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Entropic Constitutive Relation and Modeling for Fourier and Hyperbolic Heat Conductions

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Abstract: Most existing phenomenological heat conduction models are expressed by temperature and heat flux distributions, whose definitions might be debatable in heat conductions with strong non-equilibrium. The constitutive relations of Fourier and hyperbolic heat conductions are here rewritten by the entropy and entropy flux distributions in the frameworks of classical irreversible thermodynamics (CIT) and extended irreversible thermodynamics (EIT). The entropic constitutive relations are then generalized by Boltzmann–Gibbs–Shannon (BGS) statistical mechanics, which can avoid the debatable definitions of thermodynamic quantities relying on local equilibrium. It shows a possibility of modeling heat conduction through entropic constitutive relations. The applicability of the generalizations by BGS statistical mechanics is also discussed based on the relaxation time approximation, and it is found that the generalizations require a sufficiently small entropy production rate.

Keywords: entropic constitutive relation; Fourier’s law; hyperbolic heat conduction; statistical mechanics

1. Introduction

Fourier’s law of heat conduction is the most classical heat conduction model, which has been proved by numerous experiments and widely applied to engineering. As a phenomenological model, Fourier’s law describes the constitutive relation between the temperature gradient and heat flux

$$\mathbf{q}(\mathbf{x}, t) = -\lambda \nabla T(\mathbf{x}, t), \quad (1)$$

where \mathbf{q} is the heat flux, λ is the thermal conductivity and T is the temperature. For constant material properties, the governing equation of Fourier’s law is a linear parabolic equation

$$\frac{\partial T}{\partial t} = a \nabla^2 T, \quad (2)$$

where $a = \lambda / \rho c_V$ is the thermal diffusivity, ρ is the mass density and c_V is the specific heat. Equation (2) will predict a global response to a sudden thermal disturbance at some point on the body, which corresponds to infinite speeds of heat propagation. Although the amplitudes of the response will be exponentially small at distant points, it neglects the time needed for the acceleration of heat flow, as was argued by Onsager [1]. A thermal relaxation between the heat flux and temperature gradient is introduced in the Cattaneo–Vernotte (CV) model [2,3] to overcome this unphysical behavior, vis.,

$$\mathbf{q}(\mathbf{x}, t) + \tau_q \frac{\partial \mathbf{q}(\mathbf{x}, t)}{\partial t} = -\lambda \nabla T(\mathbf{x}, t), \quad (3)$$

where τ_q is the relaxation time of the heat flux. The CV model gives rise to a hyperbolic or telegraph governing equation

$$\frac{\partial T}{\partial t} + \tau_q \frac{\partial^2 T}{\partial t^2} = a \nabla^2 T, \quad (4)$$

which predicts a finite nominal wave velocity $\sqrt{a/\tau_q}$ of heat propagation. In the spirit of thermal relaxation, different non-Fourier heat conduction models were developed [4–12], i.e., the Jeffrey model [4,5], a linear superposition of Fourier's law and the CV model. The constitutive relations of these hyperbolic models can usually be rewritten as the following memory behaviors between the temperature gradient and heat flux [4],

$$\mathbf{q}(\mathbf{x}, t) = - \int_{-\infty}^t M_q(t - \eta) \nabla T(\mathbf{x}, \eta) d\eta, \quad (5)$$

where $M_q(t)$ is the memory kernel of the heat flux (or relaxation function). Different constitutive relations can be given from different choices of the memory kernels. Exponential and Dirac delta functions are the most common types. The CV model has an exponential kernel $M_q(t) = \lambda \exp\left(-\frac{t}{\tau_q}\right)$ and if the Dirac delta function $M_q(t) = \lambda \delta(t - \tau_q)$ is applied, the phase-lagging model will arise [6,7],

$$\mathbf{q}(\mathbf{x}, t + \tau_q) = -\lambda \nabla T(\mathbf{x}, t). \quad (6)$$

The power-law memory kernel $M_q(t) \propto t^{-\alpha}$ (α is a positive constant) can also be used, and fractional differential operators have also appeared [10,11]. It should be noted that wave-like transport with finite speeds of heat propagation can also be predicted by Fourier's law in the cases of temperature-dependent thermal properties. For instance, in fast (superfast) diffusion [13] $\lambda = \lambda(T) \propto \frac{1}{T^\beta}$ ($0 < \beta < 2$ and ρc_V is a constant), there also exists the travelling wave solution $T(x, t) = \Phi(x - Vt) + \Psi(x + Vt)$ with the wave velocity V , which will show hyperbolic or wave-like characteristics. Although Fourier's law can also predict finite speeds of heat propagation, non-Fourier modeling is still necessary from the point view of mathematics and physics. In mathematics, non-linear Fourier heat conduction with temperature-dependent thermal properties might not be well-posed, i.e., for the cases of $\alpha < -1$, there are no physically meaningful solutions in multi-dimensional problems [13]. In terms of physics, Fourier's law is valid in the near-equilibrium region and hyperbolic modifications are needed for reflecting effects by strong non-equilibrium. The non-Fourier effects are obvious in small-scale and super-transient heat transport, where the characteristic size and time of the system are comparable to the mean free path and relaxation time of the heat carriers, respectively. Although the non-Fourier models aim at exhibiting more detailed non-equilibrium effects than Fourier's law, their constitutive relations are still expressed by the temperature and heat flux distributions paired with their derivatives. Strictly speaking, the definitions of these macroscopic quantities and their derivatives also have certain requirements on local equilibrium. For instance, as the scale decreases to zero, it would be inappropriate to define a continuous temperature distribution or its spatial differentials for a sufficiently small scale. The definition of temperature in heat conduction in strong non-equilibrium remains a debatable open problem. Although statistical mechanics can be introduced to deal with the non-equilibrium effects on "temperature" [14], it also needs appropriate assumptions, i.e., the form of the distribution function [14]. Compared with temperature, as another fundamental concept in thermodynamics, entropy also relies on equilibrium states and large physical systems in classical thermodynamics, but there exists a universal form of entropy based on Boltzmann–Gibbs–Shannon (BGS) statistical mechanics.

$$S_{BGS} = -k_B \sum f \ln f, \quad (7)$$

where k_B is the Boltzmann constant, \sum is the summation (or integral) operator in phase space and f denotes the one-particle distribution function containing at least spatial and temporal variables.

The distribution function f describes the number density of particles in the one-particle phase space, i.e., in kinetic theory, $f = f(\mathbf{x}, t, \mathbf{v})$ with \mathbf{v} denoting the particle velocity. In this work, the distribution function is governed by the following Boltzmann transport equation without an external force field

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = C(f, f), \quad (8)$$

where $C(f, f)$ is the collision term. For pure heat conduction, there exists no macroscopic motion $\sum \mathbf{v} f = \mathbf{0}$. Analogously, the definition of the heat flux will also be debatable in heat conduction with strong non-equilibrium. Correspondingly, BGS statistical mechanics also gives a universal form for the entropy flux

$$\mathbf{J}_{BGS}^S = -k_B \sum \mathbf{v} f \ln f. \quad (9)$$

These entropic quantities with more universal applicability are also widely discussed and used in macroscopic irreversible processes including heat conduction, which shows a possibility of modeling heat conduction through entropic constitutive relations.

In this work, the constitutive relations of Fourier and hyperbolic heat conduction models are rewritten by the entropy and entropy flux distributions in the frameworks of classical irreversible thermodynamics (CIT) [1,15,16] and extended irreversible thermodynamics (EIT) [16,17]. The entropic constitutive relations are then generalized by Boltzmann–GibbsShannon (BGS) statistical mechanics, and heat conduction modeling is also discussed through entropic constitutive relations. The applicability of the generalizations by BGS statistical mechanics is also studied based on the relaxation time approximation. An inequality is then established between the phenomenological relaxation time and the relaxation time in the Boltzmann equation. Although heat conduction could exist in gas, liquid and solid bodies, wave-like heat transport is mainly observed in solids. Therefore, the medium discussed in this work is limited to solids.

2. Entropic Constitutive Relation and Modeling

2.1. Entropic Constitutive Relation for Fourier's Law

In this subsection, Fourier's law will be transformed into an entropic constitutive relation by the CIT entropy and CIT entropy flux. We start with heat conduction in the near-equilibrium region, where Fourier's law is usually valid. In this case, the framework of classical irreversible thermodynamics [1,15,16] can be applied with the local equilibrium entropy S_{eq} and entropy flux \mathbf{J}^S given by

$$S_{eq}(\mathbf{x}, t) = \int^{T(\mathbf{x}, t)} \rho c_V \frac{dT}{T}, \quad (10a)$$

$$\mathbf{J}^S(\mathbf{x}, t) = \frac{\mathbf{q}(\mathbf{x}, t)}{T(\mathbf{x}, t)}. \quad (10b)$$

Combining the above definitions with Equation (1), Fourier's law is subsequently rewritten as the following form expressed by the CIT entropy and entropy flux

$$\mathbf{J}^S(\mathbf{x}, t) = \frac{\mathbf{q}(\mathbf{x}, t)}{T(\mathbf{x}, t)} = -a \nabla S_{eq}(\mathbf{x}, t). \quad (11)$$

We now obtain an entropic constitutive relation for Fourier's law, which has the same form as Equation (1). Similar to the constitutive relation expressed by the temperature and heat flux, Equation (11) also depends on the instantaneous and local values of the CIT entropy flux and entropy gradient. In this entropic expression of Fourier's law, the thermal diffusivity could be regarded as the transport coefficient of entropy. It is not difficult to find that Equation (11) is also valid in the cases of temperature-dependent material properties, where $\lambda = \lambda(T)$ and $\rho c_V = \rho(T) c_V(T)$. In the near-equilibrium region, the framework of classical irreversible thermodynamics could approximately

agree with statistical mechanics, which means $S_{eq} \cong S_{BGS}$ and $\mathbf{J}_{BGS}^S \cong \mathbf{J}^S$. Then, a generalization of Fourier's law based on BGS statistical mechanics can be proposed as follows

$$\mathbf{J}_{BGS}^S(\mathbf{x}, t) = -a \nabla S_{BGS}(\mathbf{x}, t), \tag{12}$$

which will reduce to Fourier's law in the near-equilibrium region. By replacing the CIT entropy flux \mathbf{J}^S and CIT entropy S_{eq} by the BGS entropy flux \mathbf{J}_{BGS}^S and BGS entropy S_{BGS} , Equation (11) is generalized into a statistical form, Equation (12). $S_{BGS}(\mathbf{x}, t)$ has the same form as Equation (7) but there are more limits on the summation (or integral) operator in phase space Σ . For Equation (12), $S_{BGS}(\mathbf{x}, t)$ is the local entropy density and hence, the spatial variables should not be involved in the operator Σ . Even more, non-extensive statistical mechanics can also be introduced, i.e., the Tsallis entropy of q -indices [18] $S_q = k_B \frac{1-\Sigma f^q}{q-1}$, which will reduce to the BGS entropy as $q \rightarrow 1$. This generalized Fourier law does not rely on local equilibrium or the debatable definition of non-equilibrium temperature, which exhibits better universality than Equation (1). For the closure of the entropic expression, the entropy balance equation is needed

$$\frac{\partial S_{eq}}{\partial t} = -\nabla \cdot \mathbf{J}^S + \sigma_{CIT}, \tag{13}$$

where $\sigma_{CIT} = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) = -\frac{\mathbf{J}^S \cdot \nabla S_{eq}}{\rho c_V}$ is the CIT entropy production rate. Combining Equation (13) with Equation (11), we can obtain the following governing equation for S_{eq} :

$$\begin{aligned} \frac{\partial S_{eq}}{\partial t} &= -\nabla \cdot \mathbf{J}^S + \sigma_{CIT} = -\nabla \cdot \mathbf{J}^S - \frac{\mathbf{J}^S \cdot \nabla S_{eq}}{\rho c_V} = -\nabla \cdot (-a \nabla S_{eq}) - \frac{(-a \nabla S_{eq}) \cdot \nabla S_{eq}}{\rho c_V} \\ \Leftrightarrow \frac{\partial S_{eq}}{\partial t} &= a \nabla^2 S_{eq} + \frac{a}{\rho c_V} |\nabla S_{eq}|^2 \end{aligned} \tag{14a}$$

By taking the gradient of Equation (13), we can also obtain the governing equation for \mathbf{J}^S :

$$\begin{aligned} \nabla \left(\frac{\partial S_{eq}}{\partial t} \right) &= \nabla \left(-\nabla \cdot \mathbf{J}^S - \frac{\mathbf{J}^S \cdot \nabla S_{eq}}{\rho c_V} \right) \\ &= \frac{\partial}{\partial t} \left(\frac{-\mathbf{J}^S}{a} \right) = -\nabla \nabla \cdot \mathbf{J}^S - \nabla \left[\frac{\mathbf{J}^S \cdot \left(\frac{-\mathbf{J}^S}{a} \right)}{\rho c_V} \right] = -\nabla (\nabla \cdot \mathbf{J}^S) + \nabla \left(\frac{\mathbf{J}^S \cdot \mathbf{J}^S}{a \rho c_V} \right) \\ \Leftrightarrow \frac{\partial \mathbf{J}^S}{\partial t} + \frac{1}{\rho c_V} \nabla (\mathbf{J}^S \cdot \mathbf{J}^S) &= a \nabla (\nabla \cdot \mathbf{J}^S). \end{aligned} \tag{14b}$$

Besides parabolic or diffusion terms ($\frac{\partial S_{eq}}{\partial t}$ and $a \nabla^2 S_{eq}$), Equation (14a) also contains a nonlinear term $\frac{a}{\rho c_V} |\nabla S_{eq}|^2$. Equation (14b) will be further simplified. In Fourier heat conduction, taking the curl of \mathbf{J}^S leads to

$$\begin{aligned} \nabla \times \mathbf{J}^S &= -\nabla \times [a(T) \nabla S_{eq}(T)] \\ &= -\left[a(T) \nabla \times \nabla S_{eq}(T) + \frac{da(T)}{dT} \frac{dS_{eq}(T)}{dT} \nabla T \times \nabla T \right] = \mathbf{0}, \end{aligned} \tag{15}$$

and hence we have

$$\nabla (\mathbf{J}^S \cdot \mathbf{J}^S) = 2(\mathbf{J}^S \cdot \nabla) \mathbf{J}^S + 2\mathbf{J}^S \times (\nabla \times \mathbf{J}^S) = 2(\mathbf{J}^S \cdot \nabla) \mathbf{J}^S \tag{16a}$$

$$\nabla (\nabla \cdot \mathbf{J}^S) = \nabla^2 \mathbf{J}^S + \nabla \times (\nabla \times \mathbf{J}^S) = \nabla^2 \mathbf{J}^S. \tag{16b}$$

Then Equation (14b) is simplified into

$$\frac{\partial \mathbf{J}^S}{\partial t} + \frac{2}{\rho c_V} (\mathbf{J}^S \cdot \nabla) \mathbf{J}^S = a \nabla^2 \mathbf{J}^S, \tag{17}$$

and by setting $\mathbf{V}^S = \frac{2}{\rho c_V} \mathbf{J}^S$, a Burgers equation [19] can be obtained

$$\frac{\partial \mathbf{V}^S}{\partial t} + (\mathbf{V}^S \cdot \nabla) \mathbf{V}^S = a \nabla^2 \mathbf{V}^S. \quad (18)$$

A Burgers equation is a simplified momentum equation of the Navier–Stokes equations, which seems that \mathbf{V}^S can be considered as the velocity of entropy flow. In many existing works, vectors proportional to $\frac{\mathbf{q}}{\rho c_V T} = \frac{\mathbf{J}^S}{\rho c_V}$ are usually considered as the speeds of Fourier heat conduction [8,20–23], while here we provide an understanding from entropy transport. Although the entropy flow and fluid velocities obey the same governing equation, their corresponding terms have fundamentally different physical meanings. In Fourier heat conduction, $a \nabla^2 \mathbf{V}^S = a \nabla (\nabla \cdot \mathbf{V}^S)$ is the transport term of entropy flow and $(\mathbf{V}^S \cdot \nabla) \mathbf{V}^S = \frac{1}{2} \nabla (\mathbf{V}^S \cdot \mathbf{V}^S)$ is the term of entropy generation, related to the irreversibility of heat transfer. In contrast, for a Newtonian fluid, $a \nabla^2 \mathbf{V}^S$ is the viscous term resulting in the irreversible viscous dissipation and $(\mathbf{V}^S \cdot \nabla) \mathbf{V}^S$ is the term of convective momentum transport. When the diffusion coefficient $a \rightarrow 0$, Fourier's law predicts a steady-state distributed temperature field and the entropy flow velocity \mathbf{V}^S must be zero. However, in the inviscid limit, the fluid velocity field of a Newtonian fluid is governed by a conservation-law equation, whose solution could be unsteady and non-zero. Therefore, the similarity between the entropy flow velocity in Fourier heat conduction and the fluid velocity of a Newtonian fluid mainly is a pure mathematical property. In fact, this mathematical similarity is guaranteed by the Cole–Hopf transformation [24,25] between the entropy flux velocity \mathbf{V}^S and temperature distribution, $\mathbf{V}^S = -2a \frac{\nabla T}{T} = -2a \nabla (\ln T)$. The governing equation given by Equation (14a) or Equation (14b) cannot give a complete description of heat conduction; we also need the condition determining the solution. For general heat conduction problems, the condition determining the solution is usually given as the boundary and initial value of the temperature. Consider the initial value function $f_T(\mathbf{x})$ and the boundary value function $g_T(\mathbf{x}, t)$, which satisfy $T(\mathbf{x}, t)|_{t=0} = f_T(\mathbf{x})$, $T(\mathbf{x}, t)|_{\Gamma} = g_T(\mathbf{x}, t)$ and $f_T(\mathbf{x})|_{\Gamma} = g_T(\mathbf{x}, t)|_{t=0}$. From Equation (10a), we find that a given initial value function of the temperature can also determine an initial value function of the CIT entropy $f_S(\mathbf{x})$, $S_{eq}(\mathbf{x}, t)|_{t=0} = f_S(\mathbf{x})$. Thus, an initial value problem of the temperature also corresponds to an initial value problem of the CIT entropy. Similarly, $g_T(\mathbf{x}, t)$ also corresponds to a boundary value function of the CIT entropy, $S_{eq}(\mathbf{x}, t)|_{\Gamma} = g_S(\mathbf{x}, t)$. In summary, a boundary and initial value problem of the temperature is also a boundary and initial value problem of the CIT entropy. The solution of a specific problem reflects the effects containing three aspects: constitutive relation, condition determining the solution and entropy balance equation. Generally speaking, the entropy balance is universal in heat conduction, the condition determining the solution is given in terms of practical problems, while the constitutive relation depends directly on the heat transport regime. To reflect the features of the entropic constitutive relation, we provide a well-known type of solution for Equation (18), a solitary wave solution,

$$\mathbf{V}^S = U_S - C_1 \tanh \left[\frac{C_1}{2a} (x - U_S t + C) \right], \quad (19)$$

where U_S is the velocity of entropy transport, $C_1 \geq 0$ and C are integration constants. When $C_1 = 0$, the soliton in Equation (19) degenerates to a trivial solution and the entropy flux velocity \mathbf{V}^S equals the entropy transport velocity U_S . The implicit form of non-trivial shock structure with the natural boundary condition $\lim_{x \rightarrow \pm\infty} |\mathbf{V}^S| < +\infty$ solutions take the following form ($\mathbf{V}_{\infty 1} \neq \mathbf{V}_{\infty 2}$)

$$x - U_S t + C = \frac{2a}{\mathbf{V}_{\infty 1} - \mathbf{V}_{\infty 2}} \ln \frac{\mathbf{V}_{\infty 1} - \mathbf{V}^S}{\mathbf{V}^S - \mathbf{V}_{\infty 2}}. \quad (20)$$

According to the implicit form, we find that, as the traveling wave parameter $\xi = x - U_S t$ approaches infinity, the solitary wave tends to two asymptotic states $\mathbf{V}_{\infty 1}$ and $\mathbf{V}_{\infty 2}$. The average of the asymptotic values equals the entropy transport velocity $U_S = \frac{\mathbf{V}_{\infty 1} + \mathbf{V}_{\infty 2}}{2}$. Specifically, when

$\mathbf{V}_{\infty 1} + \mathbf{V}_{\infty 2} = 0$, meaning a zero transport velocity, it becomes a stationary soliton. The above solution shows that the entropy flow propagates with the form of a solitary wave, and the solitary wave velocity is determined by the boundary entropy flux. These features may provide possible verification for the entropic constitutive relation if the entropy transport in the heat conduction can be observed as the solitary wave of the entropy flux. Further verification can be provided through measurement of the solitary wave velocity, and we can check whether the solitary wave velocity and the corresponding asymptotic states satisfy $U_S = \frac{\mathbf{V}_{\infty 1} + \mathbf{V}_{\infty 2}}{2}$.

2.2. Entropic Constitutive Relation for Hyperbolic Heat Conduction

In this subsection, the entropic constitutive relations of hyperbolic heat conduction will be derived and discussed in the frameworks of CIT and EIT. We now consider the entropic relation for the hyperbolic heat conduction Equation (3). In the framework of classical irreversible thermodynamics, the entropic form of the CV model is given by

$$\left(1 + \frac{\tau_q}{\rho c_V} \frac{\partial S_{eq}}{\partial t}\right) \mathbf{J}^S + \tau_q \frac{\partial \mathbf{J}^S}{\partial t} = -a \nabla S_{eq}. \tag{21}$$

Compared with Equation (3), the entropic constitutive relation Equation (21) contains not only the linear relaxation term $\tau_q \frac{\partial \mathbf{J}^S}{\partial t}$ but also a nonlinear relaxation term $\frac{\tau_q}{\rho c_V} \frac{\partial S_{eq}}{\partial t} \mathbf{J}^S$. This means that a relaxation term between the temperature gradient and heat flux will result in two relaxation terms between the CIT entropy and entropy flux. For constant material properties, we have $S_{eq} = \rho c_V \ln \frac{T}{T_C}$ with T_C denoting the reference temperature. Then, we can obtain $T = T_C \exp\left(\frac{S_{eq}}{\rho c_V}\right)$ and substituting this into the governing equation of the CV model gives

$$T_C \frac{\partial \left[\exp\left(\frac{S_{eq}}{\rho c_V}\right)\right]}{\partial t} + \tau_q T_C \frac{\partial^2 \left[\exp\left(\frac{S_{eq}}{\rho c_V}\right)\right]}{\partial t^2} = a T_C \nabla^2 \left[\exp\left(\frac{S_{eq}}{\rho c_V}\right)\right]. \tag{22a}$$

The above governing equation of CIT entropy can be simplified into the following form

$$\frac{\partial S_{eq}}{\partial t} + \tau_q \frac{\partial^2 S_{eq}}{\partial t^2} + \frac{\tau_q}{\rho c_V} \left(\frac{\partial S_{eq}}{\partial t}\right)^2 = a \nabla^2 S_{eq} + \frac{a}{\rho c_V} |\nabla S_{eq}|^2. \tag{22b}$$

Compared with Equation (4), which consists of diffusion and hyperbolic wave terms, there also exist nonlinear first-order wave terms $\left(\frac{\tau_q}{\rho c_V} \left(\frac{\partial S_{eq}}{\partial t}\right)^2\right)$ and $\frac{a}{\rho c_V} |\nabla S_{eq}|^2$. Different from Fourier heat conduction, the CIT entropy flux of the CV model is not irrotational

$$\nabla \times \mathbf{J}^S = \nabla \times \left(\frac{\mathbf{q}}{T}\right) = \frac{T \nabla \times \mathbf{q} - \nabla T \times \mathbf{q}}{T^2} = \frac{1}{T^2} \left(T \nabla \times \mathbf{q} - \frac{\tau}{\lambda} \frac{\partial \mathbf{q}}{\partial t} \times \mathbf{q}\right), \tag{23}$$

owing to Equation (3). This means that Equation (16a,b) no longer hold, and therefore, the governing equation of the entropy flux cannot be changed into a form similar to the equations in fluid mechanics by the Cole–Hopf transformation. It is found that the linear relaxation between the temperature gradient and heat flux will result in nonlinear effects in the entropic expression of hyperbolic heat conduction. The above discussion of the CV model is based on the CIT entropic definitions. However, the CIT entropy production rate could be negative in hyperbolic heat conduction [26,27]. Accordingly, the CIT entropy might not be valid in hyperbolic heat conduction, which would also make Equations (19) and (20) invalid. In order to guarantee a non-negative form for the entropy production rate in hyperbolic heat conduction, $(\mathbf{q} \cdot \mathbf{q})$ is introduced as a non-equilibrium intrinsic variable of the EIT entropy [16]

$$S_{CV} = S_{eq} - \frac{\tau_q}{2\lambda T^2} \mathbf{q} \cdot \mathbf{q}, \text{ with } \lambda > 0. \tag{24}$$

The entropy flux is still given by Equation (10b), and a non-negative entropy production rate will be guaranteed by requesting that $\sigma_{CV} = \frac{\mathbf{q} \cdot \mathbf{q}}{\lambda T^2} = \frac{\mathbf{J}^S \cdot \mathbf{J}^S}{\lambda} \geq 0$. From Equation (24), we have $S_{eq} = S_{CV} + \frac{\tau_q}{2\lambda} (\mathbf{J}^S \cdot \mathbf{J}^S)$ and substituting this into Equation (21) will lead to

$$\begin{aligned} & \left(1 + \frac{\tau_q}{\rho c_V} \frac{\partial S_{eq}}{\partial t}\right) \mathbf{J}^S + \tau_q \frac{\partial \mathbf{J}^S}{\partial t} = -a \nabla S_{eq} \\ & = \mathbf{J}^S + \tau_q \frac{\partial \mathbf{J}^S}{\partial t} + \mathbf{J}^S \frac{\tau_q}{\rho c_V} \frac{\partial}{\partial t} \left[S_{CV} + \frac{\tau_q}{2\lambda} (\mathbf{J}^S \cdot \mathbf{J}^S) \right] = -a \nabla \left[S_{CV} + \frac{\tau_q}{2\lambda} (\mathbf{J}^S \cdot \mathbf{J}^S) \right] \\ & = \mathbf{J}^S + \tau_q \frac{\partial \mathbf{J}^S}{\partial t} + \frac{\tau_q^2 \mathbf{J}^S}{2\lambda \rho c_V} \frac{\partial (\mathbf{J}^S \cdot \mathbf{J}^S)}{\partial t} + \mathbf{J}^S \frac{\tau_q}{\rho c_V} \frac{\partial S_{CV}}{\partial t} = -a \nabla S_{CV} - \frac{\tau_q}{2\rho c_V} \nabla (\mathbf{J}^S \cdot \mathbf{J}^S). \end{aligned} \quad (25)$$

In Equation (25), it is found that the non-Fourier effects are reflected by four parts, the relaxation of entropy flow $\tau_q \frac{\partial \mathbf{J}^S}{\partial t}$, the relaxation of the EIT entropy $\mathbf{J}^S \frac{\tau_q}{\rho c_V} \frac{\partial S_{CV}}{\partial t}$, the relaxation of the EIT entropy generation $\frac{\tau_q^2 \mathbf{J}^S}{2\lambda \rho c_V} \frac{\partial (\mathbf{J}^S \cdot \mathbf{J}^S)}{\partial t}$ and the driving force of entropy transport caused by the EIT entropy generation difference $\frac{\tau_q}{2\rho c_V} \nabla (\mathbf{J}^S \cdot \mathbf{J}^S)$. Similar to Equation (12), the EIT entropic quantities in Equation (25) can also be replaced by the BGS entropic quantities and a generalization of the CV model will be given by

$$\begin{aligned} & \mathbf{J}_{BGS}^S + \tau_q \frac{\partial \mathbf{J}_{BGS}^S}{\partial t} + \frac{\tau_q^2 \mathbf{J}_{BGS}^S}{2\lambda \rho c_V} \frac{\partial (\mathbf{J}_{BGS}^S \cdot \mathbf{J}_{BGS}^S)}{\partial t} + \mathbf{J}_{BGS}^S \frac{\tau_q}{\rho c_V} \frac{\partial S_{BGS}}{\partial t} \\ & = -a \nabla S_{BGS} - \frac{\tau_q}{2\rho c_V} \nabla (\mathbf{J}_{BGS}^S \cdot \mathbf{J}_{BGS}^S). \end{aligned} \quad (26)$$

This generalization requires that the EIT entropy could provide a good approximation of the BGS entropy in hyperbolic heat conduction. Similar to Equation (12), Equation (26) is a generalized form of Equation (25) by replacing the CIT entropy flux \mathbf{J}^S and CIT entropy S_{eq} by the BGS entropy flux \mathbf{J}_{BGS}^S and BGS entropy S_{BGS} . \mathbf{J}_{BGS}^S and S_{BGS} also have the same forms as Equations (7) and (9) (Σ should not include the spatial variables).

The CV model lacks a fundamental proof and its physical and mathematical validity remains debatable. Nevertheless, it is considered as “the most obvious and simple generalization of Fourier’s law that will give rise to finite speeds of propagation” in reference [4]. It shows a perspective that Fourier’s law can be improved by introducing the thermal relaxation between the temperature gradient and heat flux. The thermal relaxation has been generalized or connected to many non-Fourier models. Thus, the CV model can be considered as a typical example which shows that the entropic constitutive modeling can also be applied to non-Fourier heat conduction. This is the reason that we discussed the entropic constitutive relation of the CV model. It should be emphasized that the above results rely on the near-equilibrium assumption, where the non-equilibrium temperature T_{neq} and equilibrium temperature T_{eq} are approximately equal $T_{neq} \approx T_{eq} = T$ [14]. Strictly speaking, the EIT entropic concepts should be defined by the non-equilibrium temperature. To avoid the non-equilibrium temperature, we generalized the results from the near-equilibrium region by replacing the EIT entropic concepts with the BGS entropic concepts. We assume that the entropic constitutive relations based on CIT or EIT are still applicable for BGS statistical mechanics. If the effects of the non-equilibrium temperature are considered, the entropic constitutive relations based on EIT might be different from the results in the near-equilibrium region. Then, the corresponding generalized forms in the BGS statistical mechanics would also change, which needs further discussion.

2.3. Modeling Based on the Entropic Constitutive Relation

In this subsection, we propose an entropic relaxation model by introducing a relaxation between the entropy gradient and entropy flux. The above discussion shows a possibility of modeling heat conduction through entropic constitutive relations, which exhibits better universality than the constitutive modeling expressed by the temperature and heat flux distributions. By analogy to Equation (5), a memory form between the entropy gradient and entropy flux can be proposed from the perspective of entropy,

$$\mathbf{J}^S(\mathbf{x}, t) = - \int_{-\infty}^t M_S(t - \eta) \nabla S(\mathbf{x}, \eta) d\eta, \quad (27)$$

where $M_S(t)$ is the entropic memory kernel. Different entropic constitutive models can arise from different choices of the entropic memory kernels. For an exponential kernel $M_S(t) = a \exp\left(-\frac{t}{\tau_S}\right)$ with τ_S denoting the entropic relaxation time, we can obtain an entropic relaxation model similar to Equation (3),

$$\mathbf{J}^S + \tau_S \frac{\partial \mathbf{J}^S}{\partial t} = -a \nabla S. \tag{28}$$

In the near-equilibrium region, where Equation (10a,b) are valid, the governing equation of this entropic relaxation model, Equation (28), is given by

$$\frac{\partial \mathbf{J}^S}{\partial t} + \tau_S \frac{\partial^2 \mathbf{J}^S}{\partial t^2} + \frac{\tau_S}{2\rho c_V} \frac{\partial \nabla(\mathbf{J}^S \cdot \mathbf{J}^S)}{\partial t} + \frac{\nabla(\mathbf{J}^S \cdot \mathbf{J}^S)}{\rho c_V} = a \nabla(\nabla \cdot \mathbf{J}^S). \tag{29}$$

Besides the entropic diffusion terms $\left(\frac{\partial \mathbf{J}^S}{\partial t}\right)$ and $[a \nabla(\nabla \cdot \mathbf{J}^S)]$ and the entropic relaxation term $\left(\tau_S \frac{\partial^2 \mathbf{J}^S}{\partial t^2}\right)$, Equation (29) also contains the effects by the entropy production rate $\left[\frac{\tau_S}{2\rho c_V} \frac{\partial \nabla(\mathbf{J}^S \cdot \mathbf{J}^S)}{\partial t}\right]$ and $\left[\frac{\nabla(\mathbf{J}^S \cdot \mathbf{J}^S)}{\rho c_V}\right]$. The constitutive relation in Equation (28), expressed by the heat flux and temperature distributions, is

$$\mathbf{q} + \tau_S \frac{\partial \mathbf{q}}{\partial t} - \frac{\mathbf{q} \tau_S}{T} \frac{\partial T}{\partial t} = -\lambda \nabla T, \tag{30}$$

Compared with the CV model, this entropic relaxation model avoids the mathematical possibility of non-positive absolute temperature in a well-posed problem. This is the case, because non-positive absolute temperature will result in the singularity of S , and from Equation (28), \mathbf{J}^S will also be singular, which cannot be solved by a well-posed problem of Equation (29). For the CV model, the positive boundary and initial temperatures cannot guarantee a positive solution [28,29] because the solution is also influenced by the rate of the initial temperature $\left.\frac{\partial T}{\partial t}\right|_{t=0}$. An initial value problem in $\mathbb{R}^1 \times [0, +\infty)$ with $T|_{t=0} = k_1 > 0$ and $\left.\frac{\partial T}{\partial t}\right|_{t=0} = k_2 < -\frac{k_1}{\tau}$ ($\tau_q = \tau_S = \tau$, k_1 and k_2 are constants) is taken as an example. The solution of this initial value problem for the CV model is given by

$$T_{CV} = -\tau k_2 \exp\left(-\frac{t}{\tau}\right) + \tau k_2 + k_1, \tag{31}$$

which will be non-positive after a sufficiently long time and tend to a negative value $(\tau k_2 + k_1)$ as $t \rightarrow +\infty$. In contrast, the solution predicted by the entropic relaxation model is positive for all $t > 0$, vis.,

$$T_S = k_1 \exp\left\{\frac{\tau k_2}{k_1} \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]\right\}. \tag{32}$$

Although the CV model can also be rewritten as Equation (19), the singularity of S_{eq} would not necessarily cause \mathbf{J}^S to be singular because there are two terms containing a singularity in Equation (21), which could cancel each other out. Similar to Fourier’s law, this model also has an implicit form of shock wave structure solutions with two asymptotic states $\mathbf{V}_{\infty 1}$ and $\mathbf{V}_{\infty 2}$

$$x - U_S t + C = \frac{2\left(a - \frac{\tau_S U_S^2}{2}\right)}{\mathbf{V}_{\infty 1} - \mathbf{V}_{\infty 2}} \ln \frac{\mathbf{V}_{\infty 1} - \mathbf{V}^S}{\mathbf{V}^S - \mathbf{V}_{\infty 2}} + \frac{\tau_S U_S}{2} \ln(\mathbf{V}_{\infty 1} - \mathbf{V}^S)(\mathbf{V}^S - \mathbf{V}_{\infty 2}). \tag{33}$$

One interesting conclusion is that the entropy transport velocity is still equal to the average of the asymptotic values, $U_S = \frac{\mathbf{V}_{\infty 1} + \mathbf{V}_{\infty 2}}{2}$. When the entropic relaxation is introduced, there also exists the solitary wave of \mathbf{V}^S in entropy transport and the relation between the asymptotic states and transport velocity remains unchanged. It seems that the verification of the entropic constitutive relation based on the relation $U_S = \frac{\mathbf{V}_{\infty 1} + \mathbf{V}_{\infty 2}}{2}$ is also valid for more general cases.

It should be pointed out that all of the above discussion on the entropic constitutive relations relies on the validity of the entropy balance law, i.e., Equation (13). In this work, we assume that the frameworks of CIT and EIT satisfy the entropy balance law, while their corresponding physical and mathematical validity might be debatable in the discussion of rational thermodynamics [30]. Although the entropy balance law for a general problem remains an open issue, it seems to be applicable in wave-like heat transport (second sound) [31].

3. Applicability of Generalization Based on Statistical Mechanics

In the above discussion, we have mentioned that the heat conduction models can be generalized through replacing macroscopic entropic quantities with BGS entropic quantities. However, when the deviation between the macroscopic and statistical entropies is sufficiently large, the generalization might be invalid. In this section, we will discuss the applicability or applicable range of these generalizations based on BGS statistical mechanics. For the local-equilibrium state in CIT, the distribution function $f = f_0$, where f_0 is the equilibrium distribution determined by the macroscopic quantity, i.e., temperature, and the local-equilibrium entropy in BGS statistical mechanics is given by

$$S_{eq} = -k_B \sum f_0 \ln f_0. \quad (34)$$

The difference between the BGS and local-equilibrium entropies is

$$S_{BGS} - S_{eq} = k_B \sum (f_0 \ln f_0 - f \ln f), \quad (35)$$

whose first-order expansion is

$$\begin{aligned} S_{BGS} - S_{eq} &= k_B \sum (f_0 - f) \frac{d(f \ln f)}{df} + k_B \sum o(f_0 - f) \\ &= k_B \sum (f_0 - f) (\ln f + 1) + k_B \sum o(f_0 - f). \end{aligned} \quad (36)$$

Consider the relaxation time approximation $C(f, f) = C(\tau_B) = \frac{f_0 - f}{\tau_B}$, with the relaxation time τ_B ; Equation (36) can subsequently be rewritten as

$$S_{BGS} - S_{eq} = k_B \sum \tau_B C(\tau_B) (\ln f + 1) + k_B \sum o(f_0 - f). \quad (37)$$

The BGS entropy production rate is

$$\sigma_{BGS} = -k_B \sum C(\tau_B) (\ln f + 1), \quad (38)$$

and by substituting σ_{BGS} into $(S_{BGS} - S_{eq})$, we have

$$S_{BGS} - S_{eq} = -\tau_B \sigma_{BGS} + k_B \sum o(f_0 - f). \quad (39)$$

This shows that $(S_{eq} - \tau_B \sigma_{BGS})$ can be used to approximate S_{BGS} when higher-order terms can be neglected. Thus, for the CIT entropy, generalizations like Equation (12) might be invalid for large σ_{BGS} . On the basis of this approximation, the minimum entropy production is equivalent to

$$\min(\sigma_{BGS}) \Leftrightarrow \max(S_{BGS} - S_{eq}). \quad (40)$$

S_{eq} is determined by the macroscopic equilibrium quantities, and if the maximum entropy principle [32,33] is satisfied by heat conduction, the minimum entropy production can be derived for given macroscopic descriptions. As a universal principle, the maximum entropy principle is satisfied by the distribution function under given constraints. These constraints are usually connected to several macroscopic quantities, i.e., the average kinetic energy and temperature. The CIT entropy can be defined by these macroscopic quantities and in equilibrium, it equals the BGS entropy

$S_{eq}|_{f=f_0} = S_{BGS}|_{f=f_0}$. Thus, we have $\max(S_{eq}) \Leftrightarrow \max(S_{BGS})$ in an equilibrium system and when certain local macroscopic quantities are variable, we can also apply the maximum CIT entropy to determine these local macroscopic quantities. In the near-equilibrium region, the macroscopic quantities based on local equilibrium are still applicable but there will exist a deviation between the CIT and BGS entropies. The deviation between the two entropies is estimated by the BGS entropy production rate $\max(S_{BGS} - S_{eq}) = -\tau_B \min(\sigma_{BGS})$. For non-equilibrium heat conduction, although the maximum CIT entropy will not be strictly equivalent to the maximum entropy principle, the maximum entropy principle will still be satisfied when σ_{BGS} reaches minimum and S_{eq} reaches maximum. Then, we can use the maximum CIT entropy as a first-order approximation of the maximum entropy principle if a heat conduction process can satisfy the minimum entropy production rate. In Equation (36), it is shown that the BGS entropy production rate σ_{BGS} corresponds to the first-order term $|f_0 - f|$. In the near-equilibrium region, σ_{CIT} could be considered as an estimation of σ_{BGS} and their difference is the higher-order terms. With higher-order terms neglected, we assume that the CIT entropy production rate can give a reasonably accurate estimation of the BGS entropy production rate, $\sigma_{CIT} \cong \sigma_{BGS}$ and then, a macroscopic approximation can be obtained as

$$S_{BGS} \approx S_{CIT} - \tau_B \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right). \quad (41)$$

Then, the applicability of the generalized Fourier law, Equation (12), must have sufficiently small $\mathbf{q} \cdot \nabla \left(\frac{1}{T} \right)$. Next, we focus on the EIT entropy. There exists a similar macroscopic approximation to Equation (39) between S_{CV} and S_{eq}

$$S_{CV} = S_{eq} - \frac{1}{2} \tau_q \sigma_{CV}. \quad (42)$$

If σ_{CV} is also assumed to be a reasonably accurate estimation of σ_{BGS} in hyperbolic heat conduction, we have

$$S_{BGS} - S_{CV} = -k_B \left(\tau_B - \frac{1}{2} \tau_q \right) \sigma_{BGS} + k_B \sum o(f_0 - f). \quad (43)$$

It is found that the generalization in Equation (26) needs sufficiently small σ_{BGS} or $\left| \tau_B - \frac{1}{2} \tau_q \right|$, which seems to imply that the generalization from EIT entropy has a wider applicability. Moreover, Equation (43) suggests that S_{CV} can be regarded as a modification of S_{eq} to approximate S_{BGS} . As an improvement of the CIT entropy, S_{CV} should be able to provide a better approximate degree than S_{eq} , explicitly,

$$|S_{BGS} - S_{CV}| \leq |S_{BGS} - S_{eq}|, \quad (44)$$

which is equivalent to $0 \leq \tau_q \leq 4\tau_B$. Next, we discuss whether this requirement is satisfied by the phenomenological relaxation time τ_q . $\tau_q < 0$ reflects a negative macroscopic relaxation between the heat flow and temperature difference, which is unphysical. Furthermore, taking the curl of Equation (3) gives

$$\nabla \times \mathbf{q} = (\nabla \times \mathbf{q})|_{t=0} \exp\left(-\frac{t}{\tau_q}\right), \quad (45)$$

which shows that the curl of the heat flux is exponentially growing for $\tau_q < 0$ and $(\nabla \times \mathbf{q})|_{t=0} \neq \mathbf{0}$. This exponential growth means that a heat conduction process obeying the CV model can never reach thermal equilibrium, and the non-equilibrium degree will even be increased by heat transport. Thus, a negative value for the macroscopic relaxation time of the heat flux is physically improper. On the other hand, S_{CV} is a macroscopic approximation relying on local equilibrium, and a given macroscopic description of heat conduction might correspond to different microscopic states containing non-local equilibrium. The microscopic ‘‘uncertainty’’ is increased by the macroscopic approximation and the BGS entropy for general cases will also be increased as the local equilibrium is reached. Therefore, the inequality $S_{CV} \geq S_{BGS}$ should be satisfied, which requires $\tau_q \leq 2\tau_B$. This can also be

understood more obviously from the view of exponential decay. Under the condition of $\nabla f = \mathbf{0}$, a well-known exponential decay of the deviation from the equilibrium distribution can be derived from the Boltzmann equation with the relaxation time approximation

$$\frac{f - f_0}{(f - f_0)|_{t=0}} = \exp\left(-\frac{t}{\tau_B}\right). \tag{46}$$

Set $\Delta f_0 = (f - f_0)|_{t=0}$ ($|\Delta f_0| \ll f_0$) and from Equation (44),

$$\frac{(f_0 \ln f_0 - f \ln f)}{(f_0 \ln f_0 - f \ln f)|_{t=0}} = \frac{f_0 \ln f_0 - \left(f_0 + \Delta f_0 e^{-\frac{t}{\tau_B}}\right) \ln\left(f_0 + \Delta f_0 e^{-\frac{t}{\tau_B}}\right)}{f_0 \ln f_0 - (f_0 + \Delta f_0) \ln(f_0 + \Delta f_0)}. \tag{47}$$

Consider the following two functions of ξ

$$h(\xi) = (f_0 + \xi) \ln(f_0 + \xi), \tag{48a}$$

$$g(\xi) = (f_0 + k\xi) \ln(f_0 + k\xi). \tag{48b}$$

Let $\xi = \Delta f_0$ and $k = \exp\left(-\frac{t}{\tau_B}\right)$; then we have

$$\frac{(f_0 \ln f_0 - f \ln f)}{(f_0 \ln f_0 - f \ln f)|_{t=0}} = \frac{g(0) - g(\xi)}{h(0) - h(\xi)}. \tag{49}$$

According to the differential mean value theorem, there is an $\varepsilon \in (-|\xi|, |\xi|)$ satisfying

$$\frac{(f_0 \ln f_0 - f \ln f)}{(f_0 \ln f_0 - f \ln f)|_{t=0}} = \frac{g'(\varepsilon)}{h'(\varepsilon)} = \frac{k[1 + \ln(f_0 + k\varepsilon)]}{1 + \ln(f_0 + \varepsilon)} \cong k = \exp\left(-\frac{t}{\tau_B}\right). \tag{50}$$

Then, we can also derive an exponential decay for the deviation between the BGS and CIT entropies

$$\frac{S_{BGS} - S_{eq}}{(S_{BGS} - S_{eq})|_{t=0}} = \frac{\sum(f_0 \ln f_0 - f \ln f)}{\sum(f_0 \ln f_0 - f \ln f)|_{t=0}} \cong \exp\left(-\frac{t}{\tau_B}\right). \tag{51}$$

Similarly, with the macroscopic condition of $\nabla T = \mathbf{0}$, the deviation between the EIT and CIT entropies is also exponentially decaying, vis.,

$$\frac{S_{CV} - S_{eq}}{(S_{CV} - S_{eq})|_{t=0}} = \exp\left(-\frac{2t}{\tau_q}\right). \tag{52}$$

When the distribution function reaches equilibrium, the macroscopic description of heat conduction must also reach equilibrium, but the converse may not be true. That is because a detailed balance needs a higher condition than the macroscopic equilibrium defined by phenomenological heat conduction. Accordingly, the decay in Equation (51) cannot be faster than the macroscopic decay in Equation (52), which means the macroscopic decay has a smaller or equal relaxation time, $\frac{\tau_q}{2} \leq \tau_B$. When $\tau_q = 2\tau_B$, the first-order term in Equation (43) becomes zero and to guarantee $S_{CV} \leq S_{BGS}$, the second-order term should be taken account of

$$S_{BGS} - S_{eq} = -\tau_B \sigma_{BGS} + k_B \sum \frac{(f_0 - f)^2}{2f} + k_B \sum o(f_0 - f)^2, \tag{53a}$$

$$S_{BGS} - S_{CV} = k_B \sum \frac{(f_0 - f)^2}{2f} + k_B \sum o(f_0 - f)^2. \tag{53b}$$

Equation (53b) shows that $S_{CV} \leq S_{BGS}$ will also be satisfied for $\tau_q = 2\tau_B$. The meaning of the second-order term can be better understood by introducing the relative entropy or Kullback–Leibler (KL) divergence [34] between f_0 and f

$$D_{KL}(f_0||f) = \sum f_0 \ln \frac{f_0}{f} = \sum \left[\frac{(f - f_0)^2}{2f} + o(f_0 - f)^2 \right]. \quad (54)$$

Thus, we have

$$S_{BGS} - S_{eq} = -\tau_B \sigma_{BGS} + k_B D_{KL}(f_0||f) + k_B \sum o(f_0 - f)^2, \quad (55a)$$

$$S_{BGS} - S_{CV} = k_B D_{KL}(f_0||f) + k_B \sum o(f_0 - f)^2. \quad (55b)$$

As an information-geometrical concept, the KL divergence $D_{KL}(f_0||f)$ exhibits the meaning of a second-order term, the global deviation between the distribution function and the corresponding equilibrium distribution. This conclusion also shows that compared with the entropy production rate, the effect of the non-equilibrium distribution function is the high-order small quantity, which also reflects the reasonability of the above macroscopic approximations based on local equilibrium.

4. Conclusions

1. The constitutive relations in Fourier and hyperbolic heat conductions are rewritten by the entropy and entropy flux distributions. The heat conduction models are generalized through replacing macroscopic entropic quantities with BGS entropic quantities. The generalizations can avoid the debatable definition of non-equilibrium temperature, which exhibits better universality than the constitutive relations expressed by the temperature and heat flux distributions.
2. The entropic constitutive relations provide a perspective for heat conduction modeling. Analogous to hyperbolic heat conduction, an entropic relaxation is introduced between the entropy flux and entropy gradient. In contrast with the CV model, this entropic relaxation model can avoid non-positive absolute temperature for the well-posed problems because non-positive absolute temperature will generate a singularity.
3. Based on the relaxation time approximation, it is found that the applicability of the generalizations based on BGS statistical mechanics requires a sufficiently small entropy production rate. From the physical discussions and exponential decay of the macroscopic approximations, an inequality is established between the phenomenological relaxation time and the relaxation time in the Boltzmann equation, $0 \leq \tau_q \leq 2\tau_B$.

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