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Nonequilibrium thermodynamics of phonon hydrodynamic model for nanoscale heat transport

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A phonon hydrodynamic equation has been recently derived from the kinetic theory of phonons for nanoscale heat transport at ordinary temperatures. The classical irreversible thermodynamics is no longer valid due to the failure of the local equilibrium hypothesis from temporal and spatial strong nonequilibrium effects. In the present paper, we investigate the thermodynamic consistency of the phonon hydrodynamic equation for heat transport based on the phonon kinetic theory. The macroscopic expressions of entropy density and entropy flux in the bulk region as well as interfacial entropy generation in the boundary region are derived from their mesoscopic definitions in terms of the nonequilibrium phonon distribution solution. The phonon hydrodynamic equation is demonstrated to be consistent with the second law in the frame of extended irreversible thermodynamics. This paper provides a solid mesoscopic theoretical foundation to the previous nonequilibrium thermodynamics of the phonon hydrodynamic model for heat transport in nanosystems on a macroscopic basis.

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I. INTRODUCTION

Heat transport is an irreversible process which can be described from mesoscopic as well as macroscopic levels of theoretical descriptions. The mesoscopic theoretical description is mainly based on the Boltzmann transport equation as the core of kinetic theory of microscopic particles (molecules, phonons, electrons, etc.) [1,2]. In terms of the macroscopic theoretical description, there are often two branches, namely, the heat transport equation and nonequilibrium thermodynamics. These two branches are intimately related, as the compatibility of the heat transport equation with the second law of thermodynamics is the essential issue in the latter branch [3,4]. The macroscopic theories are also deeply rooted in the mesoscopic Boltzmann transport theory [5,6]. The classical Fourier law of heat conduction assumes a linear dependence of the heat flux on the temperature gradient and has been put into the frame of classical irreversible thermodynamics (CIT) for transport processes within the near-equilibrium regime [7]. On the other hand, both Fourier's law and CIT have been derived from Chapman-Enskog expansion to the Boltzmann transport equation within first-order approximation [7].

In recent decades, with the rapid development of nanoscience and nanotechnology, there have been extensive studies on microscale and nanoscale heat transport [8–11]. The classical Fourier law fails as the characteristic size and time of the nanosystems and ultrafast processes become comparable to or even smaller than the mean free path and relaxation time of heat carriers. For instance, the violation of Fourier's law has been clearly demonstrated by the length-dependent thermal conductivity of silicon nanowires based on nonequilibrium molecular dynamics simulation [12], and the nondiffusive period-dependent decay rate in a recent transient thermal grating (TTG) experiment on nanofilms [13]. Therefore, several macroscopic non-Fourier models have been proposed as substitutes, such as the Cattaneo-Vernotte model [14,15], phonon hydrodynamic model [16,17], dual-phase-lag model [18,19], and so on. The heat transport equations in these models include additional relaxation and/or nonlocal terms beyond Fourier's law to capture the strong temporal and/or spatial nonequilibrium effects in heat transport at extreme states. Such heat transport equations are thus no longer compatible with the second law of thermodynamics in CIT [20–22]. In other words, CIT is no longer valid in strong nonequilibrium situations due to the failure of the local equilibrium hypothesis.

Among the existing macroscopic non-Fourier models, the phonon hydrodynamic model is the most promising one since it can be directly derived from mesoscopic Boltzmann transport theory [23]. When studying phonon hydrodynamic phenomena in dielectric crystals at extremely low temperature, the Guyer-Krumhansl (G-K) heat transport equation was derived from the phonon Boltzmann equation based on the eigenstate analysis [16,24], which inspires the kinetic-collective model emphasizing the collective features of momentum-conserving phonon normal scattering [25,26]. The G-K heat transport equation was later adapted to the modeling of effective thermal conductivity of nanostructures at room temperature where phonon resistive scattering dominates [17,27–29]. Thus there existed a theoretical gap between this phenomenological model [17] and the mesoscopic Boltzmann transport theory [23,30]. In our recent study [31], we have filled this theoretical gap by deriving a phonon hydrodynamic equation from the phonon Boltzmann equation for nanoscale heat transport at ordinary temperatures. On the

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other hand, there have been extensive investigations on the thermodynamic consistency of phonon hydrodynamic models based on the extended nonequilibrium thermodynamics beyond CIT, as will be summarized below.

The classical G-K heat transport equation was derived from extended irreversible thermodynamics (EIT), which elevates the dissipative variables (heat flux and the flux of heat flux) into the state variable space [32]. A generalized Prigogine's principle of minimum entropy production based on EIT was also proposed for the steady-state G-K heat transport equation [33]. To remove the infinite speed of thermal perturbation, a generalized G-K model was developed in the frame of EIT when considering also the evolution equation of the flux of heat flux [34,35]. In recent years, the G-K-like nonlocal heat transport equations in the phenomenological phonon hydrodynamic model have been verified to be compatible with the second law in extended thermodynamics based on dynamical nonequilibrium temperature [36–38]. The nonlocal heat transport equations have also been derived through the standard procedures in EIT with slightly different expressions of generalized entropy flux in several studies [39–41]. For the application in nanosystems, the heat flux boundary condition for the nonlocal heat transport equation was derived through an extension of the generalized Prigogine principle of minimum entropy production in Ref. [33] by including the boundary entropy production term [42]. In spite of the plentiful studies on the nonequilibrium thermodynamics for the phonon hydrodynamic model from a macroscopic perspective, the corresponding mesoscopic theoretical foundation has not yet been well established. Although the mesoscopic foundation of EIT has been discussed from the gas kinetic theory [43], a direct kinetic theoretical foundation for EIT of phonon heat transport far from the equilibrium state is still lacking, to the author's best knowledge.

The aim of the present paper is to explore the nonequilibrium thermodynamics of our recently developed phonon hydrodynamic model for nanoscale heat transport [31] based on the kinetic theory of phonons. We find that the heat transport equation in our recent model is compatible with the second law in the frame of EIT. In this way, we also provide a solid mesoscopic theoretical foundation for EIT of phonon hydrodynamic models. The remainder of the paper is organized as follows: the theoretical foundation of nonequilibrium thermodynamics for phonon transport is given in Sec. II; in Sec. III, the nonequilibrium thermodynamic framework for the phonon hydrodynamic equation is established from the solution of the phonon Boltzmann equation; in Sec. IV, we discuss the interfacial entropy generation, the importance of which will increase in nanosystems; the concluding remarks are finally made in Sec. V.

II. THEORETICAL FOUNDATION

In this section, the entropy balance equation for phonon transport in dielectric crystals will be first introduced from the phonon Boltzmann equation in Sec. II A. The kinetic definitions of entropy density, entropy flux, and entropy generation are thus obtained. In Sec. II B, the basic tenets of CIT for the classical Fourier law are then illustrated by deriving the macroscopic expressions of entropy density and entropy flux from their kinetic definitions.

A. Entropy balance equation for phonon transport

The quasiparticle picture is valid for phonon transport in a dielectric solid when the characteristic size of the system is much larger than the dominant phonon wavelength. In this way, the transport behavior of phonons can be described by the phonon Boltzmann equation (Peierls-Boltzmann equation) [9,44]:

$$\frac{\partial f}{\partial t} + \mathbf{v}_{\mathrm{g}} \cdot \nabla f = C(f), \tag{1}$$

where $f \equiv f(\mathbf{x}, t, \mathbf{k})$ is the phonon occupation number or phonon distribution function, with $f(\mathbf{x}, t, \mathbf{k}) d\mathbf{x} d\mathbf{k}$ denoting the probabilistic number of phonons found within the spatial interval $(\mathbf{x}, \mathbf{x} + d\mathbf{x})$ and wave-vector interval $(\mathbf{k}, \mathbf{k} + d\mathbf{k})$ at a specific time t. The phonon group velocity can be determined from the dispersion relation: $\mathbf{v}_{\mathrm{g}} = \nabla_{\mathbf{k}} \omega(\mathbf{k})$, with $\omega(\mathbf{k})$ the frequency of phonons with the wave vector $\mathbf{k}$. The collision term $C(f)$ represents the alteration of the phonon distribution function due to phonon scattering processes.

As a phonon is a kind of boson, the kinetic (or statistical mechanical) definition of entropy density is given as [6,45,46]

$$s = -k_{\mathrm{B}} \int [f \ln f - (1 + f) \ln (1 + f)] d\mathbf{k}, \tag{2}$$

with k_{B} being the Boltzmann constant. The temporal derivative of entropy density is computed from Eq. (2) as

$$\frac{\partial s}{\partial t} = -k_{\mathrm{B}} \int \left\{ \frac{\partial (f \ln f)}{\partial t} - \frac{\partial [(1 + f) \ln (1 + f)]}{\partial t} \right\} d\mathbf{k}. \tag{3}$$

With the help of the phonon Boltzmann equation (1), Eq. (3) gives rise to the entropy balance equation for phonon transport:

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}^s = \sigma^s, \tag{4}$$

where the kinetic definitions of entropy flux and entropy generation are obtained as, respectively [6,45,46],

$$\mathbf{J}^s = -k_{\mathrm{B}} \int \mathbf{v}_{\mathrm{g}} [f \ln f - (1 + f) \ln (1 + f)] d\mathbf{k}, \tag{5}$$

$$\sigma^s = -k_{\mathrm{B}} \int C(f) [\ln f - \ln (1 + f)] d\mathbf{k}. \tag{6}$$

B. Classical irreversible thermodynamics for Fourier's law

The macroscopic expressions of entropy density and entropy flux can be derived once the solution of the phonon distribution function in Eq. (1) is obtained. As a first step, we revisit the CIT for phonon heat transport in the diffusive regime in the presence of a temperature gradient, where Fourier's law is valid.

Throughout this paper, we consider heat transport at ordinary temperatures, where the phonon resistive scattering is dominant over the normal scattering. In other words, the normal scattering and hydrodynamic phonon transport usually relevant at very low temperature [16,47,48] are not taken into account. Thus the single mode relaxation time model is a very good approximation to the scattering term in Eq. (1), which is then reduced to

$$\frac{\partial f}{\partial t} + \mathbf{v}_{\mathrm{g}} \cdot \nabla f = -\frac{f - f_{\mathrm{R}}^{\mathrm{eq}}}{\tau_{\mathrm{R}}}, \tag{7}$$

where the equilibrium phonon distribution is the Bose-Einstein distribution:

$$f_{\mathrm{R}}^{\mathrm{eq}} = \frac{1}{\exp(\hbar\omega/k_{\mathrm{B}}T) - 1}. \tag{8}$$

The overall relaxation time τ_{R} in Eq. (7) has included the effects from all the intrinsic phonon resistive scattering (Umklapp scattering, imperfection scattering, etc.), and is often computed based on Matthiessen's rule [9]. Furthermore, the isotropic gray Debye phonon model is assumed for the convenience of the derivation of the macroscopic heat transport equation from the phonon Boltzmann equation [23,31].

In the diffusive regime of heat conduction, the phonon distribution function is obtained through a Chapman-Enskog expansion to Eq. (7) within first order [9]:

$$f = f_{\mathrm{R}}^{\mathrm{eq}} + \phi, \tag{9}$$

where the first-order perturbation quantity is fully expressed as

$$\phi = -\tau_{\mathrm{R}} v_{\mathrm{g}\beta} \frac{\partial T}{\partial x_\beta} \frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}. \tag{10}$$

Einstein's rule of summation is adopted hereafter. Putting Eq. (9) into the kinetic definition of heat flux, we derive Fourier's law: $\mathbf{q} = -\lambda\nabla T$, with the definition of bulk thermal conductivity:

$$\lambda = \tfrac{1}{3} C_V v_{\mathrm{g}} \Lambda, \tag{11}$$

where the phonon mean free path is defined as $\Lambda = v_{\mathrm{g}}\tau_{\mathrm{R}}$.

To compute the integration in the kinetic definitions of entropy density and entropy flux, we consider the following approximations through Taylor's expansion within second order:

$$f \ln f \approx f_{\mathrm{R}}^{\mathrm{eq}} \ln f_{\mathrm{R}}^{\mathrm{eq}} + \phi\left(1 + \ln f_{\mathrm{R}}^{\mathrm{eq}}\right) + \frac{\phi^2}{2 f_{\mathrm{R}}^{\mathrm{eq}}}, \tag{12}$$

$$\begin{aligned}(1+f)\ln(1+f) \approx{}& \left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\ln\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\\ &+ \phi\left[1 + \ln\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\right] + \frac{\phi^2}{2\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)}.\end{aligned} \tag{13}$$

Substituting Eq. (9) into the kinetic definition Eq. (2), we obtain the expression of entropy density with the help of Eqs. (12) and (13):

$$\begin{aligned} s ={}& -k_{\mathrm{B}} \int \left[f_{\mathrm{R}}^{\mathrm{eq}} \ln f_{\mathrm{R}}^{\mathrm{eq}} - \left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\ln\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\right] d\mathbf{k}\\ &- \frac{1}{2} k_{\mathrm{B}} \int \frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)} d\mathbf{k}. \end{aligned} \tag{14}$$

The second-order term in ϕ^2 is negligibly small in the near-equilibrium regime where Fourier's law is valid. As a result, Eq. (14) is reduced to exactly the equilibrium entropy density:

$$s = s_{\mathrm{eq}} = -k_{\mathrm{B}} \int \left[f_{\mathrm{R}}^{\mathrm{eq}} \ln f_{\mathrm{R}}^{\mathrm{eq}} - \left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\ln\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\right] d\mathbf{k}, \tag{15}$$

which is consistent with the local equilibrium hypothesis in CIT. Substituting Eq. (9) into the kinetic definition Eq. (5), we obtain the expression of entropy flux with the help of Eqs. (12) and (13):

$$\begin{aligned} J_\alpha^s ={}& -k_{\mathrm{B}} \int v_{\mathrm{g}\alpha} \phi\left[\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)\right] d\mathbf{k}\\ &- \frac{1}{2} k_{\mathrm{B}} \int v_{\mathrm{g}\alpha} \frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)} d\mathbf{k}. \end{aligned} \tag{16}$$

Putting the perturbation term Eq. (10) into the first term of Eq. (16), with also the aid of Fourier's law and Eq. (11), we obtain the macroscopic expression of entropy flux:

$$\mathbf{J}^s = \frac{\mathbf{q}}{T}. \tag{17}$$

The second term of Eq. (16) vansihes, as the integrand is an odd function of the wave vector. Equation (17) is exactly the classical expression of entropy flux in CIT [7].

III. NONEQUILIBRIUM THERMODYNAMICS

In this section, a brief introduction will be first given in Sec. III A to the derivation of the phonon hydrodynamic model for nanoscale heat transport at ordinary temperatures [31], which mainly refers to the non-Fourier heat conduction at extremely small spatial scale and ultrafast temporal scale. Heat transport in bulk materials with strong spatial and/or temporal nonequilibrium effects (for instance, in the TTG experiment on thick film [13], and in the frequency domain thermoreflectance experiment on bulk substrate [49]) can be also treated as "nanoscale heat transport" since it involves heat transport over an extremely small characteristic length within an extremely short time duration. In Secs. III B and III C, the obtained nonequilibrium phonon distribution solution will be then used to derive the macroscopic expressions of both entropy density and entropy flux from their kinetic definitions in Sec. II A. Finally, it will be verified that the phonon hydrodynamic equation is consistent with the second law in the frame of EIT in Sec. III D.

A. Phonon hydrodynamic model

The starting point of the derivation of the phonon hydrodynamic equation is the moment balance equations of phonons. The balance equations of energy density e and heat flux $\mathbf{q}$ are obtained by multiplying on both sides of Eq. (7) the phonon energy quanta $\hbar\omega$ and the modal heat flux $\mathbf{v}_{\mathrm{g}}\hbar\omega$, respectively, and then integrating over the wave-vector space:

$$\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{q} = 0, \tag{18}$$

$$\frac{\partial \mathbf{q}}{\partial t} + \nabla \cdot \mathbf{Q} = -\frac{\mathbf{q}}{\tau_{\mathrm{R}}}. \tag{19}$$

To have a closed mathematical description, we have to specify the flux of heat flux $\mathbf{Q}$ in terms of the four basic field variables (e and three components of $\mathbf{q}$). A regularized moment method originally put forward in rarefied gas flow [50] has been used for the closure problem in nanoscale phonon heat transport [31]. The main idea of this closure method is a perturbation expansion around a referenced nonequilibrium phonon distribution rather than the usual equilibrium one Eq. (8). The regularized moment method combines the advantages of the Chapman-Enskog method [51] and moment method [45] and overcomes some drawbacks of each method. A four-moment phonon distribution function is derived first through the maximum entropy principle as the referenced nonequilibrium distribution [31]:

$$f_4 = f_{\mathrm{R}}^{\mathrm{eq}} + \frac{3}{C_V v_{\mathrm{g}}^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T} q_\alpha v_{\mathrm{g}\alpha}. \tag{20}$$

Higher-order approximation is then derived from the balance equation of the flux of heat flux:

$$\frac{\partial Q_{\alpha\beta}}{\partial t} + \frac{\partial}{\partial x_\gamma} M_{\alpha\beta\gamma} = \frac{1}{\varepsilon \tau_{\mathrm{R}}}\left(\frac{1}{3} v_{\mathrm{g}}^2 e \delta_{\alpha\beta} - Q_{\alpha\beta}\right), \tag{21}$$

where $M_{\alpha\beta\gamma}$ represents the flux of $Q_{\alpha\beta}$, being a third-order tensor defined as $M_{\alpha\beta\gamma} = \int v_{\mathrm{g}\alpha} v_{\mathrm{g}\beta} v_{\mathrm{g}\gamma} \hbar\omega f d\mathbf{k}$. The small parameter ε comes from the scaling of the phonon Boltzmann equation and will be set to unity after the perturbation expansion:

$$Q_{\alpha\beta} = Q_{\alpha\beta}^{(0)} + \varepsilon Q_{\alpha\beta}^{(1)} + \dots. \tag{22}$$

Substituting Eq. (22) into Eq. (21), we obtain the terms of each order on the small parameter separately:

$$\varepsilon^{-1} : Q_{\alpha\beta}^{(0)} = \frac{1}{3} v_{\mathrm{g}}^2 e \delta_{\alpha\beta}, \tag{23}$$

$$\varepsilon^{0} : \left[\frac{\partial Q_{\alpha\beta}^{(0)}}{\partial t} + \frac{\partial}{\partial x_\gamma} M_{\alpha\beta\gamma}^{(0)}\right]\Bigg|_{f_4} = -\frac{1}{\tau_{\mathrm{R}}} Q_{\alpha\beta}^{(1)}. \tag{24}$$

The zeroth-order approximation Eq. (23) to the flux of heat flux corresponds exactly to the four-moment phonon distribution function Eq. (20). Furthermore, the first-order approximation is obtained by substituting Eq. (20) into Eq. (24). Combining the zeroth-order and first-order approximations, we get the explicit expression of the flux of heat flux as

$$Q_{\alpha\beta} = \frac{1}{3} v_{\mathrm{g}}^2 e \delta_{\alpha\beta} + \frac{2}{15}\tau_{\mathrm{R}} v_{\mathrm{g}}^2 \frac{\partial q_\gamma}{\partial x_\gamma}\delta_{\alpha\beta} - \frac{1}{5}\tau_{\mathrm{R}} v_{\mathrm{g}}^2\left(\frac{\partial q_\alpha}{\partial x_\beta} + \frac{\partial q_\beta}{\partial x_\alpha}\right). \tag{25}$$

The phonon hydrodynamic equation is achieved by putting Eq. (25) into the balance equation (19) of heat flux [31]:

$$\tau_{\mathrm{R}}\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \boldsymbol{\nabla} T + \frac{1}{5}\Lambda^2\left[\nabla^2 \mathbf{q} + \frac{1}{3}\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{q})\right]. \tag{26}$$

The preceding derivation in the level of moment equations has a counterpart in the level of the phonon distribution function. The perturbation expansion around f_4 in Eq. (20) gives rise to the phonon distribution function as

$$f = f_{\mathrm{R}}^{\mathrm{eq}} - \tau_{\mathrm{R}}\left(\frac{\partial f}{\partial t} + \mathbf{v}_{\mathrm{g}}\cdot\boldsymbol{\nabla} f\right)\Bigg|_{f_4}. \tag{27}$$

Substituting Eq. (20) into Eq. (27), we get the nonequilibrium phonon distribution solution corresponding to the phonon hydrodynamic equation (26):

$$f = f_{\mathrm{R}}^{\mathrm{eq}} + \phi, \tag{28}$$

where the perturbation quantity is fully expressed as

$$\phi = \frac{3}{C_V v_{\mathrm{g}}^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T} q_\alpha v_{\mathrm{g}\alpha} + \frac{\tau_{\mathrm{R}}}{C_V}\frac{\partial q_\alpha}{\partial x_\alpha}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T} - \frac{3\tau_{\mathrm{R}}}{C_V v_{\mathrm{g}}^2} v_{\mathrm{g}\alpha} v_{\mathrm{g}\beta}\frac{\partial q_\alpha}{\partial x_\beta}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}. \tag{29}$$

The phonon hydrodynamic equation (26) has a very similar mathematical form to the nonlocal heat transport equation in the phenomenological phonon hydrodynamic model [17,27–29]:

$$\tau_{\mathrm{R}}\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \boldsymbol{\nabla} T + l^2[\nabla^2 \mathbf{q} + 2\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{q})], \tag{30}$$

where l denotes a characteristic length of phonon dynamics and is often assumed as the value of the phonon mean free path. Equation (30) is actually adapted from the classical G-K hydrodynamic equation of phonon transport in dielectric crystals at low temperature [16,24]:

$$\tau_{\mathrm{R}}\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \boldsymbol{\nabla} T + \frac{1}{5} v_{\mathrm{g}}^2 \tau_{\mathrm{N}} \tau_{\mathrm{R}}[\nabla^2 \mathbf{q} + 2\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{q})], \tag{31}$$

with τ_{N} the relaxation time of phonon normal scattering. Therefore, our theoretical derivation of Eq. (26) from the phonon Boltzmann equation provides a solid kinetic foundation to the phonon hydrodynamic model for nanoscale heat transport around ordinary temperatures [31].

Finally we would like to clarify two widely used concepts in the literature: (i) hydrodynamic phonon transport (or phonon hydrodynamic phenomena) and (ii) the phonon hydrodynamic equation (or model). “Hydrodynamic phonon transport” refers to the heat transport processes where phonon normal scattering plays a dominant role. As quasimomentum is conserved in normal scattering, the behaviors of phonon transport resemble those of fluid flow, including the phonon Poiseuille flow and second sound [16,47,48]. In contrast, the “phonon hydrodynamic equation” refers to the macroscopic theoretical description of heat transport derived from the phonon Boltzmann equation [16,17,23,31]. The heat transport could be any kind, including hydrodynamic phonon transport and nanoscale heat transport at room temperatures where phonon resistive scattering dominates. The indirect correspondence between hydrodynamic phenomena and the hydrodynamic equation in phonon transport can be understood from the history of the terminology. The “hydrodynamic equations” originally referred to the fluid dynamic equations including the Euler equations and Navier-Stokes equations proposed during 18th to 19th centuries [9]. With the development of the kinetic theory of gases in the late 19th century and early 20th century, the hydrodynamic equations were derived through the classical Chapman-Enskog expansion to the Boltzmann transport equation [1]. Later the kinetic theory was extensively developed for transport processes via other microscopic particles [2,9]. Thus the macroscopic transport equations derived from the mesoscopic Boltzmann equation are often called hydrodynamic equations along the terminology in gas kinetic theory, as for phonons [16,52], electrons [53,54], photons [55,56], and so on. Although the earliest version was derived in the study of hydrodynamic phonon transport [16,52], phonon hydrodynamic equations represent, in a broader context, all the macroscopic heat transport equations derived from the phonon Boltzmann equation.

B. Kinetic derivation of entropy density

The macroscopic expression of entropy density can be obtained by substituting the nonequilibrium phonon distribution solution Eq. (28) into its kinetic definition Eq. (2). With also the help of approximations Eqs. (12) and (13), we arrive at

$$s = s_{\mathrm{eq}} - \frac{1}{2}k_{\mathrm{B}}\int \frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k}. \tag{32}$$

For nanoscale heat transport with strong nonequilibrium effects, the perturbation part Eq. (29) is expected to be non-negligible. Therefore the second term in Eq. (32) will be no longer negligibly small as in CIT, and is computed by putting Eq. (29) into it

$$\int \frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k} = \left[\begin{array}{l} \int \frac{9}{C_V^2 v_{\mathrm{g}}^4} q_\alpha q_\beta v_{\mathrm{g}\alpha} v_{\mathrm{g}\beta} \frac{\hbar\omega}{k_{\mathrm{B}}T^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}d\mathbf{k} + \int \frac{\tau_{\mathrm{R}}^2}{C_V^2}\left(\frac{\partial q_\beta}{\partial x_\beta}\right)^2 \frac{\hbar\omega}{k_{\mathrm{B}}T^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}d\mathbf{k} \\ + \int \frac{9\tau_{\mathrm{R}}^2}{C_V^2 v_{\mathrm{g}}^4}\left(\frac{\partial q_\alpha}{\partial x_\beta}\right)\left(\frac{\partial q_m}{\partial x_n}\right) v_{\mathrm{g}\alpha} v_{\mathrm{g}\beta} v_{\mathrm{g}m} v_{\mathrm{g}n} \frac{\hbar\omega}{k_{\mathrm{B}}T^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}d\mathbf{k} \\ - \int \frac{6\tau_{\mathrm{R}}^2}{C_V^2 v_{\mathrm{g}}^2}\left(\frac{\partial q_\beta}{\partial x_\beta}\right)\left(\frac{\partial q_m}{\partial x_n}\right) v_{\mathrm{g}m} v_{\mathrm{g}n} \frac{\hbar\omega}{k_{\mathrm{B}}T^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}d\mathbf{k} \end{array}\right]. \tag{33}$$

There are only four terms left on the right-hand side of Eq. (33) as the integrands in the other two terms from ϕ^2 are odd functions of the wave vector. After integration and combination, the integral Eq. (33) becomes

$$\int \frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k} = \frac{3\mathbf{q}\cdot\mathbf{q}}{C_V k_{\mathrm{B}} T^2 v_{\mathrm{g}}^2} + \frac{6}{5}\frac{\tau_{\mathrm{R}}^2}{C_V k_{\mathrm{B}} T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}, \tag{34}$$

where the symmetric traceless part of the second-order tensor $\nabla\mathbf{q}$ is fully expressed as

$$(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} = \tfrac{1}{2}[\nabla\mathbf{q} + (\nabla\mathbf{q})^{\mathrm{T}}] - \tfrac{1}{3}(\nabla\cdot\mathbf{q})\mathbf{I}, \tag{35}$$

with the superscript “T” denoting the transpose of a tensor and $\mathbf{I}$ denoting the unit tensor. Substitution of Eq. (34) into Eq. (32) yields the macroscopic expression of entropy density as

$$s = s_{\mathrm{eq}} - \frac{3\mathbf{q}\cdot\mathbf{q}}{2C_V T^2 v_{\mathrm{g}}^2} - \frac{3}{5}\frac{\tau_{\mathrm{R}}^2}{C_V T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}. \tag{36}$$

Supplemented with the kinetic definition Eq. (11) of bulk thermal conductivity, Eq. (36) is further reformulated into the following form:

$$s = s_{\mathrm{eq}} - \frac{\tau_{\mathrm{R}}}{2\lambda T^2}\mathbf{q}\cdot\mathbf{q} - \frac{\tau_{\mathrm{R}}}{5\lambda T^2}\Lambda^2(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}. \tag{37}$$

The presence of the terms in the gradients has been explored from the macroscopic perspective in some theories of weakly nonlocal thermodynamics [3,57].

C. Kinetic derivation of entropy flux

The macroscopic expression of entropy flux can be obtained by substituting the nonequilibrium phonon distribution Eq. (28) into its kinetic definition Eq. (5). With also the help of approximations Eqs. (12) and (13), we arrive at

$$J_\gamma^s = -k_{\mathrm{B}}\int v_{\mathrm{g}\gamma}\phi\left[\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\right]d\mathbf{k} - \frac{1}{2}k_{\mathrm{B}}\int v_{\mathrm{g}\gamma}\frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k}. \tag{38}$$

When putting the perturbation part Eq. (29) into Eq. (38), the first integral term on the right-hand side of Eq. (38) is reduced to

$$\int v_{\mathrm{g}\gamma}\phi\left[\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\right]d\mathbf{k} = \int v_{\mathrm{g}\alpha} v_{\mathrm{g}\gamma} q_\alpha \frac{3}{C_V v_{\mathrm{g}}^2}\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}\left[\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\right]d\mathbf{k}, \tag{39}$$

where two terms have been vanished as the integrands are odd functions of the wave vector. Since $\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln(1+f_{\mathrm{R}}^{\mathrm{eq}}) = -\hbar\omega/k_{\mathrm{B}}T$, Eq. (39) further becomes

$$\int v_{\mathrm{g}\gamma}\phi\left[\ln f_{\mathrm{R}}^{\mathrm{eq}} - \ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\right]d\mathbf{k} = -\frac{q_\gamma}{k_{\mathrm{B}}T}. \tag{40}$$

Thus the first term on the right-hand side of Eq. (38) is exactly the contribution of classical entropy flux Eq. (17). The second integral term on the right-hand side of Eq. (38) becomes increasingly important in nanoscale heat transport, and is computed by putting Eq. (29) into it

$$\int v_{\mathrm{g}\gamma}\frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k} = \int \frac{v_{\mathrm{g}\gamma}}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}\left[\frac{6\tau_{\mathrm{R}}}{C_V^2 v_{\mathrm{g}}^2} v_{\mathrm{g}\alpha} q_\alpha \frac{\partial q_\beta}{\partial x_\beta}\left(\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}\right)^2 - \frac{18\tau_{\mathrm{R}}}{C_V^2 v_{\mathrm{g}}^4} v_{\mathrm{g}\alpha} v_{\mathrm{g}m} v_{\mathrm{g}n} q_\alpha \frac{\partial q_m}{\partial x_n}\left(\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T}\right)^2\right]d\mathbf{k}, \tag{41}$$

where four terms have vanished as the integrands are odd functions of the wave vector. Since $\frac{\partial f_{\mathrm{R}}^{\mathrm{eq}}}{\partial T} = f_{\mathrm{R}}^{\mathrm{eq}}(1 + f_{\mathrm{R}}^{\mathrm{eq}})\frac{\hbar\omega}{k_{\mathrm{B}}T^2}$, Eq. (41) further becomes

$$\begin{aligned}\int v_{\mathrm{g}\gamma}\frac{\phi^2}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1 + f_{\mathrm{R}}^{\mathrm{eq}}\right)}d\mathbf{k} \\ = \frac{4\tau_{\mathrm{R}}}{5C_V k_{\mathrm{B}}T^2}q_\gamma\frac{\partial q_\beta}{\partial x_\beta} - \frac{6\tau_{\mathrm{R}}}{5C_V k_{\mathrm{B}}T^2}q_\alpha\left(\frac{\partial q_\alpha}{\partial x_\gamma} + \frac{\partial q_\gamma}{\partial x_\alpha}\right).\end{aligned} \quad (42)$$

Substituting Eqs. (40) and (42) into Eq. (38), we finally obtain the macroscopic expression of the entropy flux:

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} - \frac{2\tau_{\mathrm{R}}}{5C_V T^2}\mathbf{q}(\nabla\cdot\mathbf{q}) + \frac{3\tau_{\mathrm{R}}}{5C_V T^2}\mathbf{q}\cdot[\nabla\mathbf{q} + (\nabla\mathbf{q})^{\mathrm{T}}]. \quad (43)$$

Supplemented with the kinetic definition Eq. (11) of bulk thermal conductivity as well as Eq. (35), Eq. (43) is further reformulated into the following compact form:

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \frac{2\Lambda^2}{5\lambda T^2}\mathbf{q}\cdot(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}. \quad (44)$$

Some macroscopic physical consequences of a phenomenological entropy flux of a similar form to Eq. (44) (yet without explicit mesoscopic evaluation of the coefficient for the second term) have been examined in Ref. [40] in the context of radial heat transport through cylindrical geometry.

D. Extended irreversible thermodynamic foundation

With the explicit macroscopic expressions of entropy density and entropy flux, we will now demonstrate that the phonon hydrodynamic equation (26) is compatible with the second law in the framework of EIT. In CIT for Fourier's law, the energy density is the only one in state variable space such that the entropy density is $s_{\mathrm{eq}} = s_{\mathrm{eq}}(e)$ with the Gibbs relation:

$$T\,ds_{\mathrm{eq}} = de. \quad (45)$$

The main idea of EIT is to include also the dissipative variables into the state variable space. In the conventional scheme of EIT, the dissipative variables include the heat flux $\mathbf{q}$, the flux of heat flux $\mathbf{Q}$, and higher-order moment variables such that the entropy is defined as $s = s(e,\ \mathbf{q},\ \mathbf{Q}, \ldots)$ [43]. In the present paper, we introduce a slightly different scheme based on Eq. (37): $s = s(e, \mathbf{q}, (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}})$. Later we will show that the present scheme is equivalent to the conventional one due to the relation between the flux of heat flux and the heat flux gradient. With the help of Eq. (45), the generalized Gibbs relation is obtained from Eq. (37) as below:

$$ds = \frac{de}{T} - \frac{\tau_{\mathrm{R}}}{\lambda T^2}\mathbf{q}\cdot d\mathbf{q} - \frac{2\tau_{\mathrm{R}}}{5\lambda T^2}\Lambda^2(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : d(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}. \quad (46)$$

Equation (46) can be further rewritten as the time derivative form:

$$\frac{ds}{dt} = \frac{1}{T}\frac{de}{dt} - \frac{\tau_{\mathrm{R}}}{\lambda T^2}\mathbf{q}\cdot\frac{d\mathbf{q}}{dt} - \frac{2\tau_{\mathrm{R}}}{5\lambda T^2}\Lambda^2(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : \frac{d(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}}{dt}. \quad (47)$$

The symmetric traceless part of the tensor $\nabla\mathbf{q}$ is related to the first-order component of the flux of heat flux as $\mathbf{Q}^{(1)} = -\frac{2}{5}\tau_{\mathrm{R}}v_{\mathrm{g}}^2(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}$. The flux of heat flux Eq. (25) can be split into a trace part and a traceless part as $\mathbf{Q} = Q\mathbf{I} + \mathbf{Q}_{\mathrm{o}}$, with $Q\mathbf{I} = \mathbf{Q}^{(0)} = \frac{1}{3}v_{\mathrm{g}}^2 e\mathbf{I}$ and $\mathbf{Q}_{\mathrm{o}} = \mathbf{Q}^{(1)}$. Since the temporal variation of higher-order moment $\mathbf{Q}^{(1)}$ has been assumed to be in a smaller order of magnitude than that of heat flux in the derivation of the phonon hydrodynamic equation in Sec. III A, the third term on the right-hand side of Eq. (47) is thus negligibly small comparing to the second term. In this way, Eq. (47) is reduced to

$$\frac{ds}{dt} = \frac{1}{T}\frac{de}{dt} - \frac{\tau_{\mathrm{R}}}{\lambda T^2}\mathbf{q}\cdot\frac{d\mathbf{q}}{dt}. \quad (48)$$

With the help of energy balance equation (18), Eq. (48) is reformulated into the following form:

$$\frac{ds}{dt} = -\frac{1}{T}\nabla\cdot\mathbf{q} - \frac{\tau_{\mathrm{R}}}{\lambda T^2}\mathbf{q}\cdot\frac{d\mathbf{q}}{dt}. \quad (49)$$

Below we will derive the macroscopic expression of entropy generation based on the entropy balance equation (4) together with Eqs. (49) and (44).

With the help of the derived macroscopic expression Eq. (44) of entropy flux, the divergence of entropy flux is calculated as below:

$$\begin{aligned}\nabla\cdot\mathbf{J}^s \\ = \frac{1}{T}\nabla\cdot\mathbf{q} + \mathbf{q}\cdot\left\{\nabla\left(\frac{1}{T}\right) + \frac{\Lambda^2}{5\lambda T^2}\left[\frac{1}{3}\nabla(\nabla\cdot\mathbf{q}) + \nabla^2\mathbf{q}\right]\right\} \\ + \frac{2\Lambda^2}{5\lambda T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}},\end{aligned} \quad (50)$$

where λT^2 has been assumed as a constant as in CIT [7]. Combining Eqs. (49) and (50), we get exactly the entropy balance equation as

$$\begin{aligned}\frac{\partial s}{\partial t} + \nabla\cdot\mathbf{J}^s \\ = \frac{\mathbf{q}}{\lambda T^2}\cdot\left\{-\lambda\nabla T - \tau_{\mathrm{R}}\frac{d\mathbf{q}}{dt} + \frac{\Lambda^2}{5}\left[\frac{1}{3}\nabla(\nabla\cdot\mathbf{q}) + \nabla^2\mathbf{q}\right]\right\} \\ + \frac{2\Lambda^2}{5\lambda T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}.\end{aligned} \quad (51)$$

An identification of Eq. (51) to Eq. (4) gives rise to the macroscopic expression of entropy generation:

$$\begin{aligned}\sigma^s = \frac{\mathbf{q}}{\lambda T^2}\cdot\left\{-\lambda\nabla T - \tau_{\mathrm{R}}\frac{d\mathbf{q}}{dt} + \frac{\Lambda^2}{5}\left[\frac{1}{3}\nabla(\nabla\cdot\mathbf{q}) + \nabla^2\mathbf{q}\right]\right\} \\ + \frac{2\Lambda^2}{5\lambda T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}.\end{aligned} \quad (52)$$

Supplemented with the phonon hydrodynamic equation (26), the entropy generation expression Eq. (52) becomes

$$\sigma^s = \frac{\mathbf{q}\cdot\mathbf{q}}{\lambda T^2} + \frac{2\Lambda^2}{5\lambda T^2}(\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}} : (\nabla\mathbf{q})_{\mathrm{o}}^{\mathrm{s}}. \quad (53)$$

The non-negativeness of entropy generation is explicitly ensured: $\sigma^s \geqslant 0$ due to the quadratic form of its expression. In other words, the phonon hydrodynamic equation (26) for nanoscale heat transport at ordinary temperature is consistent with the second law in the frame of EIT.

There have been several macroscopic proposals of the EIT scheme for the phonon hydrodynamic models as introduced in Sec. I and further summarized in Table I. The flux of heat flux is usually elevated into the state variable space. The relaxation time of the flux of heat flux has been assumed negligibly small

TABLE I. Summary of extended irreversible thermodynamics for phonon hydrodynamic models. The flux of heat flux is split into a trace part and a traceless part as $\mathbf{Q} = Q\mathbf{I} + \mathbf{Q}_\text{o}$.

Entropy density	Entropy flux	Heat transport equation	Reference
$s = s(e, \mathbf{q}, \mathbf{Q}_\text{o}, Q)$	$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \frac{1}{\lambda T^2}(\mathbf{Q}_\text{o} \cdot \mathbf{q} + Q\mathbf{q})$	Eq. (31)	[32]
$s = s(e, \mathbf{q})$	$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \frac{l^2}{\lambda T^2}(\mathbf{q} \cdot \nabla\mathbf{q} + 2\mathbf{q}\nabla \cdot \mathbf{q})$	Eq. (30)	[39,41]
$s = s(e, \mathbf{q}, \mathbf{Q})$	$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \frac{l^2}{\lambda T^2}(\nabla\mathbf{q})^\text{T} \cdot \mathbf{q}$	$\tau_\text{R} \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda\nabla T + l^2\nabla^2\mathbf{q}$	[40]
$s = s\big(e, \mathbf{q}, (\nabla\mathbf{q})_\text{o}^\text{s}\big)$	$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \frac{2\Lambda^2}{5\lambda T^2}\mathbf{q} \cdot (\nabla\mathbf{q})_\text{o}^\text{s}$	Eq. (26)	Present paper

in the derivation of the G-K heat transport equation such that the flux of heat flux becomes proportional to the heat flux gradient [32,40]. Thus the present EIT scheme is actually equivalent to the conventional one. Nevertheless, the heat flux gradient is chosen as one of the state variables in the present EIT scheme since the expression Eq. (37) of entropy density is a natural production from the kinetic theory of phonons. The mesoscopic foundation of EIT has been discussed from Grad's 13-moment kinetic theory of gases, which results in the macroscopic expressions of entropy density and entropy flux, respectively [43]:

$$\rho s = \rho s_\text{eq} - \frac{m}{5pk_\text{B}T^2}\mathbf{q} \cdot \mathbf{q} - \frac{1}{4pT}\mathbf{P}_\text{o}^v : \mathbf{P}_\text{o}^v, \tag{54}$$

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} - \frac{2}{5pT}\mathbf{P}_\text{o}^v \cdot \mathbf{q}, \tag{55}$$

where p and $\mathbf{P}_\text{o}^v$ denote, respectively, the thermodynamic pressure and the viscous pressure tensor. The flux of heat flux in phonon transport plays a similar role as the viscous pressure tensor in gas transport [23]. With the aid of the linear relation between the flux of heat flux and the heat flux gradient, the expressions of entropy density Eq. (37) and entropy flux Eq. (44) have similar mathematical form as Eqs. (54) and (55) separately. Our paper represents a direct mesoscopic foundation for EIT of phonon heat transport in dielectric crystals far from the equilibrium state. In other words, in contrast to the previous extended nonequilibrium thermodynamics for heat conduction discussed from a macroscopic phenomenological perspective without a direct statistical mechanical basis [32,36–38,40,41,58], the present EIT scheme is developed from the kinetic theory of phonons in a more rigorous way.

IV. INTERFACIAL ENTROPY GENERATION

The previous section is focused on the expressions of entropy density, entropy flux, and entropy generation in the bulk region of nanosystems. Before the close of this paper, we would like to discuss the role of interfacial entropy generation at the system boundary. The interfacial entropy generation has been extensively explored in rarified gas flows, and shown to have an intimate relation with the nonequilibrium boundary conditions in the framework of irreversible thermodynamics [59,60]. On the other hand, with the increasing importance of particle-boundary scattering over the particle-particle scattering at decreasing system size, the interfacial entropy generation becomes a significant contribution to the total entropy generation in microscale gas transport [61]. In recent years, the thermodynamic consistency of the nonequilibrium boundary condition in nanoscale heat transport has been investigated in terms of the interfacial entropy generation [42,58], where both the phenomenological phonon hydrodynamic equation and heat flow boundary condition were derived from EIT on a macroscopic basis. In the present section, the macroscopic expression of interfacial entropy generation will be derived from the kinetic theory of phonons. Therefore, we provide a mesoscopic foundation to the nonequilibrium thermodynamic formulation of the boundary condition for the phonon hydrodynamic equation.

We will derive the interfacial entropy generation at the lower boundary within the in-plane phonon transport as shown in Fig. 1. Based on the entropy balance at the boundary and the kinetic definition of entropy flux in Eq. (5), the mesoscopic expression of interfacial entropy generation is obtained as

$$\sigma_\text{i}^s = -k_\text{B} \int v_{\text{g}y}[f_\text{w} \ln f_\text{w} - (1 + f_\text{w}) \ln (1 + f_\text{w})]d\mathbf{k}, \tag{56}$$

where the distribution function of phonons at the boundary is

$$f_\text{w} = \begin{cases} f^-, & \mathbf{k} \cdot \mathbf{n} < 0 \\ f^+, & \mathbf{k} \cdot \mathbf{n} > 0 \end{cases}, \tag{57}$$

with $\mathbf{n}$ the surface unit normal vector as shown in Fig. 1. The distribution function of phonons incident on the boundary can be determined from the nonequilibrium distribution solution Eq. (28) in the bulk region, which is further reduced to

$$f^- = f_\text{R}^\text{eq} + \phi, \tag{58}$$

with the perturbation quantity expressed as

$$\phi = \frac{3}{C_V v_\text{g}^2} \frac{\partial f_\text{R}^\text{eq}}{\partial T} q_{x\text{w}} v_{\text{g}x} - \frac{3\tau_\text{R}}{C_V v_\text{g}^2} v_{\text{g}x} v_{\text{g}y} \left(\frac{\partial q_x}{\partial y}\right)_\text{w} \frac{\partial f_\text{R}^\text{eq}}{\partial T}. \tag{59}$$

The distribution function of phonons leaving from the boundary is correlated to that of incident phonons through the Maxwell model of particle-boundary interaction [50]. For simplicity, the widely used fully thermalizing diffuse

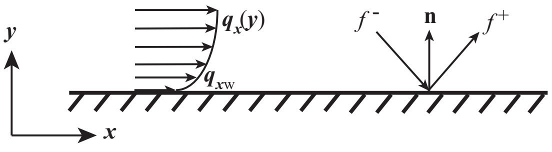

FIG. 1. Schematic of in-plane phonon transport for the derivation of interfacial entropy generation.

phonon-boundary scattering is assumed [62]:

$$f^{+} = f_{\mathrm{R}}^{\mathrm{eq}}. \tag{60}$$

Substitution of Eqs. (58) and (60) into Eq. (56) gives the interfacial entropy generation as

$$\begin{aligned}\sigma_{\mathrm{i}}^{s} = &-k_{\mathrm{B}} \int_{\Omega^{-}} v_{gy}\left(f^{-} \ln f^{-} - f_{\mathrm{R}}^{\mathrm{eq}} \ln f_{\mathrm{R}}^{\mathrm{eq}}\right) d\mathbf{k} \\ &+ k_{\mathrm{B}} \int_{\Omega^{-}} v_{gy}\left[(1+f^{-})\ln(1+f^{-})\right. \\ &\left. - \left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)\right] d\mathbf{k},\end{aligned} \tag{61}$$

where Ω^{-} represents the hemispherical wave-vector space with $\mathbf{k}\cdot\mathbf{n} < 0$. Supplemented with the approximations Eqs. (12) and (13), Eq. (61) will be reduced to

$$\begin{aligned}\sigma_{\mathrm{i}}^{s} = k_{\mathrm{B}} \int_{\Omega^{-}} v_{gy} \Bigg\{ &\phi\left[\ln\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right) - \ln f_{\mathrm{R}}^{\mathrm{eq}}\right] \\ &- \frac{\phi^{2}}{2 f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)}\Bigg\} d\mathbf{k},\end{aligned} \tag{62}$$

The first term on the right-hand side of Eq. (62) proportional to ϕ has vanishing contribution to the integral as the integrand is an odd function of k_x. Thus Eq. (62) is further simplified as

$$\sigma_{\mathrm{i}}^{s} = -\frac{1}{2} k_{\mathrm{B}} \int_{\Omega^{-}} \frac{v_{gy}\phi^{2}}{f_{\mathrm{R}}^{\mathrm{eq}}\left(1+f_{\mathrm{R}}^{\mathrm{eq}}\right)} d\mathbf{k}. \tag{63}$$

Putting Eq. (59) into Eq. (63) and completing the integration, we get the macroscopic expression of interfacial entropy generation as

$$\begin{aligned}\sigma_{\mathrm{i}}^{s} = &\frac{9}{32}\frac{q_{x\mathrm{w}}^{2}}{C_V v_{\mathrm{g}} T^{2}} + \frac{3}{32}\frac{\tau_{\mathrm{R}}^{2} v_{\mathrm{g}}}{C_V T^{2}}\left(\frac{\partial q_x}{\partial y}\right)_{\mathrm{w}}^{2} \\ &+ \frac{3}{10}\frac{\tau_{\mathrm{R}}}{C_V T^{2}} q_{x\mathrm{w}}\left(\frac{\partial q_x}{\partial y}\right)_{\mathrm{w}}.\end{aligned} \tag{64}$$

The heat flux tangential retardant boundary condition has been also derived from the principle in kinetic theory of phonons for the phonon hydrodynamic equation (26) [31]:

$$q_{x\mathrm{w}} = \frac{8}{15}\Lambda\left(\frac{\partial q_x}{\partial y}\right)_{\mathrm{w}}. \tag{65}$$

The boundary term of this form or similar forms plays a significant role in the explanation of the effective thermal conductivity of nanostructures [17,28,31]. With the help of Eq. (65), the macroscopic expression Eq. (64) of interfacial entropy generation finally becomes

$$\sigma_{\mathrm{i}}^{s} = \frac{801}{2048}\frac{\Lambda q_{x\mathrm{w}}^{2}}{\lambda T^{2}} \approx 0.4\frac{\Lambda q_{x\mathrm{w}}^{2}}{\lambda T^{2}}. \tag{66}$$

The non-negativeness of interfacial entropy generation in Eq. (66) is thus explicit, which infers that the nonequilibrium boundary condition Eq. (65) for the phonon hydrodynamic equation (26) is consistent with the second law of thermodynamics. The mathematical form as a square of boundary heat flux is exactly the same as that of boundary entropy generation in previous EIT formulation [42,58].

V. CONCLUSIONS

In this paper, we have provided the nonequilibrium thermodynamic foundation to the phonon hydrodynamic model for nanoscale heat transport at ordinary temperatures. The macroscopic expressions of entropy density Eq. (37) and entropy flux Eq. (44) are derived from their kinetic definitions in terms of the nonequilibrium phonon distribution solution. The phonon hydrodynamic equation is thus verified to be consistent with the second law in the frame of extended irreversible thermodynamics. On the other hand, we have computed the macroscopic expression of interfacial entropy generation Eq. (66) from the kinetic theory of phonons, and shown that the heat flow boundary condition for the phonon hydrodynamic equation also meets the thermodynamic requirement. This paper provides a solid mesoscopic theoretical foundation to the previous macroscopic nonequilibrium thermodynamics for the phonon hydrodynamic model in nanoscale heat transport. Our analysis could be generalized, with suitable modifications, to incorporate the contribution of phonon normal scattering and electrons to heat transfer in future work.

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