Ballistic-Diffusive Heat Conduction at Nanoscale: GENERIC Approach

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Abstract

Heat conduction in nanosize systems has to be studied in settings involving microscopic details that are not seen in the classical Fourier theory. G. Chen has suggested (Chen, Phys.Rew.Lett 86,2297 (2001)) a combination of the Cattaneo setting in which the velocity of the heat propagation is finite and the kinetic theory setting in which phonons are seen as heat carriers. In this Letter we show that if the Cattaneo and the kinetic theories are combined in a way that preserves the structure expressing their compatibility with thermodynamics (GENERIC structure) then both the Cattaneo and the kinetic equations become modified. The modified Cattaneo equations involve the term introduced by Chen and, in addition, new terms that are nonlinear in quantities that disappear at equilibrium. The kinetic equation is modified by new terms involving gradients of the heat flux and the local temperature.

1   Introduction

The thermodynamic internal energy is, from the microscopic point of view, the energy of the microscopic particles composing the macroscopic system under consideration. If our interest is focused on heat conduction then a convenient

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way of viewing the microscopic motion on a mesoscopic level is to regard the macroscopic system under consideration as a gas composed of phonons. The phonons become heat carriers. Taking this viewpoint, the one-phonon distribution function appears then as a natural state variable and the Boltzmann-like kinetic equation as a natural equation governing its time evolution. In many situations this mesoscopic description can be reduced to the Cattaneo description [1] in which states are characterized by two fields: the field of energy density and the field of heat flux. The Cattaneo description can be then still reduced in many situations to the standard Fourier description in which the state variable consists of only one scalar field, namely the the field of the energy density, and the time evolution equation is the classical diffusion equation.

An example of physical systems for which the reductions are not applicable are very small systems of the size that is comparable with the mean free path of the phonons. The heat conduction taking place in such systems appears to be different from the classical Fourier heat conduction. Chen [2] has suggested to regard the transport of heat in nanosize systems as a combination of the heat transport described by a kinetic equation (called a ballistic transport) and the heat transport governed by the Cattaneo equation. The state variables used by Chen are thus the fields of the energy density and the heat flux, describing the overall Cattaneo heat conduction, and the one-phonon distribution function describing the superposed on it ballistic component. The governing equations derived in Chen's paper are modified Cattaneo equations and a Boltzmann-like kinetic equation.

Our objective in this Letter is to work out a two-level description of heat conduction in the framework of GENERIC [3]. As a result, we obtain a set of governing equations that are guaranteed to be compatible with thermodynamics. Both the Cattaneo and the kinetic equations are modified by the appearance of new terms in which their coupling is expressed. Among the new terms appearing in the modified Cattaneo equations we recover the term introduced by Chen [2]. The other terms are quadratic and higher order in quantities that disappear at equilibrium. The kinetic equation is modified by terms involving gradients of the heat flux and the local temperature. These new terms, as well as the new terms appearing in the Cattaneo equations, become thus important only in the situations far from equilibrium. Certain symmetry in the coupling of the Cattaneo and the kinetic equations is to be expected already on the ground of the requirement that in the linear regime the Onsager-Casimir relations hold. We recall that the GENERIC structure is in fact a nonlinear extension of the Onsager-Casimir symmetry [4]. We show in this paper that it is not possible to couple the Cattaneo equations to the kinetic equation and leave the kinetic equation unchanged without violating the compatibility with thermodynamics.

This Letter is organized as follows: In Sections 2 and 3 we review the GENERIC formulations of the Cattaneo and the ballistic heat conduction. The combined formulation, the main new result of this Letter, is presented in Section 4.

2 Cattaneo description

In this section we recall results presented in [5]. We shall formulate the Cattaneo heat conduction in the GENERIC form. We choose the state variables to be:

$$(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r})), \tag{1}$$

where $s(\boldsymbol{r})$ is the field of the entropy density (per unit volume) and $\boldsymbol{w}(\boldsymbol{r})$ is the vector field conjugate (in the sense explained below) of the entropy flux. The kinematics of the state variables (1) is expressed in the Poisson bracket (see [5])

$$\begin{aligned}
\{A, B\}^{Cattaneo} &= \int d\boldsymbol{r} [s(\partial_\alpha A_s B_{w_\alpha} - \partial_\alpha B_s A_{w_\alpha}) \\
&\quad + w_\alpha(\partial_\gamma A_{w_\alpha} B_{w_\gamma} - \partial_\alpha B_{w_\alpha} A_{w_\gamma})]
\end{aligned} \tag{2}$$

where A and B are sufficiently regular real valued functions of the state variables (1), $A_{s(\boldsymbol{r})} := \frac{\delta A}{\delta s(\boldsymbol{r})}$ is the Volterra functional derivative, similarly $A_{w_\alpha(\boldsymbol{r})} := \frac{\delta A}{\delta w_\alpha(\boldsymbol{r})}$, and $\partial_\alpha := \frac{\partial}{\partial r_\alpha}$. We use hereafter the summation convention.

The state variables (1) evolve in time. The vector field generating their time evolution is a sum of a nondissipative part and a dissipative part. We shall discuss them one after the other. First, we turn our attention to the nondissipative part. According to [3], it is the Hamiltonian time evolution generated by the overall energy $E(s, \boldsymbol{w}) = \int d\boldsymbol{r} e(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$ and the kinematics (2). This means that the equations governing the nondissipative time evolution are obtained from the equations $\frac{dA}{dt} = \{A, E\}^{Cattaneo}$ that is required to hold for all A. If written explicitly, we arrive at

$$\begin{aligned}
\left(\frac{\partial s}{\partial t}\right)_{nondissip} &= -\partial_\gamma(s E_{w_\gamma}) \\
\left(\frac{\partial w_\alpha}{\partial t}\right)_{nondissip} &= -\partial_\gamma(w_\alpha E_{w_\gamma}) - w_\gamma \partial_\alpha E_{w_\gamma} - s\partial_\alpha E_s
\end{aligned} \tag{3}$$

From the first equation in (3) we see that $s E_{\boldsymbol{w}}$ has the physical interpretation of the entropy flux.

In order to introduce the dissipative part of the time evolution we pass first to the state variables

$$(e(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r})), \tag{4}$$

where $e(\boldsymbol{r})$ is the energy density. The state variables (1) and (4) are in a one-to-one relation since the entropy $S(e, \boldsymbol{w}) = \int d\boldsymbol{r} s(e(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$ is required to be a concave function of $e(\boldsymbol{r})$ and $\boldsymbol{w}(\boldsymbol{r})$, and, in addition, $S_{e(\boldsymbol{r})}$, having the physical interpretation of the inverse of the local temperature, is required to be positive for all $\boldsymbol{r}$. To guarantee that the entropy S does not decrease and the energy E is conserved in the course of the time evolution, we introduce the dissipative part of the time evolution in the form

$$\left(\frac{\partial e}{\partial t}\right)_{dissip} = 0$$

$$\left(\frac{\partial w_\alpha}{\partial t}\right)_{dissip} = \frac{\delta \Xi}{\delta S_{w_\alpha}} \tag{5}$$

where $\Xi(S_{\boldsymbol{w}})$ is a real valued function of $S_{\boldsymbol{w}(r)} := \frac{\delta S}{\delta w(r)}$ called a dissipation potential. In order that the entropy S does not decrease and the energy E the dissipation potential has to satisfy four conditions: (i) $\Xi(0) = 0$, (ii) Ξ reaches its minimum at 0, and (iii) Ξ is convex in a neighborhood of 0, and (iv) Ξ is degenerate so that the energy remains unchanged during the time evolution. As an example, we can choose Ξ as

$$\Xi(S_{\boldsymbol{w}}) = \int d\boldsymbol{r} 1/2 \Lambda S_{w_\gamma} S_{w_\gamma}, \tag{6}$$

where $\Lambda > 0$ is a phenomenological kinetic coefficient. The particular example (6) represents a restriction to states for which $S_{\boldsymbol{w}}$ is not large (we are neglecting all therm of the fourth and the higher order in $S_{\boldsymbol{w}}$) and thus, from the physical point of view, to states that are not too far from equilibrium states at which $S_{\boldsymbol{w}} = 0$). With the dissipation potential (6) the right hand side of the second equation in (5) equals $-\Lambda S_{w_\alpha}$.

If we now add the nondissipative and dissipative time evolutions we obtain (we recall that $E_s = (S_e)^{-1}$ and $E_{w_\alpha} = -(S_e)^{-1} S_{w_\alpha}$)

$$\begin{aligned}
\frac{\partial s}{\partial t} &= -\partial_\gamma(s E_{w_\gamma}) + \Lambda(E_s)^{-2} E_{w_\gamma} E_{w_\gamma} \\
\frac{\partial w_\alpha}{\partial t} &= -\partial_\gamma(w_\alpha E_{w_\gamma}) - w_\gamma \partial_\alpha E_{w_\gamma} - s \partial_\alpha E_s - \Lambda(E_s)^{-1} E_{w_\alpha}
\end{aligned} \tag{7}$$

for the state variables (1) and

$$\begin{aligned}
\frac{\partial e}{\partial t} &= -\partial_\gamma \left[S_e^{-2} \left(-s S_{w_\gamma} + w_\alpha S_{w_\alpha} S_{w_\gamma} \right) \right] \\
\frac{\partial w_\alpha}{\partial t} &= -\partial_\gamma \left(-S_e^{-1} w_\alpha S_{w_\gamma} \right) + w_\gamma \partial_\alpha (S_e^{-1} S_{w_\gamma}) - s \partial_\alpha (S_e)^{-1} + \Lambda S_{w_\alpha}
\end{aligned} \tag{8}$$

for the state variables (4). Equation (7) or Eq.(8) is a family of equations parametrized by the energy $E(s, \boldsymbol{w})$, the entropy $S(e, \boldsymbol{w})$, and the kinetic coefficient $\Lambda > 0$. In this Letter we shall leave these functions unspecified.

We make now three observations about solutions to Eq.(7) or (8):

$$(i) \quad \frac{dE}{dt} = 0$$

$$(ii) \quad \frac{dS}{dt} > 0$$

$$(iii) \text{ the solutions approach equilibrium states as } t \to \infty \tag{9}$$

The property (i) follows directly from the first equation in (8) and from $E = \int d\boldsymbol{r} e(\boldsymbol{r})$. The property (ii) follows from the first equation in (7) (note that

4

the entropy production, i.e. the second term on the right hand side of the first equation in (7), is positive because Λ has been chosen to be positive). The property (iii) follows from the observation that the function $\Phi(s, \boldsymbol{w}, T) := -S(e, \boldsymbol{w}) + 1/T \int d\boldsymbol{r} e(\boldsymbol{r})$, where T is a constant having the physical interpretation of the equilibrium temperature, plays the role of the Lyapunov function (i.e. Φ is convex and $d\Phi/dt < 0$) and equilibrium states are the states at which Φ reaches its minima.

In addition, we make an observation about the relation between Eq.(8) and the governing equations of the Fourier heat conduction. We note that if the nonlinear terms in (8) (i.e. the second term on the right hand side of the first equation in (8) and the first two terms on the right hand side of the second equation in (8)) are neglected then equations (8) become the standard governing equations of the Cattaneo heat conduction. The first equation is the local conservation law for the energy density and the second equation is the Cattaneo equation. If we assume that $\boldsymbol{w}$ evolves faster than e then we can put $\frac{\partial \boldsymbol{w}}{\partial t} \sim 0$ and the second equation in (8) becomes the Fourier constitutive relation. With this constitutive relation the first equation in (8) (with the nonlinear term, i.e. the second term on its right hand side, missing) becomes the standard heat diffusion equation.

3 Kinetic theory description

In this section we take a more microscopic viewpoint of heat conduction. We regard the system under consideration as a phonon gas. The state variable is chosen to be one-phonon distribution function $f(\boldsymbol{r}, \boldsymbol{p})$, where $\boldsymbol{p}$ is the momentum of one phonon. The kinematics of f is expressed [3] in the Poisson bracket

$$\{A, B\}^{kin.th.} = \int d\boldsymbol{r} \int d\boldsymbol{p} f \left(\partial_\gamma (A_f) \frac{\partial}{\partial p_\gamma} (B_f) - \partial_\gamma (B_f) \frac{\partial}{\partial p_\gamma} (A_f) \right), \quad (10)$$

A and B are sufficiently regular real valued functions of $f(\boldsymbol{r}, \boldsymbol{p})$. The time evolution equation corresponding to (9) (i.e. again, the equation $\frac{dA}{dt} = \{A, E\}^{Cattaneo}$ that is required to hold for all A; the function $E(f)$ denotes the energy) is

$$\left(\frac{\partial f}{\partial t} \right)_{nondissip} = -\partial_\gamma \left(f \frac{\partial}{\partial p_\gamma} E_f \right) + \frac{\partial}{\partial p_\gamma} (f \partial_\gamma E_f) \quad (11)$$

Since we want to have again a time evolution for which (9) holds, we shall choose the dissipative part of the time evolution in the same way as in (5), namely, we choose

$$\left(\frac{\partial f}{\partial t} \right)_{dissip} = \frac{\delta \Xi}{\delta S_f} \quad (12)$$

Specific forms of the dissipation potentials $\Xi(S_f)$ for which the right hand side of (12) becomes the Boltzmann collision operator, or the BGK model of the Boltzmann collision operator considered in [2], can be found in [4]. In this

Letter we shall leave the potential Ξ unspecified. We shall only require that Ξ satisfies the four conditions listed after Eq.(5).

The complete kinetic equation governing the time evolution of the distribution function $f(\boldsymbol{r}, \boldsymbol{p})$ is thus the sum of (11) and (12):

$$\frac{\partial f}{\partial t} = -\partial_\gamma \left(f \frac{\partial}{\partial p_\gamma} E_f \right) + \frac{\partial}{\partial p_\gamma} \left(f \partial_\gamma E_f \right) + \frac{\delta \Xi}{\delta S_f} \tag{13}$$

As in the previous section, we leave at this point the energy E and the entropy S unspecified. The only thing that we need is that the entropy $S(f)$ is such that it does not change in time if the time evolution of f is governed by (11). In other words, $S(f)$ has to satisfy $\{A, S\}^{kin.th} = 0$ for all A. It is well known, and easily verifiable by direct calculations, that any function of f having the form $\int d\boldsymbol{r} \int d\boldsymbol{p} \varphi(f(\boldsymbol{r}, \boldsymbol{p}))$, where $\varphi(f(\boldsymbol{r}, \boldsymbol{p})$ is a sufficiently regular pointwise function of $f(\boldsymbol{r}, \boldsymbol{p})$ has this property. Note that the entropy (14) introduced below is an example of such entropy.

Since both Eq.(7) (or Eq.(8)) and Eq.(13) share the same structure (the GENERIC structure), they also share the properties (9) of their solutions.

4   Combined description

Following Chen [2] we now want to describe the heat conduction in an extended Cattaneo setting in which, in addition to the state variables used in the Cattaneo theory, the one-phonon distribution function serves as an additional state variable characterizing the microstructure. We shall now make such extension in a way that preserves the GENERIC structure of both the Cattaneo and the kinetic equations. We shall follow the general method presented in [6].

In order to combine the Cattaneo and the kinetic theory formulations of heat conduction, we have to know first how are the Cattaneo state variables $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$ expressed in terms of the one-phonon distribution function $f(\boldsymbol{r}, \boldsymbol{p})$. From statistical mechanics of phonons [7] we know that the part of the total entropy that depends on $f(\boldsymbol{r}, \boldsymbol{p})$, we shall call it a ballistic part and denote it by the symbol S_b, is given by (we put the Boltzmann constant equal to one)

$$S_b(f) = -\int d\boldsymbol{r} \int d\boldsymbol{p} \left[f(\boldsymbol{r}, \boldsymbol{p}) \ln f(\boldsymbol{r}, \boldsymbol{p}) - (1 + f(\boldsymbol{r}, \boldsymbol{p})) \ln(1 + f(\boldsymbol{r}, \boldsymbol{p})) \right] \tag{14}$$

and consequently the ballistic part $s_b(\boldsymbol{r})$ of the local entropy is $s_b(\boldsymbol{r}) = -\int d\boldsymbol{p} [f(\boldsymbol{r}, \boldsymbol{p}) \ln f(\boldsymbol{r}, \boldsymbol{p}) - (1 + f(\boldsymbol{r}, \boldsymbol{p})) \ln(1 + f(\boldsymbol{r}, \boldsymbol{p}))]$. The expression for $\boldsymbol{w}$ follows directly from the physical interpretation of $\boldsymbol{p}$ (the phonon momentum),

$$\boldsymbol{w}(\boldsymbol{r}) = \int d\boldsymbol{p} \, \boldsymbol{p} f(\boldsymbol{r}, \boldsymbol{p}) \tag{15}$$

We introduce new state variable $(\widehat{s}(\boldsymbol{r}), \widehat{\boldsymbol{w}}(\boldsymbol{r}), \widehat{f}(\boldsymbol{r}, \boldsymbol{p}))$ by

$$\widehat{s}(\boldsymbol{r}) = s(\boldsymbol{r}) - \int d\boldsymbol{p} [f \ln f - (1 + f) \ln(1 + f)]$$

$$\widehat{\boldsymbol{w}}(\boldsymbol{r}) \quad = \quad \boldsymbol{w}(\boldsymbol{r}) + \int d\boldsymbol{p}\, \boldsymbol{p} f$$

$$\widehat{f}(\boldsymbol{r},\boldsymbol{p}) \quad = \quad f(\boldsymbol{r},\boldsymbol{p}) \tag{16}$$

The state variables $(\widehat{s}(\boldsymbol{r}), \widehat{\boldsymbol{w}}(\boldsymbol{r}))$ describe now the overall Cattaneo (called "diffusive" in [2]) heat conduction and $\widehat{f}(\boldsymbol{r},\boldsymbol{p})$ the superposed on it ballistic component. The distribution function $\widehat{f}$ corresponds to f_b in [2]. The first line in (16) follows from (14) and from the fact that the total entropy in the Cattaneo theory is given by $S = \int d\boldsymbol{r}\, s(\boldsymbol{r})$. The second line follows directly from (15). We note that the transformation $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}), f(\boldsymbol{r},\boldsymbol{p})) \to (\widehat{s}(\boldsymbol{r}), \widehat{\boldsymbol{w}}(\boldsymbol{r}), \widehat{f}(\boldsymbol{r},\boldsymbol{p}))$ is one-to-one.

The Poisson bracket expressing the kinematics of $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}), f(\boldsymbol{r},\boldsymbol{p}))$ is just a sum of the Poisson brackets (2) and (10) because the distribution function f is completely decoupled from the Cattaneo fields $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$. It is the transformation (16) where the coupling is introduced. Since (16) is a one-to-one transformation, it carries a Poisson bracket into another Poisson bracket. We can thus derive the Poisson bracket expressing the kinematics of $(\widehat{s}(\boldsymbol{r}), \widehat{\boldsymbol{w}}(\boldsymbol{r}), \widehat{f}(\boldsymbol{r},\boldsymbol{p}))$ by applying the transformation (16) to the sum of the Poisson brackets (2) and (10). After straightforward calculations (we use $A_s = A_{\widehat{s}}$; $A_{\boldsymbol{w}} = A_{\widehat{\boldsymbol{w}}}$; $A_f = A_{\widehat{f}} + \ln\left(\frac{f}{(1+f)}\right) A_{\widehat{s}} + p_\gamma A_{\widehat{\boldsymbol{w}}_\gamma}$) we arrive at (to simplify the notation we omit hereafter the hat; this means that hereafter $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$ describe the overall heat conduction and $f(\boldsymbol{r},\boldsymbol{p})$ the superposed on it microstructure)

$$\begin{aligned}
\{A, B\} \quad = \quad & \{A, B\}^{Cattaneo} + \{A, B\}^{kin.th.} \\
& + \int d\boldsymbol{r} \int d\boldsymbol{p}(f \ln f - (1+f)\ln(1+f)) \left[\frac{\partial}{\partial p_\alpha}(A_f)\partial_\alpha(B_s) \right. \\
& \left. - \frac{\partial}{\partial p_\alpha}(B_f)\partial_\alpha(A_s) \right] + \int d\boldsymbol{r} \int d\boldsymbol{p} f \left[\partial_\alpha(A_f)B_{w_\alpha} - \partial_\alpha(B_f)A_{w_\alpha} \right] \\
& - \int d\boldsymbol{r} \int d\boldsymbol{p} f p_\gamma \left[\frac{\partial}{\partial p_\alpha}(A_f)\partial_\alpha(B_{w_\gamma}) - \frac{\partial}{\partial p_\alpha}(B_f)\partial_\alpha(A_{w_\gamma}) \right] \tag{17}
\end{aligned}$$

If we now write down the time evolution equations corresponding to (17) and add to their right hand sides the dissipative parts (see Eqs.(5),(12)) we arrive at the following time evolution equations

$$\frac{\partial s}{\partial t} \quad = \quad -\partial_\alpha J_\alpha^{(s)} + \sigma$$

$$\frac{\partial w_\alpha}{\partial t} \quad = \quad -\partial_\gamma \left(w_\alpha E_{w_\gamma} + \int d\boldsymbol{p} f p_\alpha \frac{\partial}{\partial p_\gamma}(E_f) \right)$$

$$- w_\gamma \partial_\alpha(E_{w_\gamma}) - s\partial_\alpha(E_s) - \int d\boldsymbol{p} f \partial_\alpha(E_f) + \frac{\delta \Xi}{\delta(-E_s^{-1} E_{w_\alpha})}$$

$$\frac{\partial f}{\partial t} \quad = \quad -\partial_\alpha \left(f \frac{\partial}{\partial p_\alpha}(E_f) + f E_{w_\alpha} \right)$$

$$+ \frac{\partial}{\partial p_\alpha} \left(f \partial_\alpha(E_f) + f p_\gamma \partial_\alpha(E_{w_\gamma}) - (f \ln f - (1+f)\ln(1+f))\partial_\alpha(E_s) \right)$$

$$+\frac{\delta\Xi}{\delta(-E_s^{-1}E_f)} \tag{18}$$

where the entropy flux $\boldsymbol{J}^{(s)}$ is given by

$$J_\alpha^{(s)} = sE_{w_\alpha} - \int d\boldsymbol{p}(f\ln f - (1+f)\ln(1+f))\frac{\partial}{\partial p_\alpha}(E_f) \tag{19}$$

and the entropy production σ by

$$\sigma = (-E_s^{-1}E_{w_\gamma})\frac{\delta\Xi}{\delta(-E_s^{-1}E_{w_\gamma})} + \int d\boldsymbol{p}(-E_s^{-1}E_f)\frac{\delta\Xi}{\delta(-E_s^{-1}E_f)} \tag{20}$$

In terms of the state variables $(e(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}), f(\boldsymbol{r},\boldsymbol{p}))$, the governing equations (18) become (we use $\frac{\partial e}{\partial t} = E_s\frac{\partial s}{\partial t} + E_{w_\gamma}\frac{\partial w_\gamma}{\partial t} + \int d\boldsymbol{p}E_f\frac{\partial f}{\partial t}$ and $E_s = (S_e)^{-1}$, $E_{w_\alpha} = -(S_e)^{-1}$, $E_f = -(S_e)^{-1}S_f$)

$$\frac{\partial e}{\partial t} = -\partial_\gamma J_\gamma^{(e)}$$

$$\frac{\partial w_\alpha}{\partial t} = -\partial_\gamma\left(-S_e^{-1}w_\alpha S_{w_\gamma} + \int d\boldsymbol{p}fp_\alpha\frac{\partial}{\partial p_\gamma}(-S_e^{-1}S_f)\right)$$

$$\qquad -w_\gamma\partial_\alpha(-S_e^{-1}S_{w_\gamma}) - \int d\boldsymbol{p}f\partial_\alpha(-S_e^{-1}S_f) - s\partial_\alpha(S_e^{-1}) + \frac{\delta\Xi}{\delta S_{w_\alpha}}$$

$$\frac{\partial f}{\partial t} = -\partial_\alpha\left(f\frac{\partial}{\partial p_\alpha}(-S_e^{-1}S_f) - fS_e^{-1}S_{w_\alpha}\right)$$

$$\qquad +\frac{\partial}{\partial p_\alpha}\left(f\partial_\alpha(-S_e^{-1}S_f) + fp_\gamma\partial_\alpha(-S_e^{-1}S_{w_\gamma})\right.$$

$$\qquad \left.-(f\ln f - (1+f)\ln(1+f))\partial_\alpha(S_e^{-1})\right) + \frac{\delta\Xi}{\delta S_f} \tag{21}$$

where the energy flux $\boldsymbol{J}^{(e)}$ is given by

$$J_\gamma^{(e)} = S_e^{-2}\left(-sS_{w_\gamma} + \int d\boldsymbol{p}(f\ln f - (1+f)\ln(1+f))\frac{\partial}{\partial p_\gamma}(S_f)\right.$$

$$\qquad -\int d\boldsymbol{p}S_f\frac{\partial}{\partial p_\gamma}(fS_f) + S_{w_\gamma}\int d\boldsymbol{p}fS_f$$

$$\qquad \left.+S_{w_\alpha}\int d\boldsymbol{p}fp_\alpha\frac{\partial}{\partial p_\gamma}(S_f) + w_\alpha S_{w_\alpha}S_{w_\gamma}\right) \tag{22}$$

Equations (18) or (21) are families of the time evolution equations describing heat conduction in a combined Cattaneo and the kinetic theory settings. The families are parametrized by three potentials: energy $E(s, \boldsymbol{w}, f)$, entropy $S(s, \boldsymbol{w}, f)$, and the dissipation potential $\Xi(S_{\boldsymbol{w}}, S_f)$. Independently of the choice of these three potentials (except for the general requirements that S is concave and $\{A, S\} = 0$ for all A, and Ξ satisfies the four properties listed after Eq.(5)), the governing equations possess the GENERIC structure and consequently their

8

solutions have the properties (9). In other words, independently of the choice of E, S, Ξ, the families of the time evolution equations (18) or (21) are compatible with thermodynamics. We note that the ballistic phonons become equilibrated by interactions with the walls surrounding the system under consideration. Below, we shall compare Eqs.(18), (21) with the governing equations introduced by Chen in [2] and make some additional observations.

Details of solutions of (18) or (21) depend, of course, on the specific choice of the three potentials E, S, Ξ. The only specification that we shall make in this Letter concerns the ballistic parts of the entropy and the energy. As for the entropy, we have already specified it in (14). Statistical mechanics of phonons [7] provides also an expression for the ballistic part E_b of the energy.

$$E_b(f) = \nu \int d\boldsymbol{r} \int d\boldsymbol{p} |\boldsymbol{p}| f(\boldsymbol{r}, \boldsymbol{p}) \qquad (23)$$

where ν is the phonon velocity (a constant scalar). We shall assume below that the total energy and the total entropy are sums of the ballistic parts specified in (14) and (20) and Cattaneo parts, depending only on the Cattaneo fields $(s(\boldsymbol{r}), \boldsymbol{w}(\boldsymbol{r}))$. We leave the Cattaneo parts unspecified. With this assumption, we are now in position to make additional observations about Eqs. (18),(21) and about their solutions.

In order to see more clearly the physical meaning of the terms appearing in the kinetic equation (i.e. the third equation in (18) or (21)), we note that the nondissipative part of the kinetic equation can be seen as being the Liouville (continuity) equation corresponding to the ordinary differential equations

$$\left(\frac{dr_\alpha}{dt}\right)_{nondissip} = \nu\frac{p_\alpha}{|\boldsymbol{p}|} + E_{w_\alpha}$$

$$\left(\frac{dp_\alpha}{dt}\right)_{nondissip} = p_\gamma\partial_\alpha E_{w_\gamma} - \left(\ln f - \frac{1+f}{f}\ln(1+f)\right)\partial_\alpha E_s \qquad (24)$$

governing the time evolution of one phonon. Indeed, we verify easily that the continuity equation corresponding to (24) is the nondissipative part of the kinetic equation. The three terms in which the phonon time evolution is coupled to the Cattaneo time evolution (namely the second term on the right hand side of the first equation in (24) and both terms on the right hand side of the second equation in (24)) are absent in Chen's governing equations. The presence of E_{w_α} in the first equation in (21) expresses the fact that the ballistic phonons represent a part of the structure that is superposed on the Cattaneo fields. The momentum $\boldsymbol{p}$ of the ballistic phonons is the momentum in the coordinate system moving with the velocity associated with the Cattaneo heat conduction. The two terms on the right hand side of the second equation in (24) represent forces on phonons arising due to the inhomogeneity of the Cattaneo fields.

Now we turn our attention to the modified Cattaneo equations (i.e. to the first two equations in (18) or (21)). First, we note that the entropy production σ is indeed positive due to the properties of the dissipation potential listed after

Eq.(5). Next, we note that the energy flux (22) can be written as

$$
\begin{aligned}
J_\gamma^{(e)} &= (S_e)^{-1} J_\gamma^{(s)} \\
&\quad -(S_e)^{-2} \left(\int d\boldsymbol{p} S_f \frac{\partial}{\partial p_\gamma}(f S_f) + S_{w_\gamma} \int d\boldsymbol{p} f S_f \right. \\
&\quad \left. + S_{w_\alpha} \int d\boldsymbol{p} f p_\alpha \frac{\partial}{\partial p_\gamma}(S_f) + w_\alpha S_{w_\alpha} S_{w_\gamma} \right)
\end{aligned}
\tag{25}
$$

The first line in Eq.(25) is the classical relation between the entropy flux and the energy flux. The first term on the right hand side of (25) is the heat flux introduced in [2]. As seen in (19), it is a sum of two terms. The first term represents the energy flux appearing in the classical Cattaneo theory. The second term is the energy flux, introduced by Chen, that adds to the classical Cattaneo heat flux due to the coupling with the ballistic heat conduction. The remaining four terms appearing in the heat flux of our governing equations are absent in Chen's theory. They arise in our analysis as a consequence of the requirement of the GENERIC structure (the requirement of the compatibility with thermodynamics). We note that they are quadratic or higher order in derivatives of S with respect to f or $\boldsymbol{w}$. Since these derivatives equal zero at equilibrium, the four new terms become important only in the situations far from equilibrium.

Our final observation is that Eq.(25) can also be written as

$$
J_\gamma^{(e)} = (S_e)^{-1} \widehat{J^{(s)}}_\gamma
\tag{26}
$$

where the modified entropy flux $\widehat{\boldsymbol{J}^{(s)}}$ is given by

$$
\begin{aligned}
\widehat{J^{(s)}}_\gamma &= J_\gamma^{(s)} \\
&\quad -(S_e)^{-1} \left(\int d\boldsymbol{p} S_f \frac{\partial}{\partial p_\gamma}(f S_f) + S_{w_\gamma} \int d\boldsymbol{p} f S_f \right. \\
&\quad \left. + S_{w_\alpha} \int d\boldsymbol{p} f p_\alpha \frac{\partial}{\partial p_\gamma}(S_f) + w_\alpha S_{w_\alpha} S_{w_\gamma} \right)
\end{aligned}
\tag{27}
$$

The four new terms added in Eq.(25) to the heat flux are seen in Eqs.(26),(27) as new terms modifying the entropy flux.

5   Concluding remarks

The requirement that the combined Cattaneo and ballistic heat conduction possess the GENERIC structure (in other words, the requirement that the combined Cattaneo and ballistic heat conduction is compatible with thermodynamics) brings new coupling terms into the governing equations. The ballistic phonons are advected with the Cattaneo heat flux and subjected to forces that are proportional to the gradients of the Cattaneo fields. The Cattaneo equations are

modified by the appearance of additional terms in the heat flux (or alternatively in the entropy flux). One of the new terms, namely the one that appears also in Chen's theory, is the additional energy flux (or alternatively the additional entropy flux) that arises due to the ballistic heat conduction. The remaining four terms in the new heat flux (or the new entropy flux) are quadratic or higher order in the quantities that disappear at equilibrium. They become therefore important only far from equilibrium. Since the ballistic heat conduction is a process taking place far from equilibrium, the modifications of both the Cattaneo and the kinetic equations introduced in this paper are important for its theoretical description.

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