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Wigner Equations for Phonons Transport and Quantum Heat Flux

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Abstract

Starting from the quantum Liouville equation for the density operator and applying the Weyl quantization, Wigner equations for the acoustic, optical and Z phonons are deduced. The equations are valid for any solid, including 2D crystals like graphene. With the use of Moyal's calculus and its properties, the pseudo-differential operators are expanded up to the second order in $\hbar$. An energy transport model is obtained by using the moment method with closure relations based on a quantum version of the Maximum Entropy Principle by employing a relaxation time approximation for the production terms of energy and energy flux. An explicit form of the thermal conductivity with quantum correction up to $\hbar^2$ order is obtained under a long-time scaling for the most relevant phonon branches.

Keywords Wigner equations · Phonons transport · Heat flux · Quantum Maximum Entropy Principle

Mathematics Subject Classification 82C70 · 82C31 · 82D20 · 82D80 · 82D37

1 Introduction

The use of the Wigner function is one of the most promising ways to study quantum transport. Its main advantage is that a description similar to the classical or semiclassical transport is obtained in a suitable phase-space. The mean values are expectation values with respect to the Wigner function as if the latter was a probability density and the semiclassical limit of the Wigner transport equation recovers, at least formally,

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the Boltzmann transport one. There is a huge body of literature regarding the Wigner equation and the way to numerically solve it (see for example Morandi and Schürrer 2011; Muscato and Wagner 2016; Querlioz and Dollfus 2010 and references therein). However, the most of the works on the subject consider a quadratic dispersion relation for the energy. Instead, for several materials like semiconductors or semimetal, e.g., graphene, other dispersion relations must be considered (Jacoboni 2013; Jüngel 2009; Mascali and Romano 2020). From the Wigner transport equation, quantum hydrodynamical models have been obtained in Romano (2007) for charge transport in silicon in the case of parabolic bands, while in Luca and Romano (2018) the same has been devised for electrons moving in graphene.

The enhanced miniaturization of electron and mechanical devices makes the thermal effects increasingly relevant (Simoncelli et al. 2022; Sellitto et al. 2016; Jou and Restuccia 2023) requiring the use of physically accurate models. At kinetic level, a good description is the one based on the semiclassical Peierls–Boltzmann equation for each phonon branch. However, for typical lengths smaller than the phonon mean-free path also quantum effects must be considered (see for example Simoncelli et al. 2022). The Wigner equation is a natural approach that better reveals the quantum nature of phonons in such circumstances, gives the Peierls–Boltzmann equation as semiclassical limit and still keeps the structure of a kinetic formulation. In this work, the focus is on the acoustic and optical phonons dynamics with a general dispersion relation.

In order to get insights into the quantum corrections, moment equations are deduced from the corresponding Wigner equation. As in the classical case, one is led to a system of balance equations that are not closed. So, the well-known problem of getting closure relations arises, that is the issue to express the additional fields appearing in the moment equations in terms of a set of fundamental variables, e.g., the phonon energy density and energy flux. A sound way to accomplish this task is resorting to a quantum formulation of the maximum entropy principle (Jaynes 1957a) (hereafter QMEP), formulated for the first time by Jaynes (1957b). Recently, a more formal theory has been developed in a series of papers (Degond and Ringhofer 2003; Degond et al. 2005) with several applications, for example for charge transport in semiconductors (Romano 2007; Barletti 2014; Barletti and Cintolesi 2012; Luca and Romano 2019). The interested reader is also referred to Camiola et al. (2020).

We apply QMEP to the Wigner equations assuming the energy density and the energy flux for each species of phonons as basic fields. By expanding up to the second order in $\hbar$, quantum corrections to the semiclassical case (Mascali and Romano 2017) are deduced. In particular, in a long time scaling an asymptotic expression for the heat flux is obtained. The latter consists of a Fourier-like part with a highly nonlinear second-order correction in the temperature gradient. Explicit formulas for acoustic phonons in the Debye approximation are written.

The plan of the paper is as follows. In Sect. 2, the semiclassical phonon transport is summarized, while in Sect. 3 we write down the Wigner equations for phonons. Section 4 is dedicated to deducing the moment equations whose closure relations are achieved by QMEP in Sect. 5. In Sect. 6, a definition of local temperature is introduced by generalizing what has been proposed in Mascali and Romano (2017) and in the last section an asymptotic expression of the quantum correction to the heat flux is obtained for the most relevant branches of phonons.

2 Semiclassical Phonon Transport

In a crystal lattice, the transport of energy is quantized in terms of quasi-particles named phonons which are present with several branches and propagation modes. The latters vary from a material to another but in any case they are grouped in acoustic and optical phonon branches which, in turn, can oscillate in the longitudinal or transversal direction. The complete dispersion relations can be usually obtained by a numerical approach in the first Brillouin zone (FBZ) $\mathcal{B}$. However, in the applications some standard approximations are often adopted.

For the acoustic phonons, the Debye approximation for the dispersion relation $\varepsilon_\mu(\mathbf{q})$ is usually assumed, $\varepsilon_\mu(\mathbf{q}) = c_\mu|\mathbf{q}|$, $\mu = LA, TA$, where $\mathbf{q}$ is the phonon momentum. LA stands for longitudinal acoustic while TA for transversal acoustic. c_μ is the sound speed of the μ-branch. Consistently, the first Brillouin zone is extended to $\mathbb{R}^d$. Here, d is the dimension of the space; $d = 3$ for bulk crystal while $d = 2$ for graphene or similar 2D material like dichalcogenides. Sometimes also the case $d = 1$ is considered, but it represents an oversimplification from a physical point of view. We remark that the standard way to express the dispersion relation is in terms of wave-vector. However, in view of the quantum kinetic formulation which will be devised in the next sections, the phonon momentum is a more appropriate variable.

For the longitudinal optical (LO) and the transversal optical (TO) phonon, the Einstein dispersion relation, $\varepsilon_\mu(\mathbf{q}) \approx$ const, with $\mu = LO, TO$, is usually adopted. Note that under such an assumption, the group velocity of the optical phonons is negligible.

In some peculiar materials like graphene, it is customary to introduce also a fictitious branch called K-phonons constituted by the phonons having wave vectors close to the Dirac points, K or K', in the first Brillouin zone (taking the origin in the center Γ of FBZ). Also in this case the Einstein approximation is used on account of the limited variability of the phonon energy near those points. Moreover, in graphene the phonons are classified as in-plane, representing vibration parallel to the material, and out of plane, representing vibrational mode orthogonal to the material. The LA, TA, LO, TO and K phonons are in plane. The out of plane phonons belong to the acoustic branch and are named ZA phonons. For them, a quadratic dispersion relation is a good approximation: $\varepsilon_{ZA}(\mathbf{q}) = \overline{\alpha}|\mathbf{q}|^2$, where $\overline{\alpha} = \alpha/\hbar$ with $\alpha = 6.2 \times 10^7 m^2/s$ (see Mounet and Marzari 2005; Nika and Balandin 2012; Pop et al. 2012) and $\hbar$ is the reduced Planck constant.

Observe that in all the cases considered above, the dispersion relation is isotropic. Hereafter, we assume such a property for $\varepsilon_\mu(\mathbf{q})$, $\mu = LA, TA, LO, TO, K, ZA$.

The thermal transport is usually described by macroscopic models, e.g., the Fourier one, those based on the Maximum Entropy methods (Camiola et al. 2020) or on phenomenological description (Sellitto et al. 2016). A more accurate way to tackle the question is to resort to semiclassical transport equations, the so-called Peierls–Boltzmann equations, for each phonon branch for the phonon distributions $f_\mu(t, \mathbf{x}, \mathbf{q})$

$$\frac{\partial f_\mu}{\partial t} + \mathbf{c}_\mu \cdot \nabla_{\mathbf{x}} f_\mu = C_\mu, \quad \mu = LA, TA, \dots, \tag{1}$$

where $\mathbf{c}_\mu = \nabla_{\mathbf{q}}\, \varepsilon_\mu(\mathbf{q})$ is the group velocity of the μ-th phonon specie.

The phonon collision term C_μ splits into two terms

$$C_\mu = C_\mu^\mu + \sum_{\nu,\nu\neq\mu} C_\mu^\nu, \quad \mu = LA, TA, \dots. \tag{2}$$

C_μ^μ describes the phonon interaction within the same branch while C_μ^ν describes the phonon–phonon interaction between different species. To deal with the complete expressions of the C_μ's is a very complicated task even from a numerical point of view (Srivastava 1990). So, they are usually simplified by the Bhatnagar–Gross–Krook (BGK) approximation

$$C_\mu = -\frac{f_\mu - f_\mu^{LE}}{\tau_\mu(\mathbf{q})},$$

which mimics the relaxation of each phonon branch toward a common local equilibrium condition, characterized by a local equilibrium temperature T_L that is the same for each phonon population. The functions τ_μ are the phonon relaxation times

The local equilibrium phonon distributions are given by the Bose–Einstein distributions

$$f_\mu^{LE} = \left[e^{\varepsilon_\mu(\mathbf{q})/k_B T_L} - 1\right]^{-1}. \tag{3}$$

where k_B is the Boltzmann constant. Additional BGK terms can be added to include the interaction between pairs of different branches.

The modern devices, e.g., the electron ones like double gate MOSFETs (see Camiola et al. 2020), are undergoing more and more miniaturization. This implies that the characteristic scales are of the same order as the typical lengths where quantum effects become more and more relevant. Therefore, quantum effects must be included and the semiclassical phonon transport equations must be replaced by a more accurate model. Among the possible approaches, the one based on the Wigner equation has the advantage to be formulated in a phase-space, allowing us to guess the features of the solutions in analogy with the semiclassical counterpart.

A huge literature has been devoted to the application of the Wigner equations to charge transport (see Morandi and Schürrer 2011; Muscato and Wagner 2016; Querlioz and Dollfus 2010), but a limited use has been made for phonon transport. In the next sections, a transport model, based on the Wigner quasi distribution, will be devised for phonon transport in nano-structures.

3 Phonon Wigner Functions

The main point of our derivation is the kinetic description of a one-particle quantum statistical state, given in terms of one-particle Wigner functions. Let us now briefly recall the basic definitions and properties. A mixed (statistical) one-particle quantum state for an ensemble of scalar particles in $\mathbb{R}^d$ is described by a density operator $\hat{\rho}$, i.e., a bounded non-negative operator with unit trace, acting on $L^2(\mathbb{R}^d, \mathbb{C})$. Given the density operator $\hat{\rho}$ on $L^2(\mathbb{R}^d, \mathbb{C})$, the associated Wigner function, $g = g(\mathbf{x}, \mathbf{q})$, $(\mathbf{x}, \mathbf{q}) \in \mathbb{R}^{2d}$, is the inverse Weyl quantization of $\hat{\rho}$,

$$g = Op_{\hbar}^{-1}(\hat{\rho}). \tag{4}$$

We recall that the Weyl quantization of a phase-space function (a *symbol*) $a = a(\mathbf{x}, \mathbf{q})$ is the (Hermitian) operator $Op_{\hbar}(a)$ formally defined by Hall (2013)

$$Op_{\hbar}(a)\psi(\mathbf{x}) = \frac{1}{(2\pi\hbar)^d} \int_{\mathbb{R}^{2d}} a\left(\frac{\mathbf{x}+\mathbf{y}}{2}, \mathbf{q}\right) \psi(\mathbf{y}) e^{i(\mathbf{x}-\mathbf{y})\cdot\mathbf{q}/\hbar} \mathrm{d}\mathbf{y}\, \mathrm{d}\mathbf{q} \tag{5}$$

for any $\psi \in L^2(\mathbb{R}^d, \mathbb{C})$. The inverse quantization of $\hat{\rho}$ can be written as the *Wigner transform*

$$g(\mathbf{x}, \mathbf{q}) = \frac{1}{\hbar^d} \int_{\mathbb{R}^d} \rho(\mathbf{x} + \boldsymbol{\xi}/2, \mathbf{x} - \boldsymbol{\xi}/2) e^{i\mathbf{q}\cdot\boldsymbol{\xi}/\hbar} d\boldsymbol{\xi}, \tag{6}$$

of the kernel $\rho(\mathbf{x}, \mathbf{y})$ of the density operator.

The dynamics of the time-dependent phonon Wigner functions for the several phonon branches $g_\mu(\mathbf{x}, \mathbf{q}, t)$, $\mu = LA, TA, \ldots$ steams directly from the dynamics of the corresponding density operator $\hat{\rho}_\mu(t)$, i.e., from the Von Neumann or quantum Liouville equation

$$i\hbar\partial_t \hat{\rho}_\mu(t) = [\hat{H}_\mu, \hat{\rho}_\mu(t)] := \hat{H}_\mu \hat{\rho}_\mu(t) - \hat{\rho}_\mu(t) \hat{H}_\mu, \tag{7}$$

where $\hat{H}_\mu$ denotes the Hamiltonian operators of the μth phonons and $[\cdot, \cdot]$ the commutator. If $h_\mu = Op_{\hbar}^{-1}(\hat{H}_\mu)$ is the symbol associated with $\hat{H}_\mu$, then, from Eq. (7), we obtain the *Wigner equation* for each phonon species

$$i\hbar\partial_t g_\mu(\mathbf{x}, \mathbf{q}, t) = \{h_\mu, g_\mu(\mathbf{x}, \mathbf{q}, t)\}_\# := h_\mu \# g_\mu(\mathbf{x}, \mathbf{q}, t) - g_\mu(\mathbf{x}, \mathbf{q}, t) \# h_\mu. \tag{8}$$

With the symbol #, we have denoted the Moyal (or *twisted*) product which translates the product of operators at the level of symbols according to

$$a\#b = Op_{\hbar}^{-1}(Op_{\hbar}(a) Op_{\hbar}(b)), \tag{9}$$

for any pair of symbols a and b. Here, we do not tackle the analytical issues which guarantee the existence of the previous relations but limit ourselves to the remark that if two operators are in the Hilbert–Schmidt class, that is the trace there exists and it is not negative and bounded, then the product is still Hilbert–Schmidt and the Moyal calculus is well defined. In the sequel, we will suppose that such conditions are valid.

The Moyal product, under suitable regularity assumptions (see Folland 1989), possesses the following formal semiclassical expansion

$$a\#_\hbar b(\mathbf{x},\mathbf{q}) = \sum_{\alpha,\beta} \left(\frac{i\hbar}{2}\right)^{|\alpha|+|\beta|} \frac{(-1)^{|\beta|}}{\alpha!\beta!} \partial_{\mathbf{x}}^{\alpha}\partial_{\mathbf{q}}^{\beta} a(\mathbf{x},\mathbf{q}) \partial_{\mathbf{x}}^{\beta}\partial_{\mathbf{q}}^{\alpha} b(\mathbf{x},\mathbf{q}) \tag{10}$$

where $\alpha = (\alpha_1, ..., \alpha_d) \in \mathbb{N}^d$ is a multi-index, $|\alpha| = \sum_i \alpha_i$, $\alpha! = \prod_i \alpha_i!$, $\partial_{\mathbf{x}}^{\alpha} = \prod_i \partial_{x_i}^{\alpha_i}$ and similarly for $\partial_{\mathbf{q}}^{\beta}$.

The expansion (10) can be rewritten as

$$a\#_\hbar b(\mathbf{x},\mathbf{q}) = \sum_{n=0}^{\infty} \hbar^n a\#_n b \tag{11}$$

where

$$a\#_n b(\mathbf{x},\mathbf{q}) = \sum_{\alpha,\beta,|\alpha|+|\beta|=n} \left(\frac{i}{2}\right)^{n} \frac{(-1)^{|\beta|}}{\alpha!\beta!} \partial_{\mathbf{x}}^{\alpha}\partial_{\mathbf{q}}^{\beta} a(\mathbf{x},\mathbf{q}) \partial_{\mathbf{x}}^{\beta}\partial_{\mathbf{q}}^{\alpha} b(\mathbf{x},\mathbf{q}) \tag{12}$$

It is easy to see that

$$a\#_n b(\mathbf{x},\mathbf{q}) = (-1)^n b\#_n a(\mathbf{x},\mathbf{q}),$$

that is the operation $\#_n$ is commutative (respectively, anticommutative) when n is even (respectively, odd).

If we neglect, temporarily, the phonon–phonon interactions, the Hamiltonian symbol for each phonon branch is given by

$$h_\mu(\mathbf{q}) = \varepsilon_\mu(\mathbf{q}) \quad \mu = LA, TA, \ldots. \tag{13}$$

By using the Moyal calculus, one can expand the second members of the previous Wigner equations. Up to first order in $\hbar^2$, we have

$$\partial_t g_\mu(t) + S[h_\mu] g_\mu(t) = 0, \quad \mu = LA, TA, \ldots, \tag{14}$$

where[1]

$$S[h_\mu] g_\mu(\mathbf{x},\mathbf{q},t) := \mathbf{c}_\mu \cdot \nabla_{\mathbf{x}} g_\mu(\mathbf{x},\mathbf{q},t) \\ -\frac{\hbar^2}{24} \frac{\partial^3 h_\mu(\mathbf{q})}{\partial q_i \partial q_j \partial q_k} \frac{\partial^3 g_\mu(\mathbf{x},\mathbf{q},t)}{\partial x_i \partial x_j \partial x_k} + O(\hbar^4) \quad \mu = LA, TA, \ldots. \tag{15}$$

The previous equations describe only ballistic transport and include only the harmonic contribution to the Hamiltonian. In order to describe also intra and inter-branch

[1] Summation over repeated indices is understood from 1 to d.

phonon–phonon interactions, an additional anharmonic term $\hat{H}_{int}$ encompassing the high order correction to the Hamiltonian operator must be added. So doing, one gets the so-called Wigner–Boltzmann equations

$$\partial_t g_\mu(\mathbf{x}, \mathbf{q}, t) + S[h_\mu] g_\mu(\mathbf{x}, \mathbf{q}, t) = C_\mu(\mathbf{x}, \mathbf{q}, t), \quad \mu = LA, TA, \ldots, \tag{16}$$

In the quantum case, the expression of C_μ is rather cumbersome. For electron transport in semiconductors, the interested reader can see Frommlet et al. (1999). In certain regimes, it is justified to retain the same form of the semiclassical collision operator as the semiclassical case (Querlioz and Dollfus 2010).

Eq. (16) represents our starting point for the phonon transport. Note that for the optical phonons under the Einstein approximation for the energy bands one has formally the same transport equation as the semiclassical case because the group velocity vanishes.

An alternative derivation of (16) can be obtained by explicitly writing the von Neumann equation (see Luca and Romano 2019; Camiola et al. 2020 for the details). One obtains

$$\begin{aligned} &S[h_\mu] g_\mu(t) \\ &= \frac{i}{\hbar (2\pi)^d} \int_{\mathbb{R}^d_{\mathbf{x}'} \times \mathbb{R}^d_{\boldsymbol{\nu}}} \left[\varepsilon_\mu \left(\mathbf{q} + \frac{\hbar}{2} \boldsymbol{\nu}, t \right) - \varepsilon_\mu \left(\mathbf{q} - \frac{\hbar}{2} \boldsymbol{\nu}, t \right) \right] g_\mu(\mathbf{x}', \mathbf{q}, t) e^{-i(\mathbf{x}' - \mathbf{x}) \cdot \boldsymbol{\nu}} \mathrm{d}\mathbf{x}' \mathrm{d}\boldsymbol{\nu}, \end{aligned} \tag{17}$$

whose expansion is of course in agreement with the Moyal calculus.

4 Phonon Moment Equations

Getting analytical solutions to Eq. (16) is a daunting task. Therefore, viable approaches are numerical solutions based on finite differences or finite elements (Morandi and Schürrer 2011) or stochastic solutions, e.g., those obtained with a suitable modification of the Monte Carlo methods for the semiclassical Boltzmann equation (Muscato and Wagner 2016). However, it is possible to have simpler, even if approximate, models resorting to the moment method for the expectation values of interest. In fact, it is well known that, although not positive definite, the Wigner function is real and the expectation values of an operator can be formally obtained as an average of the corresponding symbol with respect to $g_\mu(\mathbf{x}, \mathbf{q}, t)$. So, for any regular enough weight function $\psi(\mathbf{q})$, let us introduce the short notation

$$< \psi >_\mu (\mathbf{x}, t) := \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \psi(\mathbf{q}) g_\mu(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q}, \tag{18}$$

which represents a partial average with respect to the phonon momentum $\mathbf{q}$.

More in general, if $a = a(\mathbf{x}, \mathbf{q})$ is a smooth *symbol*, then it is possible to prove that the expectation of the (hermitian) operator $A = Op_\hbar(a)$ satisfies[2]

$$\mathbb{E}[A] = \text{tr}(\hat{\rho}A) = \int_{\mathbb{R}^{2d}} \rho(\mathbf{x}, \mathbf{y}, t) k_A(\mathbf{x}, \mathbf{y}) \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^{2d}} a(\mathbf{x}, \mathbf{q}) g_\mu(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{q}$$
$$= \int_{\mathbb{R}^d} < a >_\mu (\mathbf{x}, t) \mathrm{d}\mathbf{x},$$

where $k_A(\mathbf{x}, \mathbf{y})$ is the kernel of A.

We want to consider a minimum set of moments whose physical meaning is well clear. In particular, we shall consider the phonon energy density and energy flux density of each branch

$$W_\mu(\mathbf{x}, t) =< h_\mu >_\mu (\mathbf{x}, t), \quad \mathbf{Q}_\mu(\mathbf{x}, t) =< h_\mu \mathbf{c}_\mu >_\mu (\mathbf{x}, t). \tag{19}$$

Note that the latter is directly related to the heat flux.

The evolution equations for $W_\mu(\mathbf{x}, t)$ and $\mathbf{Q}_\mu(\mathbf{x}, t)$ are obtained by multiplying the relative Wigner equation by $h_\mu(\mathbf{q})$, and $h_\mu(\mathbf{q})\mathbf{c}_\mu$ and integrating with respect to $\mathbf{q}$

$$\begin{aligned} \partial_t W_\mu(\mathbf{x}, t) + \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) S[h_\mu] g_\mu \,\mathrm{d}\mathbf{q} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) C_\mu \,\mathrm{d}\mathbf{q}, \\ \partial_t \mathbf{Q}_\mu(\mathbf{x}, t) + \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) \mathbf{c}_\mu S[h_\mu] g_\mu \,\mathrm{d}\mathbf{q} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) \mathbf{c}_\mu C_\mu \,\mathrm{d}\mathbf{q}. \end{aligned} \quad \mu = LA, TA, \ldots. \tag{20}$$

We implicitly assume that the resulting integrals there exist, at least in the principal value sense. In order to get some global insight from Eq. (20), we formally assume the following expansions for each phonon branch[3]

$$g_\mu(\mathbf{x}, \mathbf{q}, t) = g_\mu^{(0)}(\mathbf{x}, \mathbf{q}, t) + \hbar^2 g_\mu^{(2)}(\mathbf{x}, \mathbf{q}, t) + o(\hbar^2). \tag{21}$$

It is possible to prove, at least formally (Jüngel 2009), that the semiclassical Boltzmann equation is recovered from the Wigner equation as $\hbar \to 0^+$. Therefore, $g_\mu^{(0)}(\mathbf{x}, \mathbf{q}, t)$ can be considered as the solution f_μ of the semiclassical transport equation. Accordingly, we write

$$W_\mu = W_\mu^{(0)} + \hbar^2 W_\mu^{(2)} + o(\hbar^2), \quad \mathbf{Q}_\mu = \mathbf{Q}_\mu^{(0)} + \hbar^2 \mathbf{Q}_\mu^{(2)} + o(\hbar^2), \tag{22}$$

[2] Here we are considering a fixed instant of time.

[3] The coefficients of the odd powers in $\hbar$ are assumed zero in according to the previous Moyal expansion.

where

$$W_{\mu}^{(0)} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu g_\mu^{(0)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q}, \quad W_{\mu}^{(2)} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu g_\mu^{(2)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q},$$
$$\mathbf{Q}_{\mu}^{(0)} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu \mathbf{c}_\mu g_\mu^{(0)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q}, \quad \mathbf{Q}_{\mu}^{(2)} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu \mathbf{c}_\mu g_\mu^{(2)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q}.$$

Regarding the moments of the collision terms, only with drastic simplifications analytical expressions can be deduced. In analogy with the BGK approximation, we assume that the r.h.s. of Eq. (20) are expressed as relaxation time terms

$$\frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) C_\mu \, \mathrm{d}\mathbf{q} = -\frac{W_\mu - W_\mu^{LE}}{\tau_\mu^W} = -\frac{W_\mu^{(0)} - W_\mu^{(0)LE}}{\tau_\mu^W} - \hbar^2 \frac{W_\mu^{(2)} - W_\mu^{(2)LE}}{\tau_\mu^W} + o(\hbar^2),$$
$$\frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) \mathbf{c}_\mu C_\mu \, \mathrm{d}\mathbf{q} = -\frac{\mathbf{Q}_\mu}{\tau_\mu^{\mathbf{Q}}} = -\frac{\mathbf{Q}_\mu^{(0)} + \hbar^2 \mathbf{Q}_\mu^{(2)}}{\tau_\mu^{\mathbf{Q}}} + o(\hbar^2),$$

where

$$W_\mu^{LE} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h_\mu(\mathbf{q}) g_\mu^{LE} \, \mathrm{d}\mathbf{q}.$$

Note that we have used the fact that the local equilibrium values of the energy-flux $\mathbf{Q}_\mu^{LE}$ vanishes. The energy and energy-flux relaxation times, τ_μ^W and $\tau_\mu^{\mathbf{Q}}$, respectively, are assumed to depends on the temperature, which will be defined in the next section, of the relative branch (see for example Vallabhaneni et al. 2016).

Altogether, the resulting model is made of the following fluid-type equations

$$\begin{cases} \partial_t W_\mu + \dfrac{\partial (\mathbf{Q}_r)_\mu}{\partial x_r} - \dfrac{\hbar^2}{24} \dfrac{\partial^3 (\mathbf{T}_{ijk})_\mu}{\partial x_i \partial x_j \partial x_k} = -\dfrac{W_\mu^{(0)} - W_\mu^{(0)LE}}{\tau_\mu^W} - \hbar^2 \dfrac{W_\mu^{(2)} - W_\mu^{(2)LE}}{\tau_\mu^W} + o(\hbar^2) \\ \partial_t (\mathbf{Q}_r)_\mu + \dfrac{\partial (\mathbf{J}_{ri})_\mu}{\partial x_i} - \dfrac{\hbar^2}{24} \dfrac{\partial^3 (\mathbf{U}_{rijk})_\mu}{\partial x_i \partial x_j \partial x_k} = -\dfrac{(\mathbf{Q}_r^{(0)})_\mu + \hbar^2 (\mathbf{Q}_r^{(2)})_\mu}{\tau_\mu^{\mathbf{Q}}} + o(\hbar^2), \end{cases} \tag{23}$$

where $\mathbf{J}_\mu = \mathbf{J}_\mu^{(0)} + \hbar^2 \mathbf{J}_\mu^{(2)}$ with components

$$(\mathbf{J}_{ri}^{(0)})_\mu = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} (\mathbf{c}_r)_\mu (\mathbf{c}_i)_\mu h_\mu(\mathbf{q}) g_\mu^{(0)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q},$$
$$(\mathbf{J}_{ri}^{(2)})_\mu = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} (\mathbf{c}_r)_\mu (\mathbf{c}_i)_\mu h_\mu(\mathbf{q}) g_\mu^{(2)}(\mathbf{x}, \mathbf{q}, t) \mathrm{d}\mathbf{q},$$

and the complete symmetric tensors $\mathbf{T}_\mu$ and $\mathbf{U}_\mu$ have components

$$(\mathbf{T}_{ijk})_\mu = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} h_\mu(\mathbf{q})\frac{\partial^3 h_\mu(\mathbf{q})}{\partial q_i \partial q_j \partial q_k} g_\mu^{(0)}(\mathbf{x},\mathbf{q},t)\mathrm{d}\mathbf{q},$$
$$(\mathbf{U}_{rijk})_\mu = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} (\mathbf{c}_\mu)_r h_\mu(\mathbf{q})\frac{\partial^3 h_\mu(\mathbf{q})}{\partial q_i \partial q_j \partial q_k} g_\mu^{(0)}(\mathbf{x},\mathbf{q},t)\mathrm{d}\mathbf{q}.$$

If we split into zero and first order in $\hbar^2$, the evolution equations read

$$\partial_t W_\mu^{(0)} + \nabla_\mathbf{x}\cdot\mathbf{Q}_\mu^{(0)} = -\frac{W_\mu^{(0)} - W_\mu^{(0)LE}}{\tau_\mu^W} \tag{24}$$

$$\partial_t W_\mu^{(2)} + \nabla_\mathbf{x}\cdot\mathbf{Q}_\mu^{(2)} - \frac{1}{24}\frac{\partial^3}{\partial x_i \partial x_j \partial x_k}\left(\mathbf{T}_{ijk}\right)_\mu = -\frac{W_\mu^{(2)} - W_\mu^{(2)LE}}{\tau_\mu^W}, \tag{25}$$

$$\partial_t (\mathbf{Q}_r^{(0)})_\mu + \frac{\partial (\mathbf{J}_{ri}^{(0)})_\mu}{\partial x_i} = -\frac{(\mathbf{Q}_r^{(0)})_\mu}{\tau_\mu^\mathbf{Q}}, \tag{26}$$

$$\partial_t (\mathbf{Q}_r^{(2)})_\mu + \frac{\partial (\mathbf{J}_{ri}^{(2)})_\mu}{\partial x_i} - \frac{1}{24}\frac{\partial^3}{\partial x_i \partial x_j \partial x_k}(\mathbf{U}_{rijk})_\mu = -\frac{(\mathbf{Q}_r^{(2)})_\mu}{\tau_\mu^\mathbf{Q}}. \tag{27}$$

The zero-order equations are the model already investigated in several papers (Mascali and Romano 2020, 2017) (for specific materials see also Mascali 2022, 2023), where is proved that it is a hyperbolic system of conservation law, while the first-order corrections in $\hbar^2$ introduce dispersive terms. This is not surprising on account of the nonlocal character of the quantum evolution equations.

5 QMEP for the Closure Relations

The evolution equations (24)–(27) do not form a closed system of balance laws. If we assume the energies W_μ and the energy-fluxes $\mathbf{Q}_\mu$ as the main fields, in order to get a set of closed equations we need to express the additional fields $\mathbf{J}_\mu$, $\mathbf{T}_\mu$ and $\mathbf{U}_\mu$ as functions of W_μ and $\mathbf{Q}_\mu$. A successful approach in a semiclassical setting is that based on the Maximum Entropy Principle (MEP) (see also Camiola et al. 2020 for a complete review) which is based on a pioneering paper of Jaynes (1957a, b) who also proposed a way to extend the approach to the quantum case. The MEP in a quantum setting has been the subject of several papers (Romano 2007; Degond and Ringhofer 2003; Degond et al. 2005; Barletti 2014; Barletti and Cintolesi 2012) with several applications, e.g., to charge transport in graphene (Luca and Romano 2019; Mascali and Romano 2017). Here, we will use such an approach for phonon transport.

The starting point is the entropy for the quantum system under consideration. In Luca and Romano (2019), the authors have employed the Von-Neumann entropy which, however, does not take into account the statistical aspects. Therefore, we take as entropy a generalization of the classical one for bosons. Let us introduce the operator

$$s(\hat{\rho}_\mu) = -k_B[\hat{\rho}_\mu \ln \hat{\rho}_\mu - (1+\hat{\rho}_\mu)\ln(1+\hat{\rho}_\mu)], \tag{28}$$

which must be intended in the sense of the functional calculus. Here, k_B is the Boltzmann constant. The entropy of the μ-th phonon branch reads

$$S(\hat{\rho}_\mu) = \mathrm{Tr}\{s(\hat{\rho}_\mu)\}$$

which can be viewed as a quantum Bose–Einstein entropy.

According to MEP, we estimate $\hat{\rho}_\mu$ with $\hat{\rho}_\mu^{\mathrm{MEP}}$ which is obtained by maximizing $S(\hat{\rho}_\mu)$ under the constraints that some expectation values have to be preserved. In the semiclassical point case, one maximizes the entropy preserving the values of the moments we have taken as basic field variables

$$(W_\mu(\mathbf{x},t), \mathbf{Q}_\mu(\mathbf{x},t)) = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \boldsymbol{\psi}_\mu(\mathbf{q}) g_\mu(\mathbf{x},\mathbf{q},t)d\mathbf{q} = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \boldsymbol{\psi}_\mu(\mathbf{q}) g_\mu^{\mathrm{MEP}}(\mathbf{x},\mathbf{q},t)d\mathbf{q}, \tag{29}$$

where

$$\boldsymbol{\psi}_\mu(\mathbf{q}) = (h_\mu(\mathbf{q}), \mathbf{c}_\mu h_\mu(\mathbf{q})) \tag{30}$$

is the vector of the weight functions and g_μ^{MEP} is the Wigner function associated with $\hat{\rho}_\mu^{\mathrm{MEP}}$. In the previous relations, the time t and position $\mathbf{x}$ must be considered as fixed.

The quantum formulation of MEP is given in terms of expectation values

$$E_1(t) = \mathrm{tr}\left\{\hat{\rho}_\mu Op_\hbar(h_\mu(\mathbf{q}))\right\}(t), \quad \mathbf{E}_2(t) = \mathrm{tr}\left\{\hat{\rho}_\mu Op_\hbar(\mathbf{c}_\mu h_\mu(\mathbf{q}))\right\}(t),$$

as follows: for fixed t

$$\hat{\rho}_\mu^{\mathrm{MEP}} = \text{argument max } S(\hat{\rho}_\mu) \tag{31}$$

under the constraints

$$\mathrm{tr}\{\hat{\rho}_\mu^{\mathrm{MEP}} Op_\hbar(h_\mu(\mathbf{q}))\} = E_1(t), \quad \mathrm{tr}\{\hat{\rho}_\mu^{\mathrm{MEP}} Op_\hbar(\mathbf{c}_\mu h_\mu(\mathbf{q}))\} = \mathbf{E}_2(t), \tag{32}$$

in the space of the Hilbert–Schmidt operators on $L^2(\mathbb{R}^d, \mathbb{C})$ which are positive, with trace one and such that the previous expectation values there exist. Note that we are applying the maximization of the entropy for each phonon branch separately. In other words, we are requiring the additivity of the entropy.

If we introduce the vector of the Lagrange multipliers

$$\boldsymbol{\eta}_\mu = (\eta_{0\mu}(\mathbf{x},t), \boldsymbol{\eta}_{1\mu}(\mathbf{x},t)), \tag{33}$$

the vector of the moments

$$\mathbf{m}[\rho_\mu](\mathbf{x},\mathbf{t}) := \mathbf{m}_\mu(\mathbf{x},t) = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \boldsymbol{\psi}_\mu(\mathbf{q}) g_\mu(\mathbf{x},\mathbf{q},t)d\mathbf{q}, \tag{34}$$

and the vector of the moments which must be considered as known

$$\mathbf{M}_\mu(\mathbf{x}, t) := \left(W_\mu(\mathbf{x}, t), \mathbf{Q}_\mu(\mathbf{x}, t)\right), \tag{35}$$

the constrained optimization problem (31) and (32) can be rephrased as a saddle-point problem for the Lagrangian

$$\begin{aligned}\mathcal{L}_\mu(\hat{\rho}_\mu, \boldsymbol{\eta}_\mu) &= S(\hat{\rho}_\mu) - \int_{\mathbb{R}^d} \boldsymbol{\eta}_\mu \cdot \left(\mathbf{m}_\mu(\mathbf{x}, t) - \mathbf{M}_\mu(\mathbf{x}, t)\right) \,\mathrm{d}\mathbf{x} \\ &= S(\hat{\rho}_\mu) - \operatorname{tr}\left\{\hat{\rho}_\mu Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu(\mathbf{q}))\right\} + \int_{\mathbb{R}^d} \boldsymbol{\eta}_\mu \cdot \mathbf{M}_\mu(\mathbf{x}, t)\,\mathrm{d}\mathbf{x} \end{aligned} \tag{36}$$

in the space of the admissible $\hat{\rho}_\mu$ and smooth function $\boldsymbol{\eta}_\mu$.

If the Lagrangian $\mathcal{L}_\mu(\hat{\rho}_\mu, \boldsymbol{\eta}_\mu)$ is Gâteaux-differentiable with respect to $\hat{\rho}_\mu$, the first-order optimality conditions require

$$\delta\mathcal{L}_\mu(\hat{\rho}_\mu, \boldsymbol{\eta}_\mu)(\delta\hat{\rho}) = 0$$

for each Hilbert–Schmidt operators $\delta\hat{\rho}$ on $L^2(\mathbb{R}^d, \mathbb{C})$ which is positive, with trace one and such that the previous expectation values there exist.

The existence of the first-order Gâteaux derivative is a consequence of the following Lemma (for the proof see Nier 1993; an elementary proof in the case of discrete spectrum is given in Degond and Ringhofer 2003).

Lemma 1 *If $r(x)$ is a continuously differentiable increasing function on $\mathbb{R}^+$, then $tr\{r(\hat{\rho})\}$ is Gâteaux-differentiable in the class of the Hermitian Hilbert–Schmidt positive operators on $L^2(\mathbb{R}^d, \mathbb{C})$. The Gâteaux derivative along $\delta\rho$ is given by*

$$\delta tr\{r(\hat{\rho})\}(\delta\hat{\rho}) = tr\left\{r'(\hat{\rho})\delta\hat{\rho}\right\}. \tag{37}$$

The extremality conditions for the unconstrained minimization problem (31) and (32) are similar to that of the semiclassical case, as expressed by the following lemma (see Degond and Ringhofer 2003).

Lemma 2 *The first-order optimality condition for the minimization problem (31) and (32) is equivalent to*

$$\hat{\rho}_\mu = (s')^{-1}(Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu)) \tag{38}$$

where $(s')^{-1}$ is the inverse function of the first derivative of s.

Proof By applying Lemma 1, the Gâteaux derivative of the Lagrangian is given by

$$\delta\mathcal{L}_\mu(\hat{\rho}_\mu, \boldsymbol{\eta}_\mu)(\delta\hat{\rho}) = \operatorname{tr}\left\{\left(s'(\hat{\rho}_\mu) - Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu)\right)\delta\hat{\rho}\right\}$$

$\forall \delta \hat{\rho}$ perturbation in the class of the Hermitian Hilbert–Schmidt positive operators on $L^2(\mathbb{R}^d, \mathbb{C})$. This implies

$$s'(\hat{\rho}_\mu) = Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu).$$

□

Since the function $s(x)$ is concave, $s'(x)$ is invertible. Explicitly, we have

$$(s')^{-1}(z) = \frac{1}{e^{z/k_B} - 1},$$

and the operator solving the first-order optimality condition reads

$$\hat{\rho}^*_\mu = (s')^{-1}(Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu)) = \frac{1}{e^{Op_\hbar(\boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu)} - 1}. \tag{39}$$

where we have rescaled the Lagrange multipliers including the factor $1/k_B$. Moreover, such an operator is a point of maximum for the Lagrangian.

Now, to complete the program we have to determine, among the smooth functions, the Lagrange multipliers $\boldsymbol{\eta}_\mu$ by solving the constraint

$$\mathrm{tr}\left\{\hat{\rho}_\mu Op_\hbar(\boldsymbol{\eta}_\mu \cdot (h_\mu(\mathbf{q}), \mathbf{c}_\mu h_\mu(\mathbf{q}))\right\} - \int_{\mathbb{R}^d} \boldsymbol{\eta}_\mu \cdot \mathbf{M}_\mu(\mathbf{x}, t)\, \mathrm{d}\mathbf{x} = 0. \tag{40}$$

If such an equation has a solution $\boldsymbol{\eta}^*_\mu$, altogether the MEP density operator reads

$$\hat{\rho}^{\mathrm{MEP}}_\mu = \frac{1}{\exp\left[Op_\hbar\left(\eta^*_{0\mu}(\mathbf{x}, t) h_\mu(\mathbf{q}) + \boldsymbol{\eta}^*_{1\mu}(\mathbf{x}, t) \cdot \mathbf{c}_\mu h_\mu(\mathbf{q})\right)\right] - 1}. \tag{41}$$

To determine conditions under which Eq. (40) admits solutions is a very difficult task. Even in the semiclassical case, there are examples (see Junk 1998) of sets of moments that cannot be moments of a MEP distribution.

We will directly find out the solution at least up to first order in $\hbar^2$.

Once the MEP density function has been determined, the MEP Wigner function is given by

$$g^{\mathrm{MEP}}_\mu(\mathbf{x}, \mathbf{q}, t) = Op_\hbar^{-1}(\hat{\rho}^{\mathrm{MEP}}_\mu)$$

which can be used to get the necessary closure relations by evaluating the additional fields with g_μ replaced by g^{MEP}_μ.

We remark that the constraints (40) can be more conveniently expressed as

$$\frac{1}{(2\pi)^d} \int_{\mathbb{R}^{2d}} \boldsymbol{\eta}_\mu \cdot \boldsymbol{\psi}_\mu(\mathbf{x}, t) g^{\mathrm{MEP}}_\mu(\mathbf{x}, \mathbf{q}, t)\, d\mathbf{q}\, \mathrm{d}\mathbf{x} - \int_{\mathbb{R}^d} \boldsymbol{\eta}_\mu \cdot \mathbf{M}_\mu(\mathbf{x}, t)\, \mathrm{d}\mathbf{x} = 0$$

and indeed we will require, in analogy with the semiclassical case, the stronger conditions

$$\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \boldsymbol{\psi}_\mu(\mathbf{x},t) g_\mu^{\text{MEP}}(\mathbf{x},\mathbf{q},t)\,\mathrm{d}\mathbf{q} = \mathbf{M}_\mu(\mathbf{x},t),$$

where the Lagrange multipliers enter through $g_\mu^{\text{MEP}}(\mathbf{x},\mathbf{q},t)$.

5.1 Determination of the Lagrange Multipliers

For the sake of making lighter the notation, let us consider a single branch and drop the index μ in the Wigner function in this section. We look formally for a solution in powers of $\hbar$

$$g^{\text{MEP}} = g_0^{\text{MEP}} + \hbar g_1^{\text{MEP}} + \hbar^2 g_2^{\text{MEP}} + \ldots \tag{42}$$

firstly without taking into account the dependence of the Lagrange multipliers on $\hbar$.

Of course, on account of the properties of the Weyl quantization, g_0^{MEP} is equal to the semiclassical counterpart (Hall 2013)

$$g_0^{\text{MEP}} = \frac{1}{e^{\xi} - 1}$$

where

$$\xi = \eta_0(\mathbf{x},t)h(\mathbf{q}) + \boldsymbol{\eta}_1(\mathbf{x},t)\cdot\mathbf{c}h(\mathbf{q}).$$

In order to determine the higher order terms g_k^{MEP}, $k \geq 1$, given a symbol $a(\mathbf{x},\mathbf{q})$ let us introduce the so-called *quantum exponential* $Exp(a)$ defined as

$$Exp(a) = Op_\hbar^{-1}[exp(Op_\hbar(a))]$$

which can be expanded as

$$Exp(a) = Exp_0(a) + \hbar Exp_1(a) + \hbar^2 Exp_2(a) + \ldots \tag{43}$$

Proposition *Let $a(\mathbf{x},\mathbf{q})$ be a smooth symbol. Then, the following expansion is valid*

$$Exp(a) = \exp(a) - \frac{\hbar^2}{8}\exp(a)\left(\frac{\partial^2 a}{\partial x_i \partial x_j}\frac{\partial^2 a}{\partial q_i \partial q_j} - \frac{\partial^2 a}{\partial x_i \partial q_j}\frac{\partial^2 a}{\partial q_i \partial x_j} + \frac{1}{3}\frac{\partial^2 a}{\partial x_i \partial x_j}\frac{\partial a}{\partial q_i}\frac{\partial a}{\partial q_j} - \frac{2}{3}\frac{\partial^2 a}{\partial x_i \partial q_j}\frac{\partial a}{\partial q_i}\frac{\partial a}{\partial x_j} + \frac{1}{3}\frac{\partial^2 a}{\partial q_i \partial q_j}\frac{\partial a}{\partial x_i}\frac{\partial a}{\partial x_j}\right) + O(\hbar^4), \tag{44}$$

where Einstein's convention has been used.

The proof can be found for example in Degond et al. (2005).

By using what is proved in Barletti and Cintolesi (2012), we have

$$g_{2n+1}^{\mathrm{MEP}} = 0, \quad n \geq 0, \tag{45a}$$

$$g_{2n}^{\mathrm{MEP}} = -\sum_{m=0}^{n-1} \sum_{k+l+m=n} \frac{Exp_{2k}(\xi)\#_{2l} g_{2m}^{\mathrm{MEP}}}{e^{\xi}-1}, \quad n \geq 1 \tag{45b}$$

where $\#_{2l}$ are the even terms of the Moyal product expansion.

In particular,

$$g_1^{\mathrm{MEP}} = 0$$

and

$$g_2^{\mathrm{MEP}} = -\frac{1}{8}\frac{e^{\xi}}{(e^{\xi}-1)^3}\left[(e^{\xi}+1)\left(\frac{\partial^2\xi}{\partial x_i \partial x_j}\frac{\partial^2\xi}{\partial q_i \partial q_j} - \frac{\partial^2\xi}{\partial x_i \partial q_j}\frac{\partial^2\xi}{\partial q_i \partial x_j}\right)\right.$$
$$\left. -\frac{(e^{2\xi}+4e^{\xi}+1)}{3(e^{\xi}-1)}\left(\frac{\partial^2\xi}{\partial x_i \partial x_j}\frac{\partial\xi}{\partial q_i}\frac{\partial\xi}{\partial q_j} - 2\frac{\partial^2\xi}{\partial x_i \partial q_j}\frac{\partial\xi}{\partial q_i}\frac{\partial\xi}{\partial x_j} + \frac{\partial^2\xi}{\partial q_i \partial q_j}\frac{\partial\xi}{\partial x_i}\frac{\partial\xi}{\partial x_j}\right)\right]$$

Therefore, up to first order in $\hbar^2$ we have

$$g^{\mathrm{MEP}} = g_0^{\mathrm{MEP}} + \hbar^2 g_2^{\mathrm{MEP}}.$$

and the constraints for each phonon branch read

$$W = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\frac{h(\mathbf{q})}{e^{\xi}-1}\mathrm{d}\mathbf{q} + \hbar^2\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} h(\mathbf{q}) g_2^{\mathrm{MEP}}\mathrm{d}\mathbf{q}, \tag{46}$$

$$\mathbf{Q} = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\frac{\mathbf{c}h(\mathbf{q})}{e^{\xi}-1}\mathrm{d}\mathbf{q} + \hbar^2\frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \mathbf{c}h(\mathbf{q}) g_2^{\mathrm{MEP}}\mathrm{d}\mathbf{q}. \tag{47}$$

The previous equations form a nonlinear system of PDEs for the Lagrange multipliers whose analytical solution seems very difficult to get. Indeed, the situation is even more cumbersome because in a numerical scheme the inversion of the constraints should be performed at each time step.

A viable strategy is to use the Lagrange multipliers as field variables by rewriting the evolution equations (23) in the form

$$\frac{\partial W}{\partial \eta_k}\frac{\partial \eta_k}{\partial t} + \frac{\partial \mathbf{Q}_i}{\partial \eta_k}\frac{\partial \eta_k}{\partial x_i} - \frac{\hbar^2}{24}\left(\frac{\partial}{\partial \eta_k}\frac{\partial^2 \mathbf{T}_{ijk}}{\partial x_j \partial x_k}\right)\frac{\partial \eta_k}{\partial x_i} = -\frac{W - W^{LE}}{\tau^W}, \tag{48}$$

$$\frac{\partial \mathbf{Q}_i}{\partial \eta_k}\frac{\partial \eta_k}{\partial t} + \frac{\partial \mathbf{J}_{ir}}{\partial \eta_k}\frac{\partial \eta_k}{\partial x_r} - \frac{\hbar^2}{24}\left(\frac{\partial}{\partial \eta_h}\frac{\partial^2 \mathbf{U}_{ijkr}}{\partial x_k \partial x_r}\right)\frac{\partial \eta_h}{\partial x_j} = -\frac{Q_i}{\tau^{\mathbf{Q}}}, \tag{49}$$

getting a highly nonlinear system of PDEs.

A further simplification can be obtained by expanding the Lagrange multipliers as

$$\boldsymbol{\eta} = \boldsymbol{\eta}^{(0)} + \hbar^2 \boldsymbol{\eta}^{(2)} + o(\hbar^2).$$

Therefore, the basic fields are also expanded with respect to $\hbar^2$

$$W = W^{(0)} + \hbar^2 W^{(2)} + o(\hbar^2), \quad \mathbf{Q} = \mathbf{Q}^{(0)} + \hbar^2 \mathbf{Q}^{(2)} + o(\hbar^2)$$

where

$$\begin{aligned}
W^{(0)} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \frac{h(\mathbf{q})}{e^{\xi^{(0)}} - 1} \mathrm{d}\mathbf{q}, \\
W^{(2)} &= -\frac{1}{(2\pi)^d} \boldsymbol{\eta}^{(2)} \cdot \int_{\mathbb{R}^d} e^{\xi^{(0)}} \frac{h(\mathbf{q})\boldsymbol{\psi}}{\left(e^{\xi^{(0)}} - 1\right)^2} \mathrm{d}\mathbf{q} + \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h(\mathbf{q}) g_2^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}) \mathrm{d}\mathbf{q}, \\
Q_i^{(0)} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \frac{c_i h(\mathbf{q})}{e^{\xi^{(0)}} - 1} \mathrm{d}\mathbf{q}, \\
Q_i^{(2)} &= -\frac{1}{(2\pi)^d} \boldsymbol{\eta}^{(2)} \cdot \int_{\mathbb{R}^d} \frac{c_i \boldsymbol{\psi} e^{\xi^{(0)}} h(\mathbf{q})}{(e^{\xi^{(0)}} - 1)^2} \mathrm{d}\mathbf{q} + \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} c_i h(\mathbf{q}) g_2^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}) \mathrm{d}\mathbf{q},
\end{aligned}$$

with $\xi^{(0)} = \boldsymbol{\eta}^{(0)} \cdot \boldsymbol{\psi}$.

The balance equations become

$$\nabla_{\boldsymbol{\eta}^{(0)}} W^{(0)} \frac{\partial}{\partial t} (\boldsymbol{\eta}^{(0)})^T + \sum_{i=1}^{d} \left[\nabla_{\boldsymbol{\eta}^{(0)}} Q_i^{(0)} \frac{\partial}{\partial x_i} (\boldsymbol{\eta}^{(0)})^T \right] = -\frac{W^{(0)} - W^{(0)LE}}{\tau^W}, \tag{50}$$

$$\nabla_{\boldsymbol{\eta}^{(0)}} Q_i^{(0)} \frac{\partial}{\partial t} (\boldsymbol{\eta}^{(0)})^T + \sum_{j=1}^{d} \left[\nabla_{\boldsymbol{\eta}^{(0)}} J_{ij}^{(0)} \frac{\partial}{\partial x_j} (\boldsymbol{\eta}^{(0)})^T \right] = -\frac{Q_i^{(0)}}{\tau^{\mathbf{Q}}}, \tag{51}$$

$$\partial_t W^{(2)} + \nabla_{\mathbf{x}} \cdot \mathbf{Q}^{(2)} - \frac{1}{24} \frac{\partial^3}{\partial x_i \partial x_j \partial x_k} \mathbf{T}_{ijk}^{(0)} = -\frac{W^{(2)} - W^{(2)LE}}{\tau^W}, \tag{52}$$

$$\partial_t \mathbf{Q}_r^{(2)} + \frac{\partial \mathbf{J}_{ri}^0}{\partial x_i} - \frac{1}{24} \frac{\partial^3}{\partial x_i \partial x_j \partial x_k} \mathbf{U}_{rijk}^{(0)} = -\frac{\mathbf{Q}^{(2)}}{\tau^{\mathbf{Q}}}. \tag{53}$$

with

$$\begin{aligned}
\mathbf{T}_{ijk}^{(0)} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} h(\mathbf{q}) g_0^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}) \frac{\partial^3}{\partial q_i \partial q_j \partial q_k} h(\mathbf{q}) \mathrm{d}\mathbf{q} \\
\mathbf{U}_{rijk}^{(0)} &= \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \mathbf{c}_r h(\mathbf{q}) g_0^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}) \frac{\partial^3}{\partial q_i \partial q_j \partial q_k} h(\mathbf{q}) \mathrm{d}\mathbf{q}
\end{aligned}$$

We observe that Eqs. (50) and (51) decouple. Once they are solved, one can get the second-order term of the Lagrange multipliers from (52) and (53) which form a linear system for $\boldsymbol{\eta}^{(2)}$. This is rather beneficial from a computational point of view

Proposition 1 *At zero order in* $\hbar^2$*, the map* $\boldsymbol{\eta} \to \mathbf{M}(\boldsymbol{\eta})$ *is (locally) invertible.*

Proposition 2 *Eqs.* (50) *and* (51) *form a symmetric hyperbolic system of balance laws.*

The proofs can be found in Camiola et al. (2020).

6 Local Equilibrium Temperature

The concept of temperature out of equilibrium is a subtle topic and still a matter of debate. In the case of charge transport in semiconductors often, the phonons are considered as a thermal bath and under some reasonable assumptions one can hypothesize that the electrons are in thermal equilibrium with the bath. In general, if the dynamics of the phonons must be included, a thermal bath for these does not exist, unless a thermostated system is considered. Therefore, we need to introduce a local equilibrium temperature for the overall phonon system.

In statistical mechanics, one of the most reasonable and adopted ways to generalize the concept of temperature in a non-equilibrium state is that of relating it to the Lagrange multipliers associated with the energy constraint. For the phonon transport in graphene, an approach based on the Lagrange multipliers was followed in Mascali and Romano (2017) (which the interested reader is referred to for the details). Let us recall here the main features. At equilibrium, the phonon temperatures and the corresponding Lagrange multipliers are related by

$$k_B\, T_\mu(\mathbf{x}) = \frac{1}{\eta_{0,\mu}(\mathbf{x})} = \frac{1}{\eta^{(0)}_{0,\mu}(\mathbf{x})} - \hbar^2 \frac{\eta^{(2)}_{0,\mu}(\mathbf{x})}{(\eta^{(0)}_{0,\mu}(\mathbf{x}))^2} + o(\hbar^2).$$

If we assume that such relations hold, even out of equilibrium, the definition of the local temperature can be given in terms of the Lagrangian multipliers as follows.

Definition 1 The local temperature of a system of two or more branches of phonons is $T_{LE} := \frac{1}{k_B \eta_0^{LE}(\mathbf{x})}$, where $\eta_0^{LE}(\mathbf{x})$ is the common Lagrange multiplier that the occupation numbers of the branches, taken into account, would have if they were in the local thermodynamic equilibrium corresponding to their total energy density, that is, the following:

$$W(\eta_0^{LE}(\mathbf{x})) := \sum_\mu W_\mu(\eta_{0,\mu}(\mathbf{x})) = \sum_\mu W_\mu(\eta_0^{LE}(\mathbf{x})), \tag{54}$$

where the sum runs over all the phonon branches.

At *global equilibrium*, the temperature is constant $T = \bar{T}$ and the Wigner function reduced to the Bose–Einstein distribution

$$g_\mu = \left[e^{h_\mu(\mathbf{q})/k_B \bar{T}} - 1 \right]^{-1}, \tag{55}$$

with the same temperature for each phonon branch.

Let us consider a small perturbation $\delta T_\mu(\mathbf{x})$ of the temperature in the sense that $\delta T_\mu(\mathbf{x})/\bar{T} \ll 1$. We can expand g_μ^{MEP} in powers of $\delta T_\mu(\mathbf{x})/\bar{T}$

$$g_\mu^{\text{MEP}} = \left[e^{h_\mu(\mathbf{q})/k_B\bar{T}} - 1\right]^{-1} + \left[e^{h_\mu(\mathbf{q})/k_B\bar{T}} - 1\right]^{-2} e^{h_\mu(\mathbf{q})/k_B\bar{T}} \frac{h_\mu(\mathbf{q})}{k_B\bar{T}} \frac{\delta T_\mu(\mathbf{x})}{\bar{T}} + \hbar^2 \bar{T} \frac{\partial g_{2,\mu}^{\text{MEP}}(\bar{T})}{\partial T} \frac{\delta T_\mu}{\bar{T}} + o\left(\frac{\delta T_\mu}{\bar{T}} + \hbar^2 + \hbar^2 \frac{\delta T_\mu}{\bar{T}}\right).$$

Note that $g_{2,\mu}^{\text{MEP}}(\bar{T})$ is zero because $\dfrac{\partial \xi}{\partial x_i} = \dfrac{\partial \xi}{\partial T}\dfrac{\partial T}{\partial x_i} = 0$ in the case of uniform temperature.

7 Heat Flux in the Stationary Regime

In order to have a guess of the main features of the constitutive relations deduced with QMEP, we would like to get some asymptotic expression for the heat flux which can be compared with that in the semiclassical case. In particular, in order to devise a suitable coefficient of thermal conductivity, we try to put $(\mathbf{Q}_r)_\mu$ in form as close as possible to the Fourier one. Since in the semiclassical case, the Fourier form is obtained from the hyperbolic balance equations in the stationary regime, we consider a steady state.

In such a case, the time derivatives can be dropped and one gets

$$\mathbf{Q}_\mu = -\tau^{\mathbf{Q}} \left[\nabla_{\mathbf{x}} \cdot \mathbf{J}_\mu - \frac{\hbar^2}{(2\pi)^d} \frac{\partial^3}{\partial x_i \partial x_j \partial x_k} \int_{\mathbb{R}^d} \mathbf{c}_\mu \frac{h_\mu(\mathbf{q})}{24} g_{0,\mu}^{\text{MEP}}(\boldsymbol{\eta}_\mu^{(0)}) \frac{\partial^3}{\partial q_i \partial q_j \partial q_k} h_\mu(\mathbf{q}) \mathrm{d}\mathbf{q}\right] + o(\hbar^2). \tag{56}$$

The relation between the Lagrange multipliers and the basic fields, as seen, can hardly be inverted analytically, but a numerical procedure is necessary. However, if we consider a situation where the system is not too far from the equilibrium an expansion of the Lagrange multipliers around the equilibrium state can be performed. At equilibrium, g_μ^{MEP} is isotropic and therefore, $\boldsymbol{\eta}_{1,\mu}^{equil} = \mathbf{0}$ and in a neighborhood of the equilibrium $\boldsymbol{\eta}_{1,\mu}$ remains *small*.

More in general, in the spirit of Levermore theory of moments (Levermore 1996), we can consider the distribution depending on both energy density and energy-flux density as a perturbation of the distribution when only W_μ is the macroscopic field variable. Consistently, we assume that $\boldsymbol{\eta}_{1,\mu}$ remains *small*. Formally, we introduce an anisotropy parameter $0 < \delta \ll 1$ and require

$$\boldsymbol{\eta}_\mu = \left(\frac{1}{k_B T_\mu}, \delta \boldsymbol{\eta}_{1,\mu}\right). \tag{57}$$

Note that in this way we are not necessarily restricted to situation close to equilibrium. So the temperature can vary without any constraints. By expanding in power of

δ, one gets, at zero order in $\hbar^2$,

$$g_{0,\mu}^{\mathrm{MEP}} = \left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-1} - \delta\left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-2} e^{h_\mu(\mathbf{q})/k_B T_\mu} h_\mu(\mathbf{q}) \boldsymbol{\eta}_{1,\mu} \cdot \mathbf{c}_\mu + O(\hbar^2 + \delta^2).$$

We remark that the higher order terms do not enter the constitutive relation for $\mathbf{Q}_\mu$ and observe that $\forall \mathbf{n} \in S^d$

$$\int_{S^d} n_{i_1} n_{i_2} \cdots n_{i_r} d\Omega = 0 \quad \text{if } r \quad \text{odd},$$

S^d being the unit sphere in $\mathbb{R}^d$.

The previous relation implies

$$\int_{\mathbb{R}^d} \underbrace{\mathbf{c}_\mu \otimes \mathbf{c}_\mu \otimes \cdots \otimes \mathbf{c}_\mu}_{r \text{ times}} h_\mu(\mathbf{q}) \left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-1} \mathrm{d}\mathbf{q} = \mathbf{0}$$

if r is odd because the Bose–Einstein distribution is isotropic(remember that the dispersion relation is assumed isotropic).

At the zero order in $\hbar^2$, we have

$$\begin{aligned}
\mathbf{Q}_\mu^{(0)} &= -\tau^{\mathbf{Q}} \nabla_{\mathbf{x}} \mathbf{J}_\mu^{(0)} = -\frac{\tau^{\mathbf{Q}}}{(2\pi)^d} \nabla_{\mathbf{x}} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu(\mathbf{q}) g_{0,\mu}^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}(\mathbf{x}, \mathbf{q}, t)) \mathrm{d}\mathbf{q} + o(\delta) \\
&= -\frac{\tau^{\mathbf{Q}}}{(2\pi)^d} \nabla_{\mathbf{x}} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu(\mathbf{q}) \left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-1} \mathrm{d}\mathbf{q} + o(\delta) \\
&= -\frac{\tau^{\mathbf{Q}}}{(2\pi)^d} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu(\mathbf{q}) \frac{\partial}{\partial T_\mu} \left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-1} \mathrm{d}\mathbf{q}\, \nabla_{\mathbf{x}} T_\mu + o(\delta) \\
&= -\frac{\tau^{\mathbf{Q}}}{(2\pi)^d k_B T_\mu^2} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu^2(\mathbf{q}) \frac{e^{h_\mu(\mathbf{q})/k_B T_\mu}}{\left(e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right)^2} \mathrm{d}\mathbf{q}\, \nabla_{\mathbf{x}} T_\mu + o(\delta),
\end{aligned}$$

which can be written in the Fourier form

$$\mathbf{Q}_\mu^{(0)} = -\mathbf{K}_\mu^{(0)} \nabla_{\mathbf{x}} T_\mu$$

with the thermal conductivity tensor given by

$$\mathbf{K}_\mu^{(0)} = \frac{\tau^{\mathbf{Q}}}{(2\pi)^d k_B T_\mu^2} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu^2(\mathbf{q}) \frac{e^{h_\mu(\mathbf{q})/k_B T_\mu}}{\left(e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right)^2} \mathrm{d}\mathbf{q}.$$

It is evident that $\mathbf{K}_\mu^{(0)}$ is positive definite.

Therefore, if $h_\mu(\mathbf{q})$ is isotropic, then $\mathbf{K}_\mu^{(0)}$ is isotropic as well

$$\mathbf{K}_\mu^{(0)} = \frac{1}{d} k^{(0)} \mathbf{I},$$

with $\mathbf{I}$ identity matrix of order d and $k^{(0)}$ the zero order trace

$$k^{(0)} = \frac{\tau^{\mathbf{Q}}}{(2\pi)^d k_B T_\mu^2} \int_{\mathbb{R}^d} \left|\mathbf{c}_\mu\right|^2 h_\mu^2(\mathbf{q}) \frac{e^{h_\mu(\mathbf{q})/k_B T_\mu}}{\left(e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right)^2} \mathrm{d}\mathbf{q}.$$

The second-order correction in $\hbar^2$ reads

$$\begin{aligned}\mathbf{Q}_\mu^{(2)} &= -\frac{\tau^{\mathbf{Q}}}{(2\pi)^d} \nabla_{\mathbf{x}} \int_{\mathbb{R}^d} \mathbf{c}_\mu \otimes \mathbf{c}_\mu h_\mu(\mathbf{q}) g_{2,\mu}^{\mathrm{MEP}}(\boldsymbol{\eta}^{(0)}(\mathbf{x}, \mathbf{q}, t)) \mathrm{d}\mathbf{q} \\ &\quad + \delta \frac{\tau^{\mathbf{Q}}}{(2\pi)^d} \frac{\partial^3}{\partial x_i \partial x_j \partial x_k} \int_{\mathbb{R}^d} \mathbf{c}_\mu \frac{h_\mu(\mathbf{q})}{24} \left[e^{h_\mu(\mathbf{q})/k_B T_\mu} - 1\right]^{-2} e^{h_\mu(\mathbf{q})/k_B T_\mu} h_\mu(\mathbf{q}) \boldsymbol{\eta}_{1,\mu} \\ &\quad \cdot \mathbf{c}_\mu \frac{\partial^3}{\partial q_i \partial q_j \partial q_k} h_\mu(\mathbf{q}) \mathrm{d}\mathbf{q} + o(\delta).\end{aligned}$$

Indeed, if we are close to equilibrium the last term in the previous relation is of order $\hbar^2\delta$ and can be considered negligible for small deviations from local equilibrium. In any case, the remaining part gives a highly nonlinear correction which cannot be put in a Fourier form.

In the next subsections, we will analyze the quantum corrections in the most relevant phonon branches. Of course, the optical phonons, and in particular the K-phonons in graphene, have a zero group velocity in the Einstein approximation and, as a consequence, they do not contribute directly to the thermal diffusion even if they play an indirect role on account of the scattering with the acoustic branches.

7.1 Acoustic Phonons

In this subsection and in the next one, only the zero order terms in δ are retained in the $\hbar^2$ contribution.

In the case of the longitudinal and transversal acoustic phonons in the Debye approximation for a single branch, the corresponding symbol of the phonon Hamiltonian reads $c_{ac}|\mathbf{q}|$ and therefore,

$$\begin{aligned}k_{ac}^{(0)} &= \frac{\tau^{\mathbf{Q}}}{(2\pi)^d k_B T^2} \int_{\mathbb{R}^d} c_{ac}^4 |\mathbf{q}|^2 \frac{e^{c_{ac}|\mathbf{q}|/k_B T}}{\left(e^{c_{ac}|\mathbf{q}|/k_B T} - 1\right)^2} \mathrm{d}\mathbf{q} \\ &= \frac{\tau^{\mathbf{Q}} c_{ac}^4}{(2\pi)^d k_B T^2} \mathrm{meas}(S_d) \int_0^{+\infty} |\mathbf{q}|^{d+1} \frac{e^{c_{ac}|\mathbf{q}|/k_B T}}{\left(e^{c_{ac}|\mathbf{q}|/k_B T} - 1\right)^2} d|\mathbf{q}| \\ &= \frac{k_B \tau^{\mathbf{Q}} c_{ac}^{2-d}}{(2\pi)^d} \mathrm{meas}(S_d)\, (k_B T)^d \int_0^{+\infty} \xi^{d+1} \frac{e^\xi}{\left(e^\xi - 1\right)^2} d\,\xi \end{aligned} \tag{58}$$

with now $\xi = c_{ac}|\mathbf{q}|/k_B T$ and

$$\mathrm{meas}(S_d) = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

the measure of S_d, $\Gamma(x)$ being the Euler gamma function. The previous integral is convergent for any $d \in \mathbb{N}$. Observe that we get a dependence on the temperature proportional to T^d.

We observe that

$$
\begin{aligned}
g_2^{\mathrm{MEP}} &= -\frac{1}{8}\frac{e^\xi}{(e^\xi-1)^3}\left\{\frac{c_{ac}^2(e^\xi+1)}{k_B^2 T(\mathbf{x},t)^4|\mathbf{q}|^2}\left[\delta_{ij}|\mathbf{q}|^2\left(2\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j} - T\frac{\partial^2 T}{\partial x_i \partial x_j}\right)\right.\right.\\
&\quad \left. + q_i q_j\left(T\frac{\partial^2 T}{\partial x_i \partial x_j} - 3\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j}\right)\right]\\
&\quad \left. - \frac{c_{ac}^3(e^{2\xi}+4e^\xi+1)}{3k_B^3|\mathbf{q}|(e^\xi-1)T(\mathbf{x},t)^5}\left[(\delta_{ij}|\mathbf{q}|^2 - q_i q_j)\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j} - q_i q_j T\frac{\partial^2 T}{\partial x_i \partial x_j}\right]\right\}\\
&= -\frac{1}{8}\frac{c_{ac}^2 e^\xi}{(e^\xi-1)^3}\left\{\frac{(e^\xi+1)}{k_B^2 T(\mathbf{x},t)^4}\left[2|\nabla_{\mathbf{x}} T|^2 - T\Delta_{\mathbf{x}} T + n_i n_j\left(T\frac{\partial^2 T}{\partial x_i \partial x_j} - 3\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j}\right)\right]\right.\\
&\quad \left. - \frac{c_{ac}(e^{2\xi}+4e^\xi+1)|\mathbf{q}|}{3k_B^3(e^\xi-1)T(\mathbf{x},t)^5}\left[(\delta_{ij} - n_i n_j)\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j} - n_i n_j T\frac{\partial^2 T}{\partial x_i \partial x_j}\right]\right\}.
\end{aligned}
$$

and, therefore, the second-order correction to the heat flux is given by

$$
\mathbf{Q}^{(2)} = -\tau^{\mathbf{Q}}\nabla_{\mathbf{x}}\mathbf{J}^{(2)}
$$

with

$$
\begin{aligned}
\mathbf{J}^{(2)} &= \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\mathbf{c}_{ac}\otimes\mathbf{c}_{ac}h(\mathbf{q})g_2^{\mathrm{MEP}}\mathrm{d}\mathbf{q}\\
&= \frac{c_{ac}^2}{(2\pi)^d}\int_{\mathbb{R}^d} n_h n_k h(\mathbf{q})g_2^{\mathrm{MEP}}\mathrm{d}\mathbf{q}\,\mathbf{e_h}\otimes\mathbf{e_k} := \mathbf{J}_{hk}^{(2)}\mathbf{e_h}\otimes\mathbf{e_k}
\end{aligned}
$$

$(\mathbf{e_1}, \mathbf{e_2}, \cdots, \mathbf{e_d})$ being an orthonormal basis of $\mathbb{R}^d$.

By taking into account, the well-known formulas

$$
\begin{aligned}
&\int_{S_d} n_h n_k d\Omega = \frac{\mathrm{meas}(S_d)}{d}\delta_{hk},\\
&\int_{S_d} n_i n_j n_h n_k d\Omega = \frac{\mathrm{meas}(S_d)}{d(d+2)}(\delta_{ij}\delta_{hk} + \delta_{ih}\delta_{jk} + \delta_{ik}\delta_{jh}),
\end{aligned}
$$

the components of $\mathbf{J}^{(2)}$ read

$$
\begin{aligned}
\mathbf{J}_{hk}^{(2)} &= -\frac{c_{ac}^5}{8(2\pi)^d}\frac{\mathrm{meas}(S_d)}{d}\frac{1}{k_B^2 T^4(\mathbf{x},t)}\left(\frac{k_B T}{c_{ac}}\right)^{d+1}\\
&\quad \left\{\left[\left(\frac{2d+1}{d+2}I_1(d) - \frac{d+1}{3(d+2)}I_2(d)\right)|\nabla_x T|^2 - \left(\frac{d+1}{d+2}I_1(d) - \frac{I_2(d)}{3(d+2)}\right)T\Delta_x T\right]\delta_{hk}\right.\\
&\quad \left. + \frac{2}{3(d+2)}\left[(I_2(d) - 9I_1(d))\frac{\partial T}{\partial x_h}\frac{\partial T}{\partial x_k} + (3I_1(d) + I_2(d))T\frac{\partial^2 T}{\partial x_h \partial x_k}\right]\right\},
\end{aligned}
$$

where

$$I_1(d) = \int_0^{+\infty} \frac{e^\xi (e^\xi + 1)}{(e^\xi - 1)^3} \xi^d \mathrm{d}\xi,$$
$$I_2(d) = \int_0^{+\infty} \frac{e^\xi (e^{2\xi} + 4e^\xi + 1)}{(e^\xi - 1)^4} \xi^{d+1} \mathrm{d}\xi.$$

From the above results, one gets the second-order correction to the energy flux density

$$\begin{aligned}
(\mathbf{Q}^{(2)})_h = {} & \frac{\tau^{\mathbf{Q}}}{8(2\pi)^d} c_{ac}^{4-d} \frac{\text{meas}(S_d)}{d} k_B^{d-1} T^{d-4}(\mathbf{x}, t) \\
& \left\{ (d-3) \left(\frac{2d-5}{d+2} I_1(d) - \frac{d-1}{3(d+2)} I_2(d) \right) |\nabla_x T|^2 \frac{\partial T}{\partial x_h} \right. \\
& - \left(\frac{d^2 - d + 4}{d+2} I_1(d) - \frac{d}{3(d+2)} I_2(d) \right) T \frac{\partial T}{\partial x_h} \Delta_x T \\
& + \left(\frac{6d-8}{d+2} I_1(d) - \frac{4}{3(d+2)} I_2(d) \right) T \frac{\partial^2 T}{\partial x_h \partial x_k} \frac{\partial T}{\partial x_k} \\
& \left. + \left(\frac{1-d}{d+2} I_1(d) + \frac{1}{d+2} I_2(d) \right) T^2 \frac{\partial \Delta_x T}{\partial x_h} \right\}.
\end{aligned} \tag{59}$$

The integrals $I_1(d)$ and $I_2(d)$ are divergent in the cases $d = 1$ and $d = 2$. As a consequence, the quantum corrections are valid only in the bulk ($d = 3$) case where $I_1(3) = \pi^2$, $I_2(3) = 4\pi^2$. This peculiarity is physically related to the density of states and the form of the energy dispersion relations and cannot be ascribed to the approximation of the first Brillouin zone with all $\mathbb{R}^d$ because the singularity appears as the momentum tends to zero, that is at the center Γ of the first Brillouin zone. Since this pathology is not present for quadratic dispersion relations (see the next subsection) such as for Z-phonons, to overcome the divergence of the integrals $I_1(d)$ and $I_2(d)$, a viable way could be to quadratically regularize the dispersion relation in a suitable small neighborhood of the Γ point of the first Brillouin zone and matching it with a linear function for higher energies.

7.2 Quadratic Dispersion Relations and Z-Phonons

The Z-phonons have a quadratic dispersion relation $h_{ZA}(\mathbf{q}) = \bar{\alpha}|\mathbf{q}|^2$, which is also a rather common approximation in a neighborhood of a energy minimum, and the group velocity is $\mathbf{c}_{ZA}(\mathbf{q}) = 2\bar{\alpha}\mathbf{q}$.

One gets the following zero-order thermal conductivity

$$k_{ZA}^{(0)} = \frac{2k_B \tau^{\mathbf{Q}}}{(2\pi)^d} \frac{(k_B T)^{\frac{d}{2}+1}}{\bar{\alpha}^{\frac{d}{2}-1}} \text{meas}(S_d) \int_0^{+\infty} \frac{e^\xi}{(e^\xi - 1)^2} \xi^{\frac{d}{2}+2} \mathrm{d}\xi \tag{60}$$

with $\xi = \dfrac{\bar{\alpha}|\mathbf{q}|^2}{k_B T}$. Observe that previous integral is always convergent for any d and that $k_{ZA}^{(0)}$ depends on the temperature as $T^{\frac{d}{2}+1}$.

The second-order correction to the distribution function reads

$$g_2^{\text{MEP}} = -\frac{1}{4}\frac{\bar{\alpha}\xi}{k_B T^3}\Bigg[\frac{e^{\xi}(e^{\xi}+1)}{(e^{\xi}-1)^3}\left(2|\nabla_x T|^2 - T\Delta_x T - 2\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_j} n_i n_j\right) + \frac{e^{\xi}(e^{2\xi}+4e^{\xi}+1)}{3(e^{\xi}-1)^4}\xi\left(2T\frac{\partial^2 T}{\partial x_i \partial x_j} n_i n_j - |\nabla_x T|^2\right)\Bigg]$$

and one gets

$$\mathbf{J}_{hk}^{(2)} = -\frac{\bar{\alpha}^{2-\frac{d}{2}} k_B^{\frac{d}{2}+1} T^{\frac{d}{2}-1}}{(2\pi)^d}\frac{\text{meas}(S_d)}{2d} \left\{\left[\left(\frac{2d+2}{d+2}H_1(d) - \frac{1}{3}H_2(d)\right)|\nabla_x T|^2 - \left(H_1(d) - \frac{2}{3(d+2)}H_2(d)\right)T\Delta_x T\right]\delta_{hk} - \frac{4}{d+2}\left[H_1(d)\frac{\partial T}{\partial x_h}\frac{\partial T}{\partial x_k} - \frac{1}{3}H_2(d) T \frac{\partial^2 T}{\partial x_h \partial x_k}\right]\right\}$$

where

$$H_1(d) = \int_0^{+\infty} \frac{e^{\xi}(e^{\xi}+1)}{(e^{\xi}-1)^3}\xi^{\frac{d}{2}+2} \mathrm{d}\xi,$$
$$H_2(d) = \int_0^{+\infty} \frac{e^{\xi}(e^{2\xi}+4e^{\xi}+1)}{(e^{\xi}-1)^4}\xi^{\frac{d}{2}+3} \mathrm{d}\xi.$$

Note that the integrals $H_1(d)$ and $H_2(d)$ are convergent in the two- and three-dimensional cases which are the relevant ones from a physical point of view. For $d = 1$, they diverge, but this case can be considered as an oversimplification.

By evaluating the divergence of the completely symmetric second-order tensor $\mathbf{J}^{(2)}$, one finds out the second-order correction to the energy-flux density

$$\left(\mathbf{Q}_{ZA}^{(2)}\right)_h = \tau^{\mathbf{Q}}\frac{\bar{\alpha}^{2-\frac{d}{2}} k_B^{\frac{d}{2}+1}}{(2\pi)^d}\frac{\text{meas}(S_d)}{2d} T^{\frac{d}{2}-2} \left\{\left[\frac{d^2-3d+2}{d+2}H_1(d) - \frac{d-2}{6}H_2(d)\right]\frac{\partial T}{\partial x_h}|\nabla_x T|^2 - \left[\frac{d^2+2d+8}{2(d+2)}H_1(d) - \frac{d}{3(d+2)}H_2(d)\right]T\frac{\partial T}{\partial x_h}\Delta_x T + \left[\frac{4d}{d+2}H_1(d) - \frac{4}{3(d+2)}H_2(d)\right]T\frac{\partial T}{\partial x_k}\frac{\partial^2 T}{\partial x_h \partial x_k} - \left[H_1(d) - \frac{2}{d+2}H_2(d)\right]T^2\frac{\partial}{\partial x_h}\Delta_x T\right\}$$

Conclusions

The Wigner equation for phonons has been written in the case of a generic dispersion relation. Moment equations have been deduced and closed by QMEP. Under a long-time scaling, an expression for the heat flux with a nonlinear quantum correction has been obtained. The model is suited for the investigation in modern micro-devices where the enhanced miniaturization makes thermal effects more and more relevant.

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