Phonon Boltzmann equation non-local in space and time: the partial failure of the generalized Fourier law

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The purpose of this note is to clarify the solution of the non-local Peierls Boltzmann equation found by Hua and Lindsay (Phys. Rev. B 102, 104310 (2020)). They used methods of Cepellotti and Marzari. The response function “thermal distributor” is discussed. The new, “non-Fourier” term $\hat{B} [\hat{J}_b = -\kappa \hat{\nabla} T + \hat{B}]$ that occurs in non-local situations, gives rise also to a new term in the thermal distributor.

FOURIER LAW AND NONLOCAL CORRECTION

Transport in bulk systems, with currents small enough to linearize, is given by simple linear response functions, such as the Fourier law for thermal conductivity, $\hat{J}_b = -\kappa \hat{\nabla} T$, where the temperature is close to a background temperature $T_b$, deviating by a small correction $\vec{r} \cdot \hat{\nabla} T$, with $\hat{\nabla} T$ uniform in space. However, in small systems, the current and temperature need to be studied on distance scales less than the mean free paths of heat carriers. A sensible assumption is that a non-local Fourier law, $\hat{J}_F(\vec{r}) = - \int d\vec{r}' \kappa(\vec{r}, \vec{r}') \nabla T(\vec{r}')$ should describe the linear response. However, for non-uniform heat driving, a correction has been noticed recently. An additional, non-Fourier term $\hat{J}_{\text{non-F}}(\vec{r})$ appears. This was found recently by Hua and Lindsay [1, 2]. Hints of this can be found in earlier literature. Boltzmann theory shows how this happens. The derivation given below assumes heat carried by phonons in insulators. Similar results are expected for heat carried by electrons in metals, and also for electrical conduction. The derivation includes time-dependent driving of phonon heat.

NON-LOCAL PEIERLS BOLTZMANN EQUATION

The phonon, or Peierls, Boltzmann equation [3, 4] (PBE), linearized for small deviations from equilibrium, says that the phonon distribution $N_Q(\vec{r}, t)$ evolves according to

$$\frac{dN_Q}{dt} = \left( \frac{dN_Q}{dt} \right)_{\text{drift}} + \left( \frac{dN_Q}{dt} \right)_{\text{coll}} + \left( \frac{dN_Q}{dt} \right)_{\text{ext}},$$

where

$$\left( \frac{dN_Q}{dt} \right)_{\text{drift}} = -v_Q \cdot \hat{\nabla} T N_Q,$$

and

$$\left( \frac{dN_Q}{dt} \right)_{\text{coll}} = - \sum_{Q'} R_{QQ'} \Delta N_{Q'}(\vec{r}, t),$$

and

$$\left( \frac{dN_Q}{dt} \right)_{\text{ext}} = \frac{1}{C(T_0)} \left( \frac{dN_Q}{dT} \right)_{T_0} P_Q(\vec{r}, t).$$

The symbol $Q = (\vec{q}, j)$ enumerates the $N = 3nN_{\text{cell}}$ eigenstates of the harmonic vibrational system. The scattering operator $R_{QQ'}$ is linearized for small deviations $\Delta N_Q$ from the local equilibrium distribution, a Bose-Einstein distribution $n_Q$ at the local temperature $T(\vec{r}, t)$: $P_Q(\vec{r}, t)$ is the rate per unit volume of energy input into mode $Q$, and $T_0$ is the background temperature. The specific heat $C(T_0)$ has units energy divided by temperature $\times$ volume, and $P_Q$ has units power per volume. The external power input $P_Q$ causes mode $Q$ to increase in energy per unit time by an amount which would increase its effective temperature by $d\Delta T_Q(\vec{r}, t)/dt = P_Q(\vec{r}, t)/C$. For simple driving, with $P_Q$ independent of $Q$, the modal temperature increase $\Delta T_Q$ is the same for all modes $Q$.

Non-local Boltzmann theories require a definition of local temperature; the one that works in Boltzmann theory is that the local energy density $u(\vec{r}, t)$ is $(1/V) \sum \omega_Q n_Q(T(\vec{r}, t))$. This means that there is no energy in the deviation $\Delta N_Q \equiv N_Q(\vec{r}, t) - n_Q(T(\vec{r}, t))$. The sum $(1/V) \sum \omega_Q \Delta N_Q = 0$ defines $T(\vec{r}, t)$.

SCATTERING AND TEMPERATURE

Each scattering event conserves phonon energy:

$$\sum_Q \omega_Q (d\Delta N_Q/dt)_{\text{scatt}} = 0,$$

whether linearized in $\Delta N_Q$ or not. In linear approximation, this is equivalent to the sum rule $\sum_Q \omega_Q R_{QQ'} = 0$. The operator $\hat{R}$ (where $R_{QQ'} = \langle Q | \hat{R} | Q' \rangle$) has a left null eigenvector $| \omega \rangle \hat{R} = 0$, where $\omega_Q = \langle \omega | Q \rangle$. The vector $| \cdot \rangle$ lies in the space of harmonic eigenstates. The states $| Q \rangle$ are a complete orthonormal basis. In the coordinate space enumerated by unit cell $\ell$ at $\hat{R}_\ell$, and atom number $n$, and Cartesian coordinate $i$,

$$| \ell ni \rangle = \frac{1}{\sqrt{N_{\text{cells}}}} e^{i\vec{q} \cdot \vec{R}_\ell} \hat{c}_Q(n, i),$$

where the polarization vector $\hat{c}_Q$ is normalized, $\sum_{n,i} | \hat{c}_Q(n, i) |^2 = 1$. But $\hat{R}$ is not symmetric. The corresponding null right eigenvector is $| n(n + 1) \omega \rangle$. This is equivalent to the statement that if the distribution $N_Q = n_Q(T(\vec{r}, t)) + \Delta N_Q(\vec{r}, t)$ consists of shifting the oc-
and 7 become
\[ \omega \]

The different Fourier components are not coupled, and are treated one at a time, as if \( |X(\vec{k}, t)\rangle = |X(\vec{k}, \omega)\rangle \exp[i(\vec{k} \cdot \vec{r} - \omega t)] \). The symbol \( \omega \) is the external frequency, not to be confused with \( \hat{\omega} \) which is the operator version of the phonon frequency \( \omega_Q \). Equations 6 and 7 become
\[
[\hat{\Omega} + i(\vec{k} \cdot \vec{v} - \omega t)] |\Phi\rangle = |A(\vec{k}, \omega)\rangle
\] (9)

\[
|A\rangle = \sqrt{\frac{n(n+1)}{k_B T^2}} \left[-i(\vec{k} \cdot \vec{v} - \omega t) \Delta T |\hbar\omega\rangle + \frac{\hbar\omega}{\sqrt{C}} |P\rangle \right]
\] (10)

Mode space has so far been described in \( Q \)-representation by harmonic eigenstates \( |Q\rangle \). It is convenient to also use the "relaxon"-representation \( |\alpha\rangle \) of eigenstates \( |\gamma\rangle \) of \( \hat{\Omega} \).

\[ \hat{\Omega}|\alpha\rangle = \gamma_\alpha |\alpha\rangle \] (11)

where
\[ \langle \alpha | \beta \rangle = \delta_{\alpha \beta} \text{ and } \sum_\alpha |\alpha\rangle \langle \alpha| = \mathbb{I} \] (12)

The eigenvalues \( \gamma_\alpha \) are relaxation rates, \( \gamma_\alpha = 1/\tau_\alpha \). In this basis, Eq. 9 has the form
\[
\sum_\beta \left[ \gamma_\alpha \delta_{\alpha \beta} + i(\vec{k} \cdot \vec{v}_\alpha - \omega \delta_{\alpha \beta}) \right] |\Phi\rangle = |A_\alpha\rangle,
\] (13)

where \( |\Phi\rangle = \langle \beta |\Phi\rangle \) and \( A_\alpha = \langle \alpha |A\rangle \). There are \( N \) modes \( Q \) \( (N = 3N_{\text{cells}}n_{\text{at}} \) where \( n_{\text{at}} \) is the number of atoms in the unit cell), and Eq. 13 gives \( N \) equations for the \( N \) unknown components \( |\Phi_\gamma\rangle \) of the deviation function. But there are two fields \( (|\Delta T\rangle \text{ and } |P\rangle) \) driving the distribution out of equilibrium, of which one (typically \( |\Delta T\rangle \)) is unknown. An extra equation is needed. That equation is the definition of local temperature.

There is one null eigenvector, \( |\alpha = 0\rangle \equiv |0\rangle \) with eigenvalue \( \gamma_0 = 0 \). The vectors \( |0\rangle \) and \( |0\rangle \) deviate only by factors \( |\hat{n}(n+1)|^{1/2} \) from the null left \( (|\hbar\omega\rangle \) and right \( |d\bar{n}|/d\bar{t}| = 0 \rangle\) eigenvectors of \( \bar{R} \). In \( Q \)-representation, the null eigenvector is
\[
|0\rangle = \sqrt{n(n+1)} \frac{\hbar\omega_Q}{\sqrt{CV k_B T^2}}
\] (14)

The factor \( 1/\sqrt{VC k_B T^2} \) normalizes the state, \( |0\rangle \langle 0| = 1 \). The definition of temperature takes the form
\[
\frac{1}{V} \sum_Q \hbar\omega_Q n_Q = 0 \quad \frac{1}{V} \sum_Q \hbar\omega_Q n_Q(n+1) = \frac{C k_B T^2}{V} \Phi_0 = 0.
\] (15)

This shows that there are actually only \( N - 1 \) unknown parts of \( |\Phi\rangle \), because the \( \alpha = 0 \) component, \( 0 |\Phi\rangle = \Phi_0 \) must be zero by the definition of local temperature.

Now we can rewrite the formula for \( |A\rangle \) using Eqs. 10 and 11
\[
|A\rangle = \frac{V}{C k_B T^2} \left[ -i(\vec{k} \cdot \vec{v} - \omega t) C \Delta T \langle \vec{k}, \omega \rangle + P(\vec{k}, \omega) \right] |0\rangle
\] (16)

where \( \langle Q | \hat{P} |Q'\rangle = Q_Q \delta_{QQ'} \). Now look at the \( \alpha = 0 \) component of Eq. 13
\[
i\vec{k} \cdot \sum_{\beta \neq 0} \vec{v}_{0\beta} \Phi_\beta = A_0
\] (17)
The left hand side of Eq. (17) is
\[
\langle 0 | \hat{\mathbf{k}} \cdot \hat{\mathbf{J}} \rangle = \sqrt{\frac{V}{Ck_BT^2}} \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}
\]
(18)
where \( \hat{\mathbf{J}}(\mathbf{k}, \omega) \) is the energy (or heat) current density,
\[
(1/V) \sum_Q \hbar \omega_Q \psi_Q[N_Q(\mathbf{k}, \omega) - n_Q(\mathbf{k}, \omega)].
\]
The right hand side of Eq. (17) is
\[
\langle 0 | A \rangle = \sqrt{\frac{V}{Ck_BT^2}} (i\omega C\Delta T + \hat{P}),
\]
(19)
where \( \hat{P} = \langle 0 | \hat{P} | 0 \rangle \), or
\[
\hat{P} \equiv \sum_Q C_Q P_Q \text{ and } C_Q = \frac{1}{V} \hbar \omega_Q \frac{dn_Q}{dT},
\]
(20)
and \( C = \sum_Q C_Q \) is the total specific heat. If \( P_Q \) is independent of \( Q \), then \( P_Q = \hat{P} \) for all modes \( Q \). Thus the \( \alpha = 0 \) part of the Boltzmann equation expresses energy conservation. In \( \langle \mathbf{r}, t \rangle = 0 \) part of the Boltzmann equation expresses energy conservation. In \( \langle \mathbf{r}, t \rangle = 0 \) case, \( \hat{\Gamma} = 0 \) and \( \lambda_m = 0 \), so \( S_{\alpha\beta} = \delta_{\alpha\beta} \) and the bulk solution \( \Phi_\alpha = \gamma_\alpha^{-1} A_\alpha \) is recovered.

THE SOLUTION

The method of solution is given by Hua and Lindsay [2]. A earlier version is in a paper by Cepellotti and Marzari [10]. Rewrite Eq. (13) by rescaling the distribution function \( \Phi_\alpha \) and driving term \( A_\alpha \):
\[
\Psi_\beta = \gamma_\beta^{1/2} \Phi_\beta \text{ and } B_\alpha = \gamma_\alpha^{-1/2} A_\alpha.
\]
(22)
Equation (13) then becomes \( [\hat{1} + i\hat{\Gamma}] \Psi = |B \rangle \), or
\[
\sum_\beta [\delta_{\alpha\beta} + i\Gamma_{\alpha\beta}] \Psi_\beta = B_\alpha
\]
\[
\Gamma_{\alpha\beta} = \gamma_\alpha^{-1/2} \gamma_\beta^{-1/2} - \gamma_\alpha^{-1} \omega \delta_{\alpha\beta}
\]
(23)
The matrix \( \hat{\Gamma} \) is real-symmetric, so it has real eigenvalues, \( \lambda_m \):
\[
\hat{\Gamma}(\mathbf{k}, \omega)|\langle m \rangle \rangle = \lambda_m(\mathbf{k}, \omega)|\langle m \rangle \rangle.
\]
(24)
In this basis, Eq. (23) is \( (1 + i\lambda_m) \Psi_m = B_m \), where \( \Psi_m = \langle m | \Psi \rangle \), etc. Then the distribution function in the relaxon basis (the eigenbasis of \( \hat{\Omega} \)) is
\[
\Psi_\alpha = \sum_\beta S_{\alpha\beta} B_\beta, \text{ or } \Phi_\alpha = \sum_\beta (\gamma_\alpha^{-1/2} S_{\alpha\beta} \gamma_\beta^{-1/2}) A_\beta,
\]
where \( \langle \alpha | \hat{S} | \beta \rangle = S_{\alpha\beta} = \sum_m \langle \alpha | m \rangle \frac{1}{1 + i\lambda_m(\mathbf{k}, \omega)} \langle m | \beta \rangle \).
(25)
This is the desired solution. In the spatially homogeneous \( (\mathbf{k} = 0) \) and static \( (\omega = 0) \) case, \( \hat{\Gamma} = 0 \) and \( \lambda_m = 0 \), so \( S_{\alpha\beta} = \delta_{\alpha\beta} \) and the bulk solution \( \Phi_\alpha = \gamma_\alpha^{-1} A_\alpha \) is recovered.

HEAT CURRENT

The operator \( \hat{\Omega} \) is positive if we exclude the null space. The operator \( \hat{S} = (1 + i\hat{\Gamma})^{-1} \) is defined in this “positive” or \( p \)-space. It is convenient to define another operator in the same \( p \)-space,
\[
\hat{W} = \hat{\Omega}^{-1/2} \hat{S} \hat{\Omega}^{-1/2}
\]
\[
W_{\alpha\beta} = \gamma_\alpha^{-1/2} S_{\alpha\beta} \gamma_\beta^{-1/2}
\]
(26)
The solution of the Boltzmann equation is then
\[
|\Phi \rangle = \hat{W} |A\rangle_p
\]
(27)
where \( |A\rangle_p \) is the part of the driving term that is orthogonal to \( |0\rangle \) (and thus lies in \( p \)-space),
\[
|A\rangle_p = \sqrt{\frac{V}{Ck_BT^2}} \left[-i\mathbf{k} \cdot \hat{\mathbf{v}} C\Delta T + (\hat{P} - \hat{P} \hat{\mathbf{1}})\right] |0\rangle.
\]
(28)
As required, the inner product \( \langle 0 | A \rangle_p \) vanishes, because it has a term proportional to \( \langle 0 | \hat{\mathbf{v}} | 0 \rangle \) which is zero because \( \hat{\mathbf{v}} \) is an odd operator, and a term proportional to \( \langle 0 | (\hat{P} - \hat{P} \hat{\mathbf{1}}) | 0 \rangle \) that is zero because \( \langle 0 | \hat{P} | 0 \rangle \equiv \hat{P} \). From \( |\Phi \rangle \) we get the heat current density \( \hat{J} \),
\[
\hat{J} = \sqrt{\frac{Ck_BT^2}{V}} \langle 0 | \hat{\mathbf{v}} \Phi \rangle = \hat{J}_F + \hat{J}_{\text{non-F}}.
\]
(29)
The “generalized Fourier” component \( \hat{J}_F \) is
\[
\hat{J}_F(\mathbf{k}, \omega) = -\kappa(\mathbf{k}, \omega) \cdot (i\mathbf{k}) C\Delta T(\mathbf{k}, \omega),
\]
(30)
\[
\kappa(\mathbf{k}, \omega) = C \langle 0 | \hat{\mathbf{v}} \hat{W}(\mathbf{k}, \omega) \hat{\mathbf{v}} | 0 \rangle.
\]
(31)
The “non-Fourier” term is
\[
\hat{J}_{\text{non-F}}(\mathbf{k}, \omega) = \langle 0 | \hat{v} \hat{W}(\mathbf{k}, \omega) (\hat{P}(\mathbf{k}, \omega) - \hat{P}(\mathbf{k}, \omega) \hat{\mathbf{1}}) | 0 \rangle.
\]
(32)
This extra, non-Fourier, component of the current was found by Hua et al. [3] in an RTA treatment. A version is in the paper by Mahan and Claro [11]. In their version, there was no external insertion \( P \) except via boundary conditions. It was rederived by Hua and Lindsay.
In a more complete treatment (not using RTA). Reference gives additional parts of the non-Fourier term that arise from boundary conditions, but solved only in RTA. Boundary terms do not appear here; the present derivation, like ref. assumes an infinite homogeneous sample.

In a d.c. situation (ω = 0), the insertion term \( \hat{P}(\vec{r}) \) should have a zero spatial average: \( P(\vec{k} = 0, \omega = 0) = 0 \). Otherwise, the sample experiences net heating or cooling. The spatially homogeneous (\( \vec{k} = 0 \) part of the “non-Fourier” current is zero. Also, when \( \vec{k} = 0 \) and \( \omega = 0, \int W(0,0) = \Omega^{-1} \) and the bulk static thermal conductivity is recovered,

\[
\kappa(\vec{k} = 0, \omega = 0) = C \langle 0 | \hat{\Omega} \hat{\Omega}^{-1} | 0 \rangle.
\]

### THERMAL DISTRIBUTOR

The local temperature distribution \( T(\vec{r}, t) \) can be found from energy conservation (Eq. (21)),

\[
\Delta T(\vec{k}, \omega) = \frac{1}{i\omega C} \left[ i\vec{k} \cdot \left( \hat{J}_F(\vec{k}, \omega) + \hat{J}_{\text{non}-F}(\vec{k}, \omega) \right) - \hat{P}(\vec{k}, \omega) \right].
\]

If \( P_Q(\vec{k}, \omega) \) is independent of \( Q \) (i.e., \( \hat{P} = \hat{P} \)), the non-Fourier current is zero, and the local temperature variation is given by a simple nonlocal response function, the “thermal distributor” \( \Theta(\vec{k}, \omega) \),

\[
\Delta T(\vec{k}, \omega) = \Theta(\vec{k}, \omega) \hat{P}(\vec{k}, \omega)
\]

where

\[
\Theta(\vec{k}, \omega) = \frac{1}{\vec{k} \cdot \kappa(\vec{k}, \omega) \cdot \vec{k} - i\omega C}
\]

This is Eq. 38 of ref. The function \( \Theta \) was defined in ref. The name “thermal distributor,” has been changed from the previous name “thermal susceptibility,” and a factor of \( C \) has been removed from the definition. When \( \hat{P} \neq \hat{P} \), there is another term,

\[
\Delta T(\vec{k}, \omega) = \Theta(\vec{k}, \omega) \hat{P}(\vec{k}, \omega) - \frac{i\vec{k} \cdot \hat{J}_{\text{non}-F}(\vec{k}, \omega)}{\vec{k} \cdot \kappa(\vec{k}, \omega) \cdot \vec{k} - i\omega C}
\]

Griffin makes an interesting argument that may be related to thermal distributors. Guyer and Krumhansl noticed that Griffin’s argument is related to the mean-field method relating non-interacting to interacting electrical susceptibility.

### APPENDIX: TERMINOLOGY

Various names are given to the operator \(-\vec{v}_Q \cdot \nabla \vec{r}\): (a) “drift operator”, (b) “advection operator”, (c) “convection operator”, or (d) “diffusion operator”. Sometimes the combination \( \partial / \partial t + \vec{v}_Q \cdot \nabla \vec{r} \) is called the “drifting operator”. The process these words are describing is that the occupancy \( N_Q(\vec{r}, t + \Delta t) \), in a completely ballistic system, is the same as \( N_Q(\vec{r} - \vec{v}_Q \Delta t, t) \), so that

\[
\frac{dN_Q}{dt} = \lim_{\Delta t \to 0} \left[ \frac{N_Q(\vec{r}, t + \Delta t) - N_Q(\vec{r}, t)}{\Delta t} \right]_{\text{ballistic}}
\]

The term I use, “drift operator”, makes sense; “diffusion operator” does not.

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