34}$$

Finally, introducing Eq. (11) for $\vec{\beta}^{\rm col}$ yields again $v_{\rm SS} = v_{\rm drift}$. Let us note that a direct numerical solution of the BTE for graphene ribbons obtains a velocity for second sound in the collective limit which coincides with the drifting velocity [49].

We next show how our formalism allows us to understand: (i) why the driftless approximation supplies a wrong prediction and (ii) that a proper analysis of the heat flux projection also predicts for the SS speed the *drifting* (not driftless) velocity.

In the driftless derivation, the right-hand side of Eq. (28) identically vanishes so that the heat flux is conserved. This result is a bit surprising, because a normal collision conserves quasimomentum $\hbar\vec{k}$ but not the heat flux $\hbar\omega\vec{v}$. For instance, in a three-phonon normal collision, one generally has $\omega_1\vec{v}_1 + \omega_2\vec{v}_2 \neq \omega_3\vec{v}_3$. Two conditions are necessary for the equality to generally hold, namely linear dispersion relations (Debye approximation) and identical branches. Aside from this particular case, the energy flux generally changes direction after a normal collision. This feature has not gone unnoticed previously and led the authors of Ref. [9] to prefer the drifting velocity to the driftless solution in their analysis.

Let us note, however, that the no conservation of $\hbar\omega\vec{v}$ in collisions is not necessarily in contradiction with that the integral $\int \hbar\omega\vec{v}_\lambda N(f_\lambda) d\lambda$ vanishes, i.e., the sum of heat flux variations for all collisions in a given position could still be zero, so that the total heat flux $\vec{q}$ would still be a conserved macroscopic quantity. This apparently improbable situation is actually what happens for homogeneous and stationary cases as shown by Peierls [50], since then the solution of the BTE is the displaced distribution and $N(f^{\rm disp}) = 0$; in this case, a uniform heat flux is maintained without a temperature gradient [16].

The key issue in the present study is whether the heat flux $\vec{q}$ is conserved in unsteady and inhomogenous situations, such as in wave propagation. Our formalism sheds light on this point. According to the FDF, the distribution function is given by Eq. (4), so that the heat source term in Eq. (28) yields

$$\int \hbar\omega\vec{v}_\lambda N(\vec{\beta}_\lambda) d\lambda \cdot \vec{q} + \int \hbar\omega\vec{v}_\lambda N(\vec{\gamma}_\lambda) d\lambda \cdot \frac{\partial \vec{q}}{\partial t}. \tag{35}$$

The term in G_λ vanishes by symmetry in isotropic systems. In the collective limit, the first term vanishes because $N(\vec{\beta}^{\rm col}) \propto N(f^{\rm disp}) = 0$, as in the driftless derivation. However, the last term survives and, as a result, the heat flux *is not* generally conserved in unsteady situations, at variance with the driftless derivation. This explains why this approach provides wrong predictions for the velocity of SS.

There is yet to be seen whether the inclusion of the source term in the heat flux equation solves the conflict, i.e., whether the heat flux projection predicts for SS the drifting velocity obtained through the momentum projection. The source term can be easily evaluated with the help of the general equation for $C(\vec{\gamma}_\lambda)$, Eq. (5b), which yields

$$\int \hbar\omega\vec{v}_\lambda C(\vec{\gamma}_\lambda) d\lambda = \mathbb{I} - \frac{\tau}{\kappa} \int \hbar\omega\vec{v}_\lambda \vec{v}_\lambda \frac{\partial f_\lambda^{\rm eq}}{\partial T}, \tag{36}$$

where constraint (6a) has been used. Introducing the nonequilibrium phonon distribution (4) in the expression for the flux of the heat flux, $\vec{\bar{Q}}$ can be approximated in this limit (collective and infinite medium) to the local equilibrium one up to terms of order $\omega\tau_N$. The Flux derivatives formalism thus gives for the balance equation of the heat flux,

$$\frac{\partial \vec{q}}{\partial t} + \int \hbar\omega v_i^2 \frac{\partial f_\lambda^{\rm eq}}{\partial T} \nabla T = \left(1 - \frac{\tau}{\kappa} \int \hbar\omega v_i^2 \frac{\partial f_\lambda^{\rm eq}}{\partial T}\right) \frac{\partial \vec{q}}{\partial t}. \tag{37}$$

Remarkably, terms cancel out and one is left with Eq. (31). We thus recover a wave equation with the *drifting* speed for second sound, in agreement with the drifting derivation as consistency required.

D. Discussion

The derivation above shows that the origin of the error in the driftless derivation was to assume that the displaced distribution was a good approximation for the distribution function in the collective limit. It is the inclusion of the term in $\partial\vec{q}/\partial t$ in the distribution function that allows us to solve the inconsistency. This underlines the pertinence of using this macroscopic quantity as an independent variable in the nonequilibrium phonon distribution as assumed in the FDF. Indeed, notice that both the driftless and drifting derivations above assume the displaced phonon distribution. Despite this is not correct in unsteady or inhomogeneous situations in none of these cases, nevertheless, the drifting derivation provides good results because momentum conservation in normal collision gets rid of the term in heat flux time derivative, in contrast to what happens when projecting on the energy flux.

Interestingly, we have been able to obtain a closed expression for the source term in the heat flux balance equation, Eq. (37). It shows that, in general, the heat flux is not conserved under normal collisions. However, when resistive scattering can be neglected, the heat flux is a conserved quantity in stationary situations, not only for the homogeneous case—as studied by Peierls—but also for inhomogeneous ones, as in stationary Poiseuille flow, where $\vec{q}$ is only destroyed at boundaries. In unsteady situations, it is helpful to write the source term as $(1 - v_{\rm dless}^2/v_{\rm drift}^2)\partial\vec{q}/\partial t$. Since both velocities are generally different, the source term does not vanish and $\vec{q}$ is not conserved. Nevertheless, for linear dispersion and identical branches it becomes null, in agreement with the conservation of $\hbar\omega\vec{v}$ in each collision discussed above. Typically, $v_{\rm dless} > v_{\rm drift}$ (see for instance Eqs. (27) and (30), or Ref. [9]) so that the prefactor of $\partial\vec{q}/\partial t$ is negative. Notice, however, that the source term has not a definite sign. In a thermal wave, for instance, $\partial\vec{q}/\partial t$ changes sign and the source term with it. Accordingly, at any point in space the heat flux is created and destroyed periodically by normal collisions. Thus

the effect of normal collisions is not to destroy heat flux but to introduce a delay in the heat flux.

Let us finally comment that Hardy introduced the driftless SS velocity by assuming a general odd perturbation describing situations not restricted to the collective limit [39]. Then the phonon distribution is not necessarily the displaced one thus the name driftless second sound. In his heuristic derivation, Hardy considered a RTA model (therefore out from the collective limit) with a constant relaxation time. Our model also yields the driftless SS speed under these approximations, since in RTA $\kappa = C_V \langle v_i^2 \rangle \tau$. However, our model is not restricted to these approximations and it generally sets $v_{\rm SS}^2 = \frac{\kappa}{C_V \tau}$.

E. Low-dimensional materials

The study of SS in the collective limit performed above is based on the results of Sec. III. However, the applicability of those results requires that the integrals appearing therein do not diverge. This issue is delicate in low-dimensional systems due to the dispersion relations of flexural modes. In stress-free 2D materials, harmonic models of flexural modes display dispersion relations $\omega_{\rm flex} \propto k^2$; as a result, the normalization constant of vectors $|\phi_i^1>$ yields $\int k^3/\omega^2 dk \propto \int 1/k\, dk$ which diverges for infinite samples. This divergence led [6] to use the driftless expression for SS in graphene. As mentioned above, the coupling of out-of-plane and in-plane modes renormalizes the dispersion relation of flexural modes so that at low frequencies $\omega_{\rm flex} \propto k^{3/2}$ [51,52] and the divergence disappears. The renormalized dispersion relation was used in the numerical solution of the BTE performed in Ref. [49] obtaining in the collective limit thermal waves with propagation velocity equal to the drifting expression, in agreement with our formalism.

Nevertheless, the $\omega \propto k^{3/2}$ dependence and, in general, dispersion relations $\omega \propto k^\delta$ with $\delta > 1$ exhibit a problem when applied to the displaced distribution in the thermodynamic limit. The latter yields negative values for small frequencies [41,53] so that displaced distribution cannot be a correct solution at these frequencies. This contrasts, however, with iterative solutions of the BTE for graphene and other 2D substances, which seem to provide displaced distributions [6,7]. This might be due to the finite wave-vector lower bound used in the discretization of the reciprocal space, which may not reach the region of negative values. The question arises of which is the appropriate phonon distribution in the collective limit in this situation. Whichever it is, the substitution of the corresponding $\vec{\beta}_\lambda^{\rm col}$ in the root expressions of Sec. III would yield the transport coefficients. In a recent paper [54], the authors address this issue and find that for large 2D samples the drift velocity is negligible and SS propagates with a (driftless) velocity given by $v_{\rm SS}^2 = \frac{\kappa}{C\tau_q}$, where τ_q is the relaxation time of the heat flux, in agreement with our expression (32). Let us note in passing that the latter driftless velocity does not necessarily coincide with the classical expression of the driftless velocity, Eq. (29).

Finally, under strain, dispersion relations of flexural modes in 2D materials seem to become linear at low wave vectors [55,56] so that convergence of normalization constant is guaranteed. However, the convergence of the thermal conductivity in this case is still unclear both computationally and experimentally [53,54,56]. In 1D, also theoretical models often provide divergent thermal conductivities, though the inclusion of three-phonon scattering to second order seem to yield finite values [53]. The latter property is required for the application of the present approach in its current form.

V. CONCLUDING REMARKS

From the fundamental point of view, a macroscopic heat transport model generalizing Fourier's law down to smaller scales would provide a unifying description of nonlocal effects in heat transport and shed light on the phenomenology that these give rise. From the practical viewpoint it would allow us to study smaller space and timescales and address physical situations of experimental interest at low computational cost and thus make a useful tool for engineering optimization and design without resorting to the complexities of the BTE equation, whose application is generally limited to simple geometries. Recently, the GKE has been derived from the BTE for general collision operators and dispersion relations at moderate Knudsen numbers through a new method, the FDF, and applied to the kinetic limit [31]. In this paper we have extended its application to the collective limit, which has allowed us to validate the formalism by comparison with previous literature and supply additional understanding of the collective limit through a simpler mathematical method. The FDF recovers Guyer and Krumhansl transport coefficients for a single Debye branch and extends the results to general dispersion relations and branches. Interestingly, it provides a phonon distribution in this limit which differs from the commonly used displaced distribution by including two new terms. One contains the spatial derivatives of the heat flux, analogous to the viscous term appearing in fluids, and accounts for thermal viscous flow. The other one contains the time derivative of the heat flux and allows us to solve an old riddle between drifting and driftless velocities for second sound in this limit. This term conciliates drifting and driftless derivations, which now yield both the same expression for the second-sound speed, the drifting one, which is also the result supplied by the FDF. It is shown that although heat flux is not generally conserved under normal collisions, the source term in the equation for the heat flux is proportional to the time derivative of the heat flux, so that heat flux does conserve in steady sate. This includes the well-known homogeneous case analyzed by Peierls but also nonhomogeneous cases such as Poiseuille flow.

In most derivations of the macroscopic equations from the BTE, the starting point is to propose an expansion of the nonequilibrium distribution around the displaced distribution [19,24,33,38–41,44,57]. Often, this expansion is on the basis of eigenvectors of the symmetrized normal collision operator, as in the classical works of Guyer and Krumhansl and Hardy. Subsequently, under some approximations the equations for their prefactors are found, which are eventually related to macroscopic quantities, such as energy and momentum density, thus yielding the hydrodynamic equations. In the FDF framework used in this paper, the macroscopic equations are derived from a completely different perspective. Instead of expanding the phonon distribution in terms of eigenvectors, we

propose its expansion on appropriate macroscopic variables. In this way, the unknowns are the mode-dependent prefactors of the macroscopic quantities, just the opposite strategy of previous methods. The phonon distribution function assumed in the FDF, Eq. (4), states clearly that these are independent variables, and the derived macroscopic equations are consistent with this property.

Ansatz (4) implicitly assumes that after a fast timescale the system relaxes to a pseudoequilibrium distribution of the form of ansatz (4). Accordingly, the heat flux and their derivatives are slow variables which as time goes will eventually die out if the experimental conditions allow it. Ultimately, the validity of this ansatz depends on the agreement with experiments. In the collective limit, the classical experiments and theoretical analyses are consistent with it as we have seen. In the kinetic limit abundant experiments on silicon described and predicted by the GKE are also consistent with the ansatz.

The FDF is limited to moderate Knudsen numbers, when higher-order derivatives may be neglected. This prevents its application in its present form to the ballistic regime and study the effect of close boundaries or small length scales, including the study of the Knudsen minimum or the temperature dependence of the effective thermal conductivity before the maximum. In the collective limit, the smallness of normal scattering times allows the model to capture a fully developed Poiseuille flow. However, in kinetic substances the condition of small Knudsen numbers only permits to see Poiseuille flow close enough to boundaries. For silicon, it has been found that the GKE with *ab initio* calculated values for ℓ correctly describe experiments for system scales $L > 2\ell$, while for smaller L, the GKE overestimates viscous effects. In germanium, second sound has been observed in frequency-domain thermoreflectance experiments where a fast-varying heat power is directly supplied to the sample in a thin 15-nm surface layer; this corresponds to large Knudsen numbers and then far beyond the applicability of the model [32]. In these experiments, viscous effects seem to be highly suppressed thus unlocking the memory effects grasped in the relaxation time τ. The agreement of the predicted values for τ in the 100–300 K range indicates the usefulness of the present approach beyond its region of applicability and also the need of further efforts to understand the interplay of spatial and temporal effects at high Knudsen numbers.

Finally, in most real substances such as graphite or graphene where normal collisions are dominant, resistive collisions are also expected to play an important role, so that they are placed somewhere between the collective and the kinetic limits. The study of the FDF in this intermediate regime is the aim of future work.

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APPENDIX A: SYMMETRIZED SCATTERING MATRIX

The linearized BTE can be symmetrized by introducing a reference temperature T_0, defining $f_\lambda^0 = f_\lambda^{\rm eq}(T_0)$, and rescaling the phonon deviation from equilibrium $n_\lambda = f_\lambda - f_\lambda^0$ as follows:

$$n_\lambda^* = \frac{n_\lambda}{\sqrt{f_\lambda^0\left(f_\lambda^0+1\right)}}. \tag{A1}$$

Then the BTE writes

$$\frac{\partial n_\lambda^*}{\partial t} + \vec{v}_\lambda \cdot \vec{\nabla} n_\lambda^* = -\sum_{\lambda'} \Omega_{\lambda\lambda'}^* n_{\lambda'}^*, \tag{A2}$$

where Ω^* is the symmetric, self-adjoint, scattering operator [19]

$$\Omega_{\lambda\lambda'}^* = \sqrt{\frac{f_{\lambda'}^0\left(f_{\lambda'}^0+1\right)}{f_\lambda^0\left(f_\lambda^0+1\right)}}\,\Omega_{\lambda\lambda'}. \tag{A3}$$

Analogously, one can define the symmetrized normal N^* and resistive R^* scattering operators, with $\Omega^* = N^* + R^*$.

The distribution function can be expressed in terms of the eigenvectors of the symmetrized normal scattering operator N^*, which is an orthogonal basis of the phase density space, and take advantage that four of these eigenvectors are known, namely ϕ_λ^0 and $\phi_{\alpha\lambda}^1$ (α is the index of the spatial component) [19]. They are related to the equilibrium and displaced Bose-Einstein distributions, respectively, and read

$$\phi_\lambda^0 = c_0\,\hbar\omega\sqrt{f_\lambda^0\left(f_\lambda^0+1\right)} \tag{A4}$$

$$\phi_{\alpha\lambda}^1 = c_1\,\hbar k_\alpha\sqrt{f_\lambda^0\left(f_\lambda^0+1\right)}, \tag{A5}$$

with c_i normalization constants so that $<\phi_\lambda^0|\phi_\lambda^0> = <\phi_{\alpha\lambda}^1|\phi_{\alpha\lambda}^1> = 1$, and the scalar product is defined as $<f\,|\,g> = V\int f(\lambda)g(\lambda)\,d\lambda$. The eigenvalues of these eigenvectors are zero, which indicates that they describe equilibrium states under N scattering.

APPENDIX B: SECOND TIME DERIVATIVE

The heat flux equation (7b) indeed includes a term in the second time derivative of the heat flux, $\tau_p^2\frac{\partial^2\vec{q}}{\partial t^2}$, which for finite Knudsen can be typically neglected as we see in this Appendix. Coefficient τ_p^2 writes [31]:

$$\tau_p^2 = -\frac{\int \hbar\gamma_x k_x d\lambda}{\int \hbar k_x C(\beta_x) d\lambda}. \tag{B1}$$

According to Eq. (B1), τ_p directly vanishes for identical Debye branches because of constraint (6b), in agreement with Guyer and Krumhansl. For general dispersion relations, it can be written as $\tau_p^2 = \tilde{\tau}_N\tau$ by defining

$$\tilde{\tau}_N = \frac{\int \hbar\gamma_x^{\rm col} k_x d\lambda}{\int \hbar k_x \beta_x^{\rm col} d\lambda}. \tag{B2}$$

The latter is a difference of averages of τ_N, so that $\tilde{\tau}_N$ is of order $\langle\tau_N\rangle$ (or smaller). Then, the quotient of the second and first time derivative terms is $\omega\tau_p^2/\tau \approx \omega\langle\tau_N\rangle$. This is much smaller than 1 in the collective limit, so that the second time derivative can be neglected and one recovers the GKE.

[1] L. Mezhov-Deglin, Zh. Eksp. Teor. Fiz. **49**, 66 (1965) [Sov. Phys. JETP **22**, 47 (1966)].
[2] C. C. Ackerman, B. Bertman, H. A. Fairbank, and R. A. Guyer, Phys. Rev. Lett. **16**, 789 (1966).
[3] H. E. Jackson, C. T. Walker, and T. F. McNelly, Phys. Rev. Lett. **25**, 26 (1970).
[4] V. Narayanamurti and R. C. Dynes, Phys. Rev. Lett. **28**, 1461 (1972).
[5] D. W. Pohl and V. Irniger, Phys. Rev. Lett. **36**, 480 (1976).
[6] A. Cepellotti, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, and N. Marzari, Nat. Commun. **6**, 6400 (2015).
[7] S. Lee, D. Broido, K. Esfarjani, and G. Chen, Nat. Commun. **6**, 6290 (2015).
[8] A. Cepellotti and N. Marzari, Phys. Rev. Mater. **1**, 045406 (2017).
[9] S. Lee and L. Lindsay, Phys. Rev. B **95**, 184304 (2017).
[10] Z. Ding, J. Zhou, B. Song, V. Chiloyan, M. Li, T. H. Liu, and G. Chen, Nano Lett. **18**, 638 (2018).
[11] S. Huberman, R. A. Duncan, K. Chen, B. Song, V. Chiloyan, Z. Ding, A. A. Maznev, G. Chen, and K. A. Nelson, Science **364**, 375 (2019).
[12] Y. Machida, A. Subedi, K. Akiba, A. Miyake, M. Tokunaga, Y. Akahama, K. Izawa, and K. Behnia, Sci. Adv. **4**, eaat3374 (2018).
[13] Y. Machida, N. Matsumoto, T. Isono, and K. Behnia, Science **367**, 309 (2020).
[14] Z. Ding, K. Chen, B. Song, J. Shin, A. A. Maznev, K. A. Nelson, and G. Chen, Nat. Commun. **13**, 285 (2022).
[15] R. Peierls, Ann. Phys. **395**, 1055 (1929).
[16] J. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, UK, 1963)
[17] A. Cepellotti and N. Marzari, Nano Lett. **17**, 4675 (2017).
[18] C. Hua, L. Lindsay, X. Chen, and A. J. Minnich, Phys. Rev. B **100**, 085203 (2019).
[19] R. A. Guyer and J. A. Krumhansl, Phys. Rev. **148**, 766 (1966).
[20] J. A. Johnson, A. A. Maznev, J. Cuffe, J. K. Eliason, A. J. Minnich, T. Kehoe, Clivia M. Sotomayor Torres, G. Chen, and K. A. Nelson, Phys. Rev. Lett. **110**, 025901 (2013).
[21] R. B. Wilson and D. G. Cahill, Nat. Commun. **5**, 5075 (2014).
[22] K. M. Hoogeboom-Pot, J. N. Hernandez-Charpak, X. Gu, T. D. Frazer, E. H. Anderson, W. Chao, R. W. Falcone, R. Yang, M. M. Murnane, H. C. Kapteyn, and D. Nardi, Proc. Natl. Acad. Sci. USA **112**, 4846 (2015).
[23] A. Ziabari, P. Torres, B. Vermeersch, Y. Xuan, X. Cartoixà, A. Torelló, J.-H. Bahk, Y. R. Koh, M. Parsa, P. D. Ye, F. X. Alvarez, and A. Shakouri, Nat. Commun. **9**, 255 (2018).
[24] Y. Guo and M. Wang, Phys. Rev. B **97**, 035421 (2018).
[25] P. Torres, A. Ziabari, A. Torelló, J. Bafaluy, J. Camacho, X. Cartoixà, A. Shakouri, and F. X. Alvarez, Phys. Rev. Mater. **2**, 076001 (2018).
[26] A. Beardo, M. Calvo-Schwarzwälder, J. Camacho, T. G. Myers, P. Torres, L. Sendra, F. X. Alvarez, and J. Bafaluy, Phys. Rev. Appl. **11**, 034003 (2019).
[27] A. Beardo, M. G. Hennessy, L. Sendra, J. Camacho, T. G. Myers, J. Bafaluy, and F. X. Alvarez, Phys. Rev. B **101**, 075303 (2020).
[28] S. Alajlouni, A. Beardo, L. Sendra, A. Ziabari, J. Bafaluy, J. Camacho, Y. Xuan, F. X. Alvarez, and A. Shakouri, Nano Res. **14**, 945 (2021).
[29] A. Beardo, J. L. Knobloch, L. Sendra, J. Bafaluy, T. D. Frazer, W. Chao, J. N. Hernandez-Charpak, H. C. Kapteyn, B. Abad, M. M. Murnane, F. X. Alvarez, and J. Camacho, ACS Nano **15**, 13019 (2021).
[30] A. Beardo, S. Alajlouni, L. Sendra, J. Bafaluy, A. Ziabari, Y. Xuan, J. Camacho, A. Shakouri, and F. X. Alvarez, Phys. Rev. B **105**, 165303 (2022).
[31] L. Sendra, A. Beardo, P. Torres, J. Bafaluy, F. X. Alvarez, and J. Camacho, Phys. Rev. B **103**, L140301 (2021).
[32] A. Beardo, M. López-Suárez, L. A. Pérez, L. Sendra, M. I. Alonso, C. Melis, J. Bafaluy, J. Camacho, L. Colombo, R. Rurali, F. X. Alvarez, and J. S. Reparaz, Sci. Adv. **7**, eabg4677 (2021).
[33] M. J. Fryer and H. Struchtrup, Contin. Mech. Thermodyn. **26**, 593 (2014).
[34] Y. Guo and M. Wang, Phys. Rep. **595**, 1 (2015).
[35] S. Chapman and T. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1953).
[36] H. Grad, Commun. Pure Appl. Math. **2**, 331 (1949).
[37] H. Struchtrup, *Macroscopic Transport Equations for Rarefied Gas Flows* (Springer, Berlin, 2005).
[38] J. Sussmann and A. Thellung, Proc. Phys. Soc. **81**, 1122 (1963).
[39] R. J. Hardy, Phys. Rev. B **2**, 1193 (1970).
[40] R. J. Hardy and D. L. Albers, Phys. Rev. B **10**, 3546 (1974).
[41] M. Simoncelli, N. Marzari, and A. Cepellotti, Phys. Rev. X **10**, 011019 (2020).
[42] B. Vermeersch, J. Carrete, N. Mingo, and A. Shakouri, Phys. Rev. B **91**, 085202 (2015).
[43] J.-P. M. Péraud and N. G. Hadjiconstantinou, Phys. Rev. B **84**, 205331 (2011).
[44] R. A. Guyer and J. A. Krumhansl, Phys. Rev. **148**, 778 (1966).
[45] A. Cepellotti and N. Marzari, Phys. Rev. X **6**, 041013 (2016).
[46] P. Klemens, *Solid State Physics* (Academic Press, New York, 1958).
[47] H. Hall, *Solid State Physics* (Wiley, New York, 1974).
[48] X. Li and S. Lee, Phys. Rev. B **97**, 094309 (2018).
[49] X.-P. Luo, Y.-Y. Guo, M.-R. Wang, and H.-L. Yi, Phys. Rev. B **100**, 155401 (2019).
[50] R. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, UK, 1955).
[51] E. Mariani and F. von Oppen, Phys. Rev. Lett. **100**, 249901(E) (2008).
[52] A. K. Majee and Z. Aksamija, Phys. Rev. B **93**, 235423 (2016).
[53] X. Gu, Y. Wei, X. Yin, B. Li, and R. Yang, Rev. Mod. Phys. **90**, 041002 (2018).
[54] M.-Y. Shang, W.-H. Mao, N. Yang, B. Li, and J.-T. Lü, Phys. Rev. B **105**, 165423 (2022).
[55] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
[56] Y. Kuang, L. Lindsay, S. Shi, X. Wang, and B. Huang, Int. J. Heat Mass Transf. **101**, 772 (2016).
[57] R. N. Gurzhi, J. Exp. Theor. Phys. **46**, 719 (1964).