

Temperature in nonequilibrium states and non-Fourier heat conduction

Yuan Dong (董源), Bing-Yang Cao (曹炳阳), and Zeng-Yuan Guo (过增元)*

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China

(Received 11 December 2012; published 22 March 2013)

Macroscopic models beyond Fourier's law for fast-transient heating and heat transport in nanosystems have been proposed. Consequently, some basic quantities such as entropy and temperature need to be modified. From the viewpoint of the thermomass theory, we show that in nonequilibrium systems where heat conduction occurs, the static pressure of thermomass is lower than the total pressure, corresponding to a nonequilibrium temperature lower than the local-equilibrium temperature. The definition of entropy is also modified since the phonon kinetic energy conserves the ability to do work. The nonequilibrium temperature based on the thermomass theory is close to that in the extended irreversible thermodynamics. The microscopic foundation is explored through a phonon Boltzmann derivation. The higher-order contributions to the distribution function are found to be responsible for such modification of temperature. Therefore, the thermomass model gives not only non-Fourier conduction law, but also a physical picture about modified state variables in nonequilibrium states.

DOI: [10.1103/PhysRevE.87.032150](https://doi.org/10.1103/PhysRevE.87.032150)

PACS number(s): 05.70.Ln, 63.20.kg, 66.70.-f, 05.60.Cd

I. INTRODUCTION

It has been experimentally realized that the Fourier's law for heat conduction cannot accurately describe the heat transport in extreme conditions [1–3], e.g. ultra-fast laser heating [4,5] or heat transport in nanoscale systems including nanowires [6], nanofilms [7], nanotubes [8–11] and graphene layers [12]. Macroscopic modifications to Fourier's law have been proposed by adding relaxational and nonlocal terms, such as the Cattaneo-Vernotte (CV) [13–15] and dual phase lag [16,17] models. Guyer and Krumhansl [18,19] solved the phonon Boltzmann equation by a linear assumption and obtained a heat transport model (GK model) with the transient and nonlocal terms. The nonlocal term, $\nabla^2 \mathbf{q}$, where \mathbf{q} is the heat flux vector, is analogous to the viscous dissipation term in the Navier-Stokes equation. In this sense, the GK model and its nonlinear extensions are called phonon hydrodynamic models [18–24].

Macroscopic models similar to phonon hydrodynamics have also been proposed based on the extended irreversible thermodynamics (EIT) [25–34], rational extended thermodynamics (RET) [35], and thermomass theory [36–44]. The EIT obtains generalized heat conduction models by introducing additional state variables, such as heat flux, into the expression of entropy. As a result the concept of nonequilibrium temperature, β , is proposed [28–30]. This temperature takes into account the effects of transient relaxation and deviation due to heat flux, and the transport equation is in appearance classical, i.e., $\mathbf{q} = -\kappa \nabla \beta$, where κ is the thermal conductivity. The RET [35] also derives general constitutive equations for heat conduction by introducing additional state variables. The RET uses state variables which are strictly local while the EIT allows them to be nonlocal [45]. The thermomass theory [36–44] indicates that the thermal energy is equivalent to a small amount of mass, called thermomass, according to Einstein's mass-energy equivalence relation $E = mc^2$. The thermomass contributes to the total rest mass of a system,

and is frame invariant [46,47]. When the body velocity is much less than the light speed, the motion of the thermomass can be described by Newton's law and the frame invariance holds as in nonrelativistic continuum mechanics. In dielectric bulk materials, the thermomass is represented by the phonon gas and can be treated as a weighable compressible fluid. The heat transport is thus regarded as the motion of phonon gas with a drift velocity, u_h . The momentum balance equation of phonon gas gives a generalized heat transport model, which agrees with phonon hydrodynamics models. The nonlocal behaviors predicted by the EIT models agree with those in the thermomass model in many aspects, and some characteristic numbers for non-Fourier heat conduction were postulated by both theories, in analogy with fluid mechanics [30].

As mentioned above, the nonequilibrium temperature plays an important role in EIT, where the local-equilibrium hypothesis is said to be too restrictive for nonequilibrium transports. It is logical because traditionally the temperature defined in classical thermodynamics has many requirements, such as the energy equipartition among all degrees of freedom. However, the extent of nonequilibrium should be further specified for an explicit physical meaning of the nonequilibrium temperature. In this paper, we will discuss the nonequilibrium temperature and its role in non-Fourier heat conduction from the viewpoint of the thermomass model and phonon Boltzmann equation. Comparisons among different theories will be carried out to deepen the understanding of the heat transports and state variables in nonequilibrium states.

II. TEMPERATURE IN NONEQUILIBRIUM STATES DEFINED BY EIT

The nonequilibrium temperature is a key concept in the framework of EIT, which preserves the compatibility of non-Fourier heat transport with thermodynamics [25–34]. The heat transport equation in classical theory is Fourier's law,

$$\mathbf{q} = -\kappa \nabla T, \quad (1)$$

*Corresponding author: demgzy@tsinghua.edu.cn

where κ is the thermal conductivity. Consider a uniform condensed body and assume that the internal energy depends on the temperature only and the thermophysical properties (ρ , C_V) are constant. Combining Eq. (1) with the energy conservation equation,

$$\frac{\partial e}{\partial t} = \rho C_V \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}, \quad (2)$$

we get a parabolic evolution equation for temperature,

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho C_V} \nabla^2 T, \quad (3)$$

where ρ is the density and C_V is the specific heat. This equation implies that a sudden temperature perturbation is instantly felt everywhere in a material, which cannot be true since the information spreads in a finite speed. Thus the transport equation has been re-formed, for instance, as the Cattaneo-Vernotte (CV) model [13–15],

$$\tau \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\kappa \nabla T, \quad (4)$$

where τ is the relaxation time. The CV model leads to a hyperbolic evolution equation,

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{\kappa}{\rho C_V} \nabla^2 T, \quad (5)$$

with a propagation speed of heat waves, $(\kappa/\rho C_V \tau)^{1/2}$. The predicted wavelike behavior of heat is partly verified by the experiments in low temperature solids [48,49]. Other transport models with relaxation terms are also proposed, such as the dual phase lag model [16,17], to characterize more precisely the transports in fast-transient cases. Jou *et al.* [25–34] have checked the thermodynamic compatibility of Eq. (4), and found that the classical expression for entropy can decrease in a relaxation process to equilibrium in an isolated system, which violates the second law. To mend this paradox, a modified expression for entropy is derived, containing the contribution not only of internal energy but also the square of heat flux,

$$s_{\text{EIT}}(e, \mathbf{q}) = s_{\text{eq}}(e) - \frac{1}{2} \frac{\tau}{\kappa T^2} \mathbf{q} \cdot \mathbf{q}, \quad (6)$$

and the entropy production is

$$\sigma_{\text{EIT}}^s = \frac{1}{\kappa T^2} \mathbf{q} \cdot \mathbf{q}, \quad (7)$$

which keeps semipositive definite for heat waves. The nonequilibrium temperature, θ , is derived since the expression for entropy is modified,

$$\theta^{-1} = \left(\frac{\partial s}{\partial e} \right)_{v, \mathbf{q}} = T_{\text{eq}}^{-1} - \frac{1}{2} \frac{\partial(\tau/\kappa T_{\text{eq}}^2)}{\partial e} \mathbf{q} \cdot \mathbf{q}, \quad (8)$$

where the subscript v, \mathbf{q} means the derivative is made at constant volume and heat flux. In the Debye model for phonons it is easy to show that the coefficients of $\mathbf{q} \cdot \mathbf{q}$ in the second term are positive so that θ is lower than the local-equilibrium temperature T_{eq} . The subscript “eq” is added to T to stress that it is defined in an equilibrium system, i.e., with all transport fluxes, such as \mathbf{q} , stagnated. Assuming that τ is independent

of T_{eq} , we get

$$\begin{aligned} \theta &= \frac{1}{T_{\text{eq}}^{-1} + \tau/\kappa C_V T_{\text{eq}}^3 \mathbf{q} \cdot \mathbf{q}} \\ &= T_{\text{eq}} [1 - \tau/\rho \kappa C_V T_{\text{eq}}^2 \mathbf{q} \cdot \mathbf{q} + o(q^2)]. \end{aligned} \quad (9)$$

EIT predicts that the thermodynamic equilibrium is not maintained for two systems, with the same T_{eq} , but different \mathbf{q} , meaning θ takes the place of T_{eq} in the zeroth law of thermodynamics [25]. The difference between T_{eq} and θ is small in most cases, because τ is very small. For CO_2 at 300 K and 0.1 atm, with a heat flux of 10^9 W/m², the difference $T - \theta$ is 9.6×10^{-2} K [27].

Note that the extended entropy, Eq. (6), is defined based on the relaxational transport laws, Eq. (4). But the deviation of entropy and temperature for nonequilibrium states may also exist for steady situations, where Eq. (4) reduces to the Fourier’s law. For instance, the Gedanken experiment [25,27] indicates that the thermometer actually gives the nonequilibrium temperature, which deviates from the local-equilibrium one with a steady heat flux passing through the perpendicular direction. The nonequilibrium molecular dynamics calculation [50] and the theoretical study on forced oscillators [34] reveal that the kinetic (or equipartition) temperature can be significantly different from the operational temperature (the criteria of thermodynamic equilibrium in measurements) in nonequilibrium steady states, where the entropy should also be revisited. Therefore, the nonequilibrium temperature should have a physical essence independent of whether the transport processes are transient or not. In the following sections, we will discuss the effect of transport equations on the nonequilibrium temperature based on the thermomass model.

III. NON-FOURIER HEAT CONDUCTION BASED ON THE THERMOMASS THEORY

The thermomass theory [36–44] was proposed in recent years based on the Einstein’s mass-energy equivalence relation. In relativity theory, the rest mass, or proper mass, of a system composed of free particles is defined as [46,47]

$$\begin{aligned} m_{0, \text{sys}} &= \sum_i \frac{E_i}{c^2} \approx \sum_i \frac{m_{0,i} c^2 + (1/2) m_{0,i} u_i^2}{c^2} + o(u_i^2/c^2), \\ \text{if } \sum_i m_{0,i} u_i &= 0, \end{aligned} \quad (10)$$

where the subscript i means the i th particle, m_0 is the rest mass, u is the velocity, c is the vacuum light speed, and E is the energy. Equation (10) shows that the rest mass of a system contains the kinetic energy, divided by c^2 , when the terms in higher orders of u_i^2/c^2 are negligible. For a rest condensed dielectric matter, the rest mass contains the equivalent mass of the phonon gas, i.e.,

$$m_{0, \text{sys}} = \sum_i \frac{m_{0,i} c^2 + \int_k \hbar \omega dk}{c^2} + o\left(\int_k \hbar \omega dk / c^2\right), \quad (11)$$

where k is the wave vector, \hbar is the reduced Planck constant, and ω is the frequency of phonons. The sum of the phonon energy is the internal energy for a condensed dielectric matter.

Therefore, we can define the phonon gas density as [36–44]

$$\rho_h = \frac{\rho C_V T}{c^2}. \quad (12)$$

The heat transport is treated as a weighable compressible fluid, passing through the media with the drift velocity,

$$\mathbf{u}_h = \frac{\mathbf{q}}{\rho C_V T}. \quad (13)$$

The thermomass theory establishes a picture for heat transport that it is the motion of phonon gas, which is driven by the pressure gradient, and impeded by the media, like the motion of fluid in a porous media. Therefore, the balance equations for mass and momentum are obtained as in fluid mechanics,

$$\frac{\partial \rho_h}{\partial t} + \nabla \cdot (\rho_h \mathbf{u}_h) = 0, \quad (14)$$

$$\rho_h \frac{\partial \mathbf{u}_h}{\partial t} + (\rho_h \mathbf{u}_h \cdot \nabla) \mathbf{u}_h + \nabla p_h = \mathbf{f}_h. \quad (15)$$

Equation (14) is actually the energy conservation. The momentum balance equation, Eq. (15), describes the heat transport. The phonon gas pressure, p_h , is derived for the dielectric media,

$$p_h = \gamma_G \rho_h C_V T = \frac{\gamma_G \rho (C_V T)^2}{c^2}, \quad (16)$$

where γ_G is the Grüneisen parameter. The similar concept is proposed as the “phonon pressure” in Ref. [51]. Parallel to the Darcy’s law, the friction force per volume, \mathbf{f}_h , is proportional to the flux density,

$$\mathbf{f}_h = -\chi \rho_h \mathbf{u}_h. \quad (17)$$

When the acceleration effect is negligible, Eq. (15) reduces to Fourier’s law. Then the parameter in Eq. (17) is $\chi = 2\gamma_G \rho C_V^2 T / \kappa$. Thus, the general heat conduction equation is derived from Eq. (15),

$$\tau_{\text{TM}} \frac{\partial \mathbf{q}}{\partial t} + 2(\mathbf{l} \cdot \nabla) \mathbf{q} - b \kappa \nabla T + \kappa \nabla T + \mathbf{q} = 0, \quad (18)$$

with

$$\tau_{\text{TM}} = \frac{\kappa}{2\gamma_G \rho C_V^2 T}, \quad (19a)$$

$$\mathbf{l} = \frac{\mathbf{q} \kappa}{2\gamma_G C_V (\rho C_V T)^2} = \mathbf{u}_h \tau_{\text{TM}}, \quad (19b)$$

$$b = \frac{q^2}{2\gamma_G \rho^2 C_V^3 T^3} = \text{Ma}_h^2, \quad (19c)$$

where τ_{TM} is the lagging time between the temperature gradient and the heat flux, and \mathbf{l} is a characteristic length of heat transport. Nonlocal behavior appears when \mathbf{l} is comparable with the system size [38]. Ma_h is the Mach number of phonon gas flow characterizing the effect of flow compressibility, $\text{Ma}_h = u_h/v_s$, with v_s the speed of the second sound, $v_s = (2\gamma_G C_V T)^{1/2}$. With a material derivative $D/Dt = \partial/\partial t + 2(\mathbf{u}_h \cdot \nabla)$, Eq. (18) can be written as

$$\tau_{\text{TM}} \frac{D\mathbf{q}}{Dt} + \mathbf{q} = -\kappa (1 - b) \nabla T, \quad (20)$$

which can be regarded as an extension of the CV model, Eq. (4). The main differences between Eqs. (20) and (4) are that the material derivative replaces the partial derivative, and the

effective conductivity reduces by a parameter $1 - b$. The first modification accounts for the convective part due to the phonon gas motion in rest solids, which is also adopted by Ref. [30]. If the rigid solid is moving, Christov and Jordan [52] proposed a material derivative containing the solid media velocity $\mathbf{u} \cdot \nabla$ to remove the paradox in second-sound propagation. For a more general expression, Müller and Ruggeri [35] proposed, based on the 13-momentum distribution for heat conduction in gases, to replace the time derivative of the heat flux by $\partial q_i / \partial t + q_k (\partial u_i / \partial x_k) - 2q_k W_{ik}$, which has two additional terms where u_i is the fluid velocity and W is the angular velocity matrix. The first additional term, $q_k (\partial u_i / \partial x_k)$, is from the requirement of objectivity, the so-called Jaumann derivative. It characterizes the convective effect due to the fluid motion, which agrees with the thermomass model with the phonon gas velocity included in u_i . The second additional term, $-2q_k W_{ik}$, can be rewritten as $-2c^2 (\rho_h u_h)_k W_{ik}$ using Eqs. (12) and (13) and can be regarded as a Coriolis inertia term due to the effects of rotation. The second modification is related to the effective temperature for heat conduction, which will be further discussed in the following section.

IV. NONEQUILIBRIUM TEMPERATURE BASED ON THE THERMOMASS THEORY

It has been realized that the extrapolation of the zeroth and second laws of thermodynamics to nonequilibrium states requires careful treatment [25]. Here, we will investigate this extrapolation based on the thermomass theory, as well as its consequences on the definition of nonequilibrium temperature.

A. The zeroth law

In classical thermodynamics, the zeroth law gives the criterion of thermal equilibrium. It makes the temperature a measurable quantity, and justifies the use of temperature scale. In EIT theory, the nonequilibrium temperature, θ , instead of T , is suggested to be the criterion of thermal equilibrium [25–27]. That means two systems with the same T but different θ will transfer heat from one to the other. According to Eqs. (8) and (9), the presence of heat flux will reduce θ in a nonequilibrium system, making it possible to receive heat flow from an equilibrium system with the same T .

In the thermomass theory, the heat flow is driven by the static pressure gradient of phonon gas, ∇p_h . The two systems are in the local thermodynamic equilibrium with the same p_h . For systems with different material properties, namely, density, specific heat, or Grüneisen parameter, the balance condition is not simply given by p_h , but by the intrinsic phonon gas pressure as stated in porous hydrodynamics [53]. The intrinsic pressure is independent of material properties, and is only a monotonic function of temperature. However, for simplicity and illustration, we limit our discussion to materials with the same and constant properties.

For a gas flow, the static pressure is the actual pressure of the fluid, which is associated not with its motion but with its state [54]. The total pressure is larger than the static pressure by the dynamic pressure, which is related to the kinetic energy of the gas. Since the phonon gas is treated as a compressible fluid, its static pressure is related to the total pressure or the

stagnation pressure by the Bernoulli's equation,

$$\varepsilon \frac{p_h}{\rho_h} + \frac{1}{2} u_h^2 = \varepsilon \frac{p_{h,t}}{\rho_h}, \quad (21)$$

where ε is the specific heat ratio, and equals 2 for phonon gas since $p_h \rho_h^{-2} = \text{const}$ in adiabatic processes. Since the pressure of the phonon gas is directly connected with the temperature, the total pressure is

$$p_{h,t} = \frac{\gamma_G \rho (C_V T_t)^2}{c^2}, \quad (22)$$

where T_t is the total temperature of the phonon gas. Therefore, the relation between the static temperature, T , and the total temperature, T_t , is obtained from Eq. (21),

$$T = T_t - \frac{1}{4} \frac{q^2}{\gamma_G C_V (\rho C_V T)^2} = T_t - \frac{1}{2} \frac{\tau_{TM}}{\kappa \rho C_V T} q^2. \quad (23)$$

This agrees with the equation describing the relation between T and T_t for gas dynamics,

$$\frac{T_t}{T} = 1 + \frac{\varepsilon - 1}{2} \text{Ma}_h^2, \quad (24)$$

with the Mach number defined in Eq. (19c).

Equations (21) and (23) show that during motion the static pressure of the phonon gas decreases from the stagnant pressure, making T lower than T_t . Heat transfer occurs between two points with the same T_t but different T , since T is the actual criterion of balance. Compared with the EIT statement, the nonequilibrium temperature, θ , is the static temperature, T , while the equilibrium temperature, T_{eq} , is the total temperature, T_t . It is logical because T_{eq} is supposed to contain the whole energy of the element, and equal θ when the heat flux is stagnated. The difference between T and T_t is from the kinetic energy of the phonon gas. It agrees with the EIT statement that with a fixed T_{eq} , the nonequilibrium temperature, θ , decreases with the increase of heat flux. In inviscid gas dynamics, the stagnation process is reversible. For steady phonon gas flow, if the reversible transport takes place, namely, $f_h = 0$ in Eq. (15), we obtain Eq. (21) by a direct integration, which means a conservation of kinetic and potential energies. However, Eq. (23) is slightly different from Eq. (9) by a numerical parameter, $1/2$. We will discuss this difference in the next section.

For one-dimensional steady heat conduction, i.e., \mathbf{q} is constant with time and space, Eq. (20) is simplified as

$$\begin{aligned} \mathbf{q} &= -\kappa (1 - b) \nabla T \\ &= -\kappa \nabla \left(T + \frac{1}{2} \frac{\tau_{TM}}{\kappa \rho C_V T} q^2 \right) + o(q^2) \\ &= -\kappa \nabla T_t + o(q^2). \end{aligned} \quad (25)$$

It shows that for large heat flux, the effective conductivity decreases. Such behavior is attributed to the acceleration of the phonon gas, which is caused by the reduced pressure and density due to the friction, like the gas flow in a microtube [55]. Analyses based on semiempirical temperature also obtain such a reduction of κ for steady heat conduction [28–30]. In particular, the semiempirical temperature model predicts a

nonlocal behavior by defining [28–30]

$$\dot{\beta} = -\frac{1}{\tau} (\beta - \theta) + \frac{q^2}{\kappa \rho C_V T}. \quad (26)$$

The second term on the right-hand side is called nonlocal because q is proportional to $\nabla \beta$; $q = -\kappa \nabla \beta$. Making a gradient of Eq. (26) gives

$$\tau \frac{Dq}{Dt} + q = -\kappa \left(1 - \frac{\tau q^2}{\kappa \rho C_V T^2} \right) \nabla \theta, \quad (27)$$

which agrees with Eq. (20) and θ is identical to the static temperature, T . The material derivative D/Dt predicts the second sound will travel more slowly in the direction of heat flow than in the opposite direction. The nonlinear term $(1 - \tau q^2 / \kappa \rho C_V T^2)$ on the right-hand side of Eq. (27) originates from the nonlocal term in Eq. (26) and implies a reduction in thermal conductivity for higher temperature gradients. In steady state, β is identical to the total temperature, T_t , while the relation $q = -\kappa \nabla \beta$ agrees with Eq. (25).

B. The second law

From the thermomass viewpoint, the entropy production during heat transports is due to the dissipation rate of the mechanical energy of phonon gas, which is the product of drift velocity and friction force [42,43],

$$\frac{dE_h}{dt} + \nabla \cdot \mathbf{J}_{Eh} = \mathbf{f}_h \cdot \mathbf{u}_h = -\frac{2\gamma_G C_V q^2}{\kappa c^2}, \quad (28)$$

where E_h is the mechanical energy of the phonon gas, which is the sum of potential and kinetic energies,

$$E_h = p_h + \frac{1}{2} \rho_h u_h^2, \quad (29)$$

and \mathbf{J}_{Eh} is the flux of E_h . The ratio of the phonon gas energy over the available energy, namely, exergy, is $\xi = 2\gamma_G C_V T / c^2$. Noticing that the entropy production measures the dissipation rate of the available energy, divided by T , we can derive from Eq. (28)

$$\sigma_{TM}^s = -\frac{\mathbf{f}_h \cdot \mathbf{u}_h}{T \xi} = -\frac{1}{T} \mathbf{f}_h \cdot \mathbf{u}_h \left/ \left(\frac{2\gamma_G C_V T}{c^2} \right) \right. = \frac{1}{\kappa T^2} \mathbf{q} \cdot \mathbf{q}, \quad (30)$$

which agrees with Eq. (7). The full derivative of entropy density s should be

$$\begin{aligned} \frac{ds}{dt} &= -\nabla \cdot \mathbf{J}_s + \sigma_{TM}^s = -\nabla \cdot \left(\frac{\mathbf{q}}{T} \right) + \sigma_{TM}^s \\ &= \frac{\mathbf{q}}{\kappa T^2} \cdot (\mathbf{q} + \kappa \nabla T) - \frac{\nabla \cdot \mathbf{q}}{T}, \end{aligned} \quad (31)$$

where \mathbf{J}_s is the entropy flux. Here the expression of \mathbf{J}_s is only for heat conduction problems, and is adequate for most ordinary materials except multipolar materials as depicted by Müller [56]. Recently it is also shown that a nonlocal correction should be made on the entropy flux if the generalized heat transport equation containing the Laplacian term of heat flux is adopted, for example, in nanoscale structures [57]. The contribution of such correction to the nonequilibrium temperature is worth exploration and will be discussed in further work. The term $\mathbf{q} + \kappa \nabla T$ in Eq. (31) corresponds to

$\nabla p_h - f_h$ in Eq. (15), which means the difference between the driving and friction forces, namely, the inertia force. Based on Eq. (15), we have

$$\begin{aligned} \frac{\mathbf{q}}{\kappa T^2} \cdot (\mathbf{q} + \kappa \nabla T) &= \frac{1}{\xi} \frac{q}{\rho C_V T^2} (\nabla p_h + f_h) \\ &= -\frac{u_h}{\xi T} \frac{D\rho_h u_h}{Dt} = -\frac{\tau_{TM}}{\kappa T^2} \mathbf{q} \cdot \frac{D\mathbf{q}}{Dt}, \end{aligned} \quad (32)$$

where D/Dt is the material derivative. The term $-\nabla \cdot \mathbf{q}/T$ in Eq. (31) is connected to the energy balance equation

$$\rho C_V \frac{\partial T_t}{\partial t} = -\nabla \cdot \mathbf{q}, \quad (33)$$

where T_t is used because \mathbf{q} includes both the potential and kinetic energy flux. The integration of Eq. (31) gives

$$s = \rho C_V \ln T_t - \frac{1}{2} \frac{\tau_{TM}}{\kappa T^2} q^2 + o(q^2). \quad (34)$$

Equation (34) agrees with Eq. (6), and shows that the contribution of the nonequilibrium temperature to local entropy, namely the second term in Eq. (34), is proportional to the kinetic energy of the thermomass,

$$\frac{1}{2} \frac{\tau_{TM}}{\kappa T^2} q^2 = \frac{1}{2} \rho_h u_h^2 / \xi T. \quad (35)$$

It manifests that the entropy decreases because of the kinetic energy of phonon gas, which stores the available energy. The kinetic energy of phonon gas is a local state variable, which does not depend on the transport process. As long as there is a heat flux, Eq. (34) is applicable. In ordinary cases the inertia (acceleration) of the thermomass is negligible compared with the driving or friction terms and then Eq. (15) reduces to Fourier's law. Therefore the magnitude of Eq. (32) is much less than $-\nabla \cdot \mathbf{q}/T$, which indicates that the time variation of the kinetic energy of phonon gas flow is negligible compared with the time variation of the internal energy. In this case, the contribution of the kinetic energy to the local entropy still exists, but vanishes with a time derivative in Eq. (31), and the entropy production rate, Eq. (30), reduces to the classical form.

In classical thermodynamics, the internal energy is expressed by the temperature, $e = \rho C_V T$. When the system is moving, each molecule will have an additional kinetic energy. In gas dynamics, the internal energy of a gas element is expressed by a static temperature, not including the kinetic energy of the gas element. In this sense, the local internal energy density during heat transport should remove the contribution of the kinetic energy of the phonon gas. Combined with Eq. (23), the internal energy is lower than the total energy, $\rho C_V T_t$:

$$e = \rho C_V T = \rho C_V \left[T_t - \frac{1}{2} \frac{\tau_{TM}}{\kappa \rho C_V T} q^2 + o(q^2) \right] < e_t. \quad (36)$$

Recall that the thermomass theory obtains the generalized entropy, Eq. (34), which can be further derived by inserting

Eq. (23):

$$\begin{aligned} s &= \rho C_V \ln T_t - \frac{1}{2} \frac{\tau_{TM}}{\kappa T^2} q^2 \\ &= \rho C_V \ln \left\{ T_t \left[1 - \frac{1}{2} \frac{\tau_{TM}}{\rho C_V \kappa T^2} q^2 + o(q^2) \right] \right\} \\ &= \ln e. \end{aligned} \quad (37)$$

Therefore, the relation between energy and entropy has a traditional form,

$$T^{-1} = ds/de = ds/\rho C_V dT. \quad (38)$$

If the classical expression for e is applied, $e_t = \rho C_V T_t$, then the temperature will be

$$\begin{aligned} \theta = de_t/ds &= T \frac{dT_t}{dT} = T \left(1 - \frac{1}{2} \frac{\tau_{TM}}{\kappa \rho C_V T^2} q^2 \right) \\ &= T_t \left(1 - \frac{\tau_{TM}}{\kappa \rho C_V T^2} q^2 \right) + o(q^2), \end{aligned} \quad (39)$$

which is consistent with Eq. (9). It manifests that the relation between the temperature, T , and the total temperature, T_t , is slightly different from that between θ_{EIT} and T_{eq} , by a parameter of 1/2. They are derived from the same expression of entropy, Eq. (37). The difference comes from the differential of internal energy, de . In EIT, the internal energy is still defined by the equilibrium temperature, T_{eq} , containing all the molecular energies of a system. In thermomass theory, the internal energy is defined by a static temperature, T , removing the drift kinetic energy. It is logical since the internal energy, in other words, the static temperature, should be independent of motion. Therefore, both the thermomass theory and EIT get a temperature lower than the equilibrium or total temperature, with a slight difference in the numerical parameter.

There is another interpretation to nonequilibrium entropy based on the general entropy production, Eq. (34), by an EIT approach [27]. Consider a medium element with heat flux \mathbf{q}_0 . When it is suddenly isolated, the heat flux will experience a decay process,

$$\tau \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = 0, \quad (40)$$

and the entropy approaches the equilibrium value. Equation (40) is a balance between the inertia and friction forces by Eq. (15). Therefore, the difference between the nonequilibrium and equilibrium entropies is

$$s_{eq} - s_{neq} = \int_0^\infty \sigma^s dt = \int_0^\infty \frac{q_0^2 \exp(-2t/\tau)}{\kappa T^2} dt = \frac{\tau q_0^2}{2\kappa T^2}. \quad (41)$$

Equation (41) gives the entropy change by dissipating the whole kinetic energy since the exponential decay of heat flux, Eq. (40), dissipates the kinetic energy of phonon gas without changing the potential energy. This shows that we can obtain the nonequilibrium entropy as a state variable, Eq. (34), by a transient transport equation, Eq. (40), because Eq. (41) measures the kinetic energy of phonon gas by a virtual relaxation to local equilibrium.

V. A PHONON BOLTZMANN DERIVATION

In dielectric solids, heat conduction laws can be derived from the phonon Boltzmann equation [18–24,41],

$$\mathbf{D}f(\mathbf{k}, \mathbf{x}, t) = \mathbf{C}f(\mathbf{k}, \mathbf{x}, t), \quad (42)$$

where f is the distribution function of phonons, \mathbf{k} is the wave vector, and \mathbf{D} and \mathbf{C} are the drift and collision operators, respectively. The macroscopic variables, such as internal energy density E and heat flux \mathbf{q} , are obtained by an integral over the phase space of \mathbf{k} ,

$$E = \sum_n \int_{\mathbf{k}} \hbar\omega^n f^n, \quad (43)$$

$$q_i = \sum_n \int_{\mathbf{k}} \hbar\omega^n \frac{\partial \omega^n}{\partial k_i} f^n = \sum_n \int_{\mathbf{k}} \hbar\omega^n v_i^n f^n, \quad (44)$$

where n is the index of phonon branches, such as the transversal acoustic and longitudinal acoustic, v is the group velocity, and ω is the frequency. The integral is over the whole \mathbf{k} space and then summed over all branches.

Solutions of Eq. (42) are proposed by many researchers, such as the GK model, which adopts a linear assumption on the distribution function. Banach and Larecki [23] and Jiaung and Ho [24] considered higher-order expansions of f and derived more general governing equations for heat conduction. These transport equations are called phonon hydrodynamic models because of the similarity to fluid governing equations. In a previous paper [41], we showed that the thermomass transport equation, Eq. (18), can be obtained by a second-order expansion of distribution function and regarded as a nonlinear solution of Eq. (42), containing the convective term as in fluid dynamics.

In equilibrium states, the distribution function of phonons is the Planck distribution, f_E ,

$$f_E = \frac{1}{\exp(\hbar\omega/k_B T) - 1}, \quad (45)$$

where k_B is the Boltzmann constant. In nonequilibrium steady states, when there is only normal scattering for phonons, the quasimomentum of phonon gas is conserved and f is the displaced Planck distribution, f_D ,

$$f_D = \frac{1}{\exp[(\hbar\omega - \hbar\mathbf{k} \cdot \mathbf{u})/k_B T] - 1}, \quad (46)$$

where \mathbf{u} is the drift velocity of phonon gas, related to the drift velocity in the present macroscopic model, $\mathbf{u} = (3/4)\mathbf{u}_h$, in a three-dimensional isotropic media. The collision operator in Eq. (42) contains two mechanisms, namely, the resistive scattering, with the characteristic time, τ_R , which tends to relax f to f_E , while the normal scattering, with the characteristic time, τ_N , tends to relax f to f_D . Therefore, Eq. (42) can be rewritten as

$$\left(\frac{\partial}{\partial t} + \mathbf{v}^n \cdot \nabla \right) f^n = \frac{f_E^n - f^n}{\tau_R} + \frac{f_D^n - f^n}{\tau_N}, \quad (47)$$

In general, the relaxation times, τ_R and τ_N , are dependent with the wave vector, \mathbf{k} . However, we assume they are constant for simplicity. Multiplying Eq. (49) by $\hbar\omega$ and $\hbar\omega v_i$, respectively

and integrating it in k space yields

$$\frac{\partial \int_{\mathbf{k}} f^n \hbar\omega^n}{\partial t} + \int_{\mathbf{k}} \mathbf{v}^n \cdot \nabla f^n \hbar\omega^n = 0, \quad (48)$$

$$\begin{aligned} \frac{\partial \int_{\mathbf{k}} f^n \hbar\omega^n v_i^n}{\partial t} + \int_{\mathbf{k}} \mathbf{v}^n \cdot \nabla f^n \hbar\omega^n v_i^n \\ = \frac{\int_{\mathbf{k}} (f_E^n - f^n) \hbar\omega^n v_i^n}{\tau_R} + \frac{\int_{\mathbf{k}} (f_D^n - f^n) \hbar\omega^n v_i^n}{\tau_N}. \end{aligned} \quad (49)$$

The collision term vanishes in Eq. (48) since every collision must keep energy conservative. If f is approximated by a second-order expansion of f_D ,

$$\begin{aligned} f &= f_E + \frac{\partial f_D}{\partial \mathbf{u}} \Big|_{\Delta \mathbf{u}=0} \Delta \mathbf{u} + \frac{1}{2} \frac{\partial^2 f_D}{\partial \mathbf{u}^2} \Big|_{\Delta \mathbf{u}=0} (\Delta \mathbf{u})^2 + o[(\Delta \mathbf{u})^2] \\ &= f_E + \frac{\partial f_E}{\partial \omega} (\mathbf{k} \cdot \mathbf{u}) + \frac{1}{2} \frac{\partial^2 f_E}{\partial \omega^2} (\mathbf{k} \cdot \mathbf{u})^2 + o[(\Delta \mathbf{u})^2] \\ &= f_E + f_+ + f_{++} + o[(\Delta \mathbf{u})^2], \end{aligned} \quad (50)$$

we get the transport equation by integral of Eq. (49),

$$\frac{\partial q_i}{\partial t} + \frac{15}{16} \nabla_j \frac{q_i q_j}{E} + \frac{1}{3} \nabla_i \int_{\mathbf{k}} f_E^s \hbar\omega (v^s)^2 = -\frac{q_i}{\tau_R}. \quad (51)$$

The second term on the left-hand side comes from the integral of f_{++} , and corresponds to the convective term in Eq. (18).

With the distribution function of Eq. (50), regarding that f_E and f_{++} are even functions in k space while f_+ is odd, the integral of Eq. (48) becomes

$$\frac{\partial \int_{\mathbf{k}} (f_E^n + f_{++}^n) \hbar\omega}{\partial t} + \int_{\mathbf{k}} \mathbf{v}^n \cdot \nabla f_+^n \hbar\omega = 0. \quad (52)$$

The first term is traditionally interpreted as the time derivative of internal energy, and the second term is the divergence of heat flux. If the internal energy is expressed by T , then the integral of f_E is just a portion of the total energy, namely,

$$\int_{\mathbf{k}} f_E^n \hbar\omega = \rho C_V T < \rho C_V T_t. \quad (53)$$

The difference between T and T_t is

$$T = T_t - \frac{1}{\rho C_V} \int_{\mathbf{k}} f_{++}^n \hbar\omega. \quad (54)$$

The second term on the right-hand side of Eq. (54) is proportional to q^2 since it contains the term \mathbf{u}^2 . The integral in Eq. (54) is

$$\int_{\mathbf{k}} f_{++}^n \hbar\omega = \int_{\mathbf{k}} \hbar\omega \frac{1}{2} \frac{\partial^2 f_E^n}{\partial \omega^2} (\mathbf{k} \cdot \mathbf{u})^2 = \int_{\mathbf{k}} \frac{3\mathbf{u}^2}{(v^s)^2} \hbar\omega f_E^n. \quad (55)$$

Guyer and Krumhansl give that the square of v^s is related to the relaxation time and heat conductivity by [19]

$$\frac{1}{(v^s)^2} = \frac{\tau \rho C_V}{3\kappa}, \quad (56)$$

so Eq. (54) turns out to be

$$T = T_t - \frac{9}{16} \frac{\tau}{\kappa} \frac{q^2}{\rho C_V T} + o(q^2), \quad (57)$$

which is close to the macroscopic derivation, Eq. (23).

Compared with the discussion in Sec. IV B, we find that the energy conservation relation, Eq. (48), can be interpreted as

the conservation of total energy, which includes an equilibrium contribution, from f_E , and a nonequilibrium contribution, from f_{++} . The first part is the real internal energy, while the second part is actually the kinetic energy of heat, which agrees with Eq. (33).

The present derivation only focuses on the heat conduction in dielectric solids, where the thermomass is represented by the phonon gas. For gases the “thermon” is attached on the molecules or atoms, for metals it resides on the electron gas, while for semiconductors it is carried by both phonon and electron gases. For a more general statistical derivation for the nonequilibrium temperature in these systems, a possible way is starting from the non-Fourier heat conduction. Fourier’s law is mostly based on the linear part of the distribution function (e.g., molecular velocity distribution, electron state function), and the non-Fourier heat conduction originates from its higher orders. The higher orders of distribution function will not only cause the nonlinearity of the transport function, but also affect the local state variables. Further investigation is in preparation and expected to confirm such anticipations.

VI. CONCLUDING REMARKS

The thermodynamic equilibrium refers to either the local equilibrium or the global equilibrium, corresponding to the local-equilibrium temperature or the global-equilibrium temperature. The temperature in classical definitions requires an equilibrium system, which is the global-equilibrium temperature. The heat conduction occurs with temperature gradient, which is obviously not in global but local equilibrium. Otherwise, there is no way to define temperature. Thus, the local-equilibrium temperature should be used in Fourier’s law and the internal energy. When the system is sufficiently far from the global equilibrium the non-global-equilibrium contributions should be taken into consideration. From the viewpoint of thermomass theory, we show that the driving force of heat transport is due to the gradient of local-equilibrium pressure, i.e., the static pressure of phonon gas. The total pressure, or stagnation pressure, is higher than the static pressure by

a dynamic pressure. The static temperature, T , and total temperature, T_t , can be obtained through the relation between the pressure and the temperature. The static temperature, T , is the nonequilibrium temperature, θ , defined in EIT, which is a local-equilibrium state variable independent of phonon gas motion, and is the actual criterion of balance. The total temperature, T_t , is the equilibrium temperature, T_{eq} , accounting for both the potential and kinetic energy in a local element.

In extreme conditions such as the fast-transient heating or huge heat flux density, Fourier’s law is deviated since the dynamic effect of phonon gas becomes significant. The classical entropy production is no longer semipositive definite, seeming to break the second law. With the difference between T and T_t considered, we show that the non-Fourier conduction law in steady states has a similar form to Fourier’s law expressed by T_t , which agrees with the EIT postulates [28–30]. The effective thermal conductivity is reduced because the acceleration of phonon gas consumes part of the driving force. The entropy is overestimated if expressed by T_t , since the extra available energy is conserved by the dynamic temperature. With the clarified static temperature, T , the entropy keeps semipositive in heat waves and its relation to the internal energy and temperature still holds as $1/T = \partial s / \partial e$.

A phonon Boltzmann derivation shows that the high-order terms of distribution function not only give birth to the convective term in the transport equation but also have an effect on the expression of the internal energy. It agrees with the above analysis that the total energy, which is conserved in transport, can be split into a local-equilibrium part and a dynamical part by an integral over the phase space of wave vectors, which further verifies the macroscopic results based on the thermomass theory.

ACKNOWLEDGMENTS

This work is financially supported by National Natural Science Foundation of China (Grants No. 51076080 and No. 51136001) and Tsinghua University Initiative Scientific Research Program.

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