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Memory behaviors of entropy production rates in heat conduction

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HIGHLIGHTS

- Memory behaviors are found for different entropy production rates in heat conduction.
- The corresponding memory kernels and initial effects decay exponentially.
- The memory behaviors predict a special relation of the thermal relaxation times.
- The global non-equilibrium degree also has exponential memory dependences.

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ABSTRACT

Based on the relaxation time approximation and first-order expansion, memory behaviors in heat conduction are found between the macroscopic and Boltzmann–Gibbs–Shannon (BGS) entropy production rates with exponentially decaying memory kernels. In the frameworks of classical irreversible thermodynamics (CIT) and BGS statistical mechanics, the memory dependency on the integrated history is unidirectional, while for the extended irreversible thermodynamics (EIT) and BGS entropy production rates, the memory dependences are bidirectional and coexist with the linear terms. When macroscopic and microscopic relaxation times satisfy a specific relationship, the entropic memory dependences will be eliminated. There also exist initial effects in entropic memory behaviors, which decay exponentially. The second-order term are also discussed, which can be understood as the global non-equilibrium degree. The effects of the second-order term are consisted of three parts: memory dependency, initial value and linear term. The corresponding memory kernels are still exponential and the initial effects of the global non-equilibrium degree also decay exponentially.

1. Introduction

As a fundamental concept in thermodynamics, entropy is widely applied to macroscopic irreversible phenomena. The principle of entropy increase [1–3] in thermodynamics provides the tendency for irreversible phenomena, i.e., heat conduction, but it cannot describe the non-equilibrium processes in sufficient details. For instance, Clausius statement of the second law [4,5] only governs the direction of heat transfer between two different temperatures, while the details is not given, i.e., the transport rate. Thus, supplemental constitutive models are needed for complete descriptions and predictions.

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The macroscopic description of heat conduction is usually proposed by the constitutive modeling between the heat flux and temperature distributions, and the most classical constitutive relation is Fourier's law,

$$\mathbf{q} + \lambda \nabla T = 0, \tag{1}$$

where $\mathbf{q}$ is the heat flux, T is the temperature and λ is the thermal conductivity. Based on local-equilibrium macroscopic quantities, Fourier's law is discussed in the framework of classical irreversible thermodynamics (CIT) [6–8]. The local CIT entropy S_{CIT} and entropy flux $\mathbf{J}^{\mathbf{S}}$ are defined as follows (pure heat conduction)

$$S_{CIT} = \int \rho c_V \frac{dT}{T}, \tag{2a}$$

$$\mathbf{J}^{\mathbf{S}} = \frac{\mathbf{q}}{T}, \tag{2b}$$

where ρ is the mass density and c_V is the specific heat. The local CIT entropy production rate is then derived from the following entropy balance equation

$$\sigma_{CIT} = \frac{\partial S_{CIT}}{\partial t} + \nabla \cdot \mathbf{J}^{\mathbf{S}} = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right). \tag{3}$$

From Eq. (3), it is found that the positive thermal conductivity can always guarantee a non-negative form for the CIT entropy production rate. As a phenomenological model, Fourier's law is proved by numerous experiments and widely applied to engineering. However, its parabolic governing equation predicts an infinite propagation speed of thermal disturbance, which seems unphysical for neglecting the time needed for the acceleration of heat flow [9]. For improvement, a relaxation between the temperature gradient and heat flux is introduced into the constitutive relation in the Cattaneo–Vernotte (CV) model [10,11]

$$\mathbf{q} + \tau_{CV} \frac{\partial \mathbf{q}}{\partial t} + \lambda \nabla T = 0, \tag{4}$$

where τ_{CV} is the thermal relaxation time of heat flux. Eq. (4) leads to a hyperbolic governing equation, and wave-like transport with a finite speed arises from the hyperbolic heat conduction. It should be noted that the infinite transport speed of Fourier heat conduction only exists under the condition of constant physical properties, which results in a linear parabolic equation. For the non-linear cases, i.e., $\lambda = \lambda(T) \propto T^{\alpha} (\alpha \neq 0$ is a constant), Fourier's law can also predict finite transport speed and in fast (superfast) diffusion ($-2 < \alpha < 0$) [12], there even exist hyperbolic or wave-like characteristics either, for instance, the traveling wave solution $T(x, t) = \Phi(x - ct) + \Psi(x + ct)$ with c denoting the wave velocity. Even so, non-Fourier constitutive modeling is still necessary because non-linear Fourier heat conduction is not as well-posed as the linear case. The existence of solutions could be dimensional dependent and for $\alpha < -1$, there are no physically meaningful solutions in multi-dimensional problems [12]. Accordingly, the generalizations like introducing thermal relaxation may provide a perspective to overcome these defects of Fourier's law. In the spirit of thermal relaxation, hyperbolic heat conduction has been developed into different types [13–16]. Many of these heat conduction models have been summarized and understood as the following memory behaviors between the temperature gradient and heat flux [17,18]

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

where $Q(t - \eta)$ is the memory kernel (or relaxation function). For most hyperbolic models including the CV model, the memory kernels are exponential. The power-law type $Q(t) \propto t^{-\gamma} (\gamma$ is a positive constant) can also be applied, which will give rise to fractional differential operators [19].

One of the main arguments about the hyperbolic CV model is that the local CIT entropy generation could be negative [20–22]. Non-equilibrium effects have been considered to cause this unphysical behavior in the framework of extended irreversible thermodynamics (EIT). To reflect the non-equilibrium effects in EIT entropy, heat flux is introduced as an intrinsic variable [8,23–25]

$$S_{CV} = S_{CIT} - \frac{\tau_{CV}}{2\lambda T^2} \mathbf{q} \cdot \mathbf{q}. \tag{6}$$

The corresponding entropy flux is still Eq. (2b), and then a non-negative form of the EIT entropy production rate will be guaranteed $\sigma_{CV} = \frac{\mathbf{q} \cdot \mathbf{q}}{\lambda T^2}$. At the microscopic level, foundation of statistical mechanics can be established for Eqs. (5) and (2b) by Grad's method [8], and hence we assume that Eq. (2b) can provide a sufficiently accurate estimation for the local entropy flux. In statistical mechanics, the Boltzmann–Gibbs–Shannon (BGS) entropy [26,27] is the most widely used entropic definition

$$S_{BGS} = -k_B \sum f \ln f, \tag{7}$$

where k_B is the Boltzmann's constant, $\sum$ is the summation (or integral) operator in the phase space and f denotes the one-particle distribution function containing at least spatial and temporal variables. Besides spatial and temporal variables, there would also exist other variables, i.e., the particle velocity. The extensive BGS statistical mechanics is not applicable to the cases with long memory or long-range interactions, and in order to overcome these limitations, non-extensive statistical mechanics are proposed [28–30]. In this work, memory relations similar to Eq. (5) between the BGS and macroscopic entropy production rates are established based on the relaxation time approximation [31,32]. It is shown that the BGS and EIT entropy production rates have similar memory dependences on the CIT entropy production rates, which could provide an understanding for relations between macroscopic and statistical mechanics entropic definitions. Similar to the heat flux in non-Fourier heat conduction, the BGS (or EIT) entropy production rate will also be effected by the history of macroscopic quantities. The EIT entropic structure, which considers the non-equilibrium effects, is equivalent to introducing a memory modification to give more accurate macroscopic estimations for the statistical entropic definitions. What is more, when macroscopic and microscopic relaxation times satisfy a specific relationship, extended irreversible thermodynamics and BGS statistical mechanics will lead to similar temporal behaviors for entropic definitions.

2. First-order approximation

The local-equilibrium temperature in Eq. (2a) corresponds an equilibrium distribution f_0, and then the local-equilibrium CIT entropy can be rewritten by BGS statistical mechanics

$$S_{CIT} = -k_B \sum f_0 \ln f_0. \tag{8}$$

The difference between the BGS and CIT entropies is given as follows

$$S_{BGS} - S_{CIT} = k_B \sum \left(f_0 \ln f_0 - f \ln f\right). \tag{9}$$

For the existence of macroscopic descriptions, the distribution function should be close to the equilibrium distribution with sufficiently small $|f_0 - f|$, and hence the following first-order expansion can be taken

$$S_{BGS} - S_{CIT} = k_B \sum \left(f_0 - f\right)\left(\ln f + 1\right) + k_B \sum o\left(f_0 - f\right). \tag{10}$$

Consider the Boltzmann equation without external force field

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = C\left(f, f\right), \tag{11a}$$

where $C(f,f)$ is the collision term and $\mathbf{v}$ is the particle velocity. One commonly used model for $C(f,f)$ in transport processes is the relaxation time approximation [31,32] $C(f,f) = \frac{f_0 - f}{\tau_B}$ with τ_B denoting the relaxation time. Eq. (11a) and the relaxation time approximation will give rise to the following entropy production rate

$$\sigma_{BGS} = -k_B \sum C\left(f, f\right) \ln f = -k_B \sum \left(\frac{f_0 - f}{\tau_B}\right) \ln f, \tag{11b}$$

and Eq. (10) can subsequently be rewritten as

$$S_{BGS} - S_{CIT} = -\tau_B \sigma_{BGS} + k_B \sum o\left(f_0 - f\right). \tag{12}$$

Substituting Eq. (12) into the following entropy balance equation

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

and we can obtain

$$\sigma_{CIT} = \sigma_{BGS} + \tau_B \frac{\partial \sigma_{BGS}}{\partial t}. \tag{14}$$

Eq. (14) shows a relaxation relation between the CIT and BGS entropy generations, which is similar to the constitutive relation in the CV model. Like the heat flux depended on the integrated history of the temperature gradient [17,18], there is also a memory dependence for the BGS entropy production rate

$$\sigma_{BGS}\left(\mathbf{x}, t\right) = \frac{1}{\tau_B} \int_{-\infty}^{t} \sigma_{CIT}\left(\mathbf{x}, \eta\right) \exp\left(-\frac{t-\eta}{\tau_B}\right) d\eta. \tag{15}$$

It is shown that σ_{BGS} is not determined by the instantaneous values of σ_{CIT} but its integrated history, which exhibits a memory behavior with an exponentially decaying memory kernel. For the convergence of the above generalized integral, $\sigma_{CIT}\left(\mathbf{x}, -\infty\right) = 0$ must be satisfied. When the lower limit of the integral is zero, the initial CIT entropy production rate will also have an effect on the memory dependence. Generally speaking, the time domains of most heat conduction problems are $[0, +\infty)$ and we first neglect the initial effects in this section. As the lower limit of the integral is modified into zero, the memory dependence without the initial effects is given by

$$\sigma_{BGS}\left(\mathbf{x}, t\right) = \frac{1}{\tau_B} \int_{0}^{t} \sigma_{CIT}\left(\mathbf{x}, \eta\right) \exp\left(-\frac{t-\eta}{\tau_B}\right) d\eta = \frac{1}{\tau_B} \sigma_{CIT} * \exp\left(-\frac{t}{\tau_B}\right), \tag{16}$$

where $*$ is the time convolution operation. The exponentially decaying convolution kernel means that the weights of σ_{CIT} at different moments are unequal. For σ_{BGS} at a fixed moment t_0, the closer that t is to t_0, the more weight that $\sigma_{CIT}(\mathbf{x}, t)$ has. Thus, the entropic memory of a fixed moment is decreasing over time.

The BGS entropy production rate is non-negative while according to Eq. (14), σ_{CIT} could be negative as σ_{BGS} decays rapidly enough. The critical situation is $\sigma_{BGS} + \tau_B \frac{\partial \sigma_{BGS}}{\partial t} = 0$, which corresponds an exponential decay of σ_{BGS}

$$\sigma_{BGS}(\mathbf{x}, t) = \sigma_{BGS}(\mathbf{x}, 0) \exp\left(-\frac{t}{\tau_B}\right). \tag{17}$$

In this case, $\sigma_{CIT} \equiv 0$ with the irreversible heat conduction processes happening and therefore, the CIT entropy generation can no longer describe the irreversibility of heat conduction. Accordingly, the exponential decay in Eq. (17) might correspond to the maximum decay rate for theoretical applicability of classical irreversible thermodynamics. If a macroscopic description of heat conduction predicts σ_{CIT} decaying faster than Eq. (17), classical irreversible thermodynamics would not be applicable for this problem.

From Eqs. (6) and (12), the first-order relation between the BGS and EIT entropies can be obtained as follows

$$S_{BGS} - S_{CV} = -\tau_B \sigma_{BGS} + \frac{1}{2}\tau_{CV}\sigma_{CV} + k_B \sum o\left(f_0 - f\right). \tag{18}$$

Then, the fist-order relation between the three entropies is derived as

$$\sigma_{CIT} = \sigma_{BGS} + \tau_B \frac{\partial \sigma_{BGS}}{\partial t} = \sigma_{CV} + \frac{\tau_{CV}}{2}\frac{\partial \sigma_{CV}}{\partial t}, \tag{19}$$

and when the initial entropy generation is neglected, we have

$$\sigma_{CV} = \frac{2}{\tau_{CV}}\sigma_{CIT} * \exp\left(-\frac{2t}{\tau_{CV}}\right), \tag{20a}$$

$$\sigma_{BGS} = \frac{\tau_{CV}}{2\tau_B}\sigma_{CV} + \left(1 - \frac{\tau_{CV}}{2\tau_B}\right)\frac{1}{\tau_B}\sigma_{CV} * \exp\left(-\frac{t}{\tau_B}\right), \tag{20b}$$

$$\sigma_{CV} = \frac{2\tau_B}{\tau_{CV}}\sigma_{BGS} + \left(1 - \frac{2\tau_B}{\tau_{CV}}\right)\frac{2}{\tau_{CV}}\sigma_{BGS} * \exp\left(-\frac{2t}{\tau_{CV}}\right). \tag{20c}$$

Similar to the Eq. (16), σ_{CV} also indicates a unidirectional memory dependence on the integrated history of σ_{CIT} with an exponential entropic memory kernel $\exp\left(-\frac{2t}{\tau_{CV}}\right)$. Like the non-Fourier constitutive relations between the temperature gradient and heat flux, the memory behavior between the CIT entropy production rate σ_{CIT} and its macroscopic phenomenological generalization σ_G could also be summarized as $\sigma_G = Q_e * \sigma_{CIT}$ with Q_e denoting the entropic memory kernel. Then, different generalizations of the CIT entropic forms can also be given through different choices of Q_e. Different the relation between σ_{CIT} and σ_{BGS} (or σ_{CV}), Eqs. (20b) and (20c) show that the memory dependences between σ_{CV} and σ_{BGS} are bidirectional. What is more, we can also find that the memory dependences coexist with the linear terms in Eqs. (20b) and (20c). When $\tau_{CV} = 2\tau_B$, the entropic memory terms even disappear and the difference between σ_{CV} and σ_{BGS} will be high-order term of $|f - f_0|$. Thus, the EIT entropic structure can be understood as an improvement of the CIT entropy by eliminating partial memory dependence between σ_{CIT} and σ_{BGS}, and the memory modification will provide more accurate macroscopic estimations for the statistical entropic definitions.

3. Initial effects and second-order term

When the initial effects are taken account of, the above entropic memory relations will change into the following forms:

$$\sigma_{BGS} = \frac{1}{\tau_B}\sigma_{CIT} * \exp\left(-\frac{t}{\tau_B}\right) + \sigma_{BGS}|_{t=0} \exp\left(-\frac{t}{\tau_B}\right), \tag{21a}$$

$$\sigma_{CV} = \frac{2}{\tau_{CV}}\sigma_{CIT} * \exp\left(-\frac{2t}{\tau_{CV}}\right) + \sigma_{CV}|_{t=0} \exp\left(-\frac{2t}{\tau_{CV}}\right), \tag{21b}$$

$$\sigma_{BGS} = \frac{\tau_{CV}}{2\tau_B}\sigma_{CV} + \left(1 - \frac{\tau_{CV}}{2\tau_B}\right)\frac{1}{\tau_B}\sigma_{CV} * \exp\left(-\frac{t}{\tau_B}\right) + \left.\left(\sigma_{BGS} - \frac{\tau_{CV}\sigma_{CV}}{2\tau_B}\right)\right|_{t=0} \exp\left(-\frac{t}{\tau_B}\right), \tag{21c}$$

$$\sigma_{CV} = \frac{2\tau_B}{\tau_{CV}}\sigma_{BGS} + \left(1 - \frac{2\tau_B}{\tau_{CV}}\right)\frac{2}{\tau_{CV}}\sigma_{BGS} * \exp\left(-\frac{2t}{\tau_{CV}}\right) + \left.\left(\sigma_{CV} - \frac{2\tau_B\sigma_{BGS}}{\tau_{CV}}\right)\right|_{t=0} \exp\left(-\frac{2t}{\tau_{CV}}\right). \tag{21d}$$

It is shown that the initial effects decay exponentially and accordingly, the initial effects can be neglected after a sufficiently long time $t \gg \tau_B, \frac{1}{2}\tau_{CV}$. For the entropic memory relations between σ_{CIT} and σ_{BGS} (or σ_{CV}), the initial effects are only determined by the initial values $\sigma_{BGS}|_{t=0}$ (or $\sigma_{CV}|_{t=0}$), while in the relations between σ_{CV} and σ_{BGS}, both of their initial values appear. When $\tau_{CV} = 2\tau_B$, the entropic memory dependences disappear and there only exists the initial term

$$\sigma_{BGS} - \sigma_{CV} = (\sigma_{BGS} - \sigma_{CV})|_{t=0} \exp\left(-\frac{t}{\tau_B}\right). \tag{22}$$

Therefore, if the phenomenological thermal relaxation time τ_{CV} equals to $2\tau_B$, σ_{CV} can provide an accurate first-order estimation for σ_{BGS} after sufficiently long time.

The above approximations are based on the first-order term of $(f_0 - f)$ in Eq. (9), and the second-order term $(f_0 - f)^2$ will be discussed in the following part. With higher-order terms neglected, the second-order approximations between the BGS and macroscopic entropies are given by

$$S_{BGS} - S_{CIT} = -\tau_B\sigma_{BGS} + k_B \sum \frac{(f_0 - f)^2}{2f} + k_B \sum o(f_0 - f)^2, \tag{23a}$$

$$S_{BGS} - S_{CV} = -\tau_B\sigma_{BGS} + \frac{1}{2}\tau_{CV}\sigma_{CV} + k_B \sum \frac{(f_0 - f)^2}{2f} + k_B \sum o(f_0 - f)^2. \tag{23b}$$

By introducing the relative entropy or Kullback–Leibler (KL) divergence [33] between f_0 and f, the second-order term $\sum \frac{(f_0-f)^2}{2f}$ can be rewritten as

$$\mathrm{D}_{KL} = \mathrm{D}_{KL}(f_0 \,||f\,) = \sum f_0 \ln\frac{f_0}{f} = \sum\left[\frac{(f - f_0)^2}{2f} + o(f_0 - f)^2\right], \tag{24}$$

and then we have

$$S_{BGS} - S_{CIT} = -\tau_B\sigma_{BGS} + k_B\mathrm{D}_{KL} + k_B \sum o(f_0 - f)^2, \tag{25a}$$

$$S_{BGS} - S_{CV} = -\tau_B\sigma_{BGS} + \frac{1}{2}\tau_{CV}\sigma_{CV} + k_B\mathrm{D}_{KL} + k_B \sum o(f_0 - f)^2. \tag{25b}$$

As an information-geometrical concept measuring the distance between distributions, the KL divergence D_{KL} provides a more specific understanding and meaning of the second-order term, the global deviation between the distribution function and its corresponding equilibrium distribution. Briefly speaking, D_{KL} can be considered as the global non-equilibrium degree, which is one-order smaller than $\tau_B\sigma_{BGS}$. Substituting Eqs. (25a) and (25b) into the entropy balance equation gives

$$\sigma_{CIT} = \sigma_{BGS} + \tau_B\frac{\partial\sigma_{BGS}}{\partial t} - k_B\frac{\partial\mathrm{D}_{KL}}{\partial t} = \sigma_{CV} + \frac{\tau_{CV}}{2}\frac{\partial\sigma_{CV}}{\partial t}, \tag{26}$$

and the following memory relationships can be subsequently obtained

$$\sigma_{BGS} = \frac{1}{\tau_B}\left(\sigma_{CIT} - \frac{k_B\mathrm{D}_{KL}}{\tau_B}\right) * \exp\left(-\frac{t}{\tau_B}\right) + \left.\left(\sigma_{BGS} - \frac{k_B\mathrm{D}_{KL}}{\tau_B}\right)\right|_{t=0} \exp\left(-\frac{t}{\tau_B}\right) + \frac{k_B\mathrm{D}_{KL}}{\tau_B}, \tag{27a}$$

$$\begin{aligned}\sigma_{BGS} =& \frac{\tau_{CV}}{2\tau_B}\sigma_{CV} + \frac{1}{\tau_B}\left[\left(1 - \frac{\tau_{CV}}{2\tau_B}\right)\sigma_{CV} - \frac{k_B\mathrm{D}_{KL}}{\tau_B}\right] * \exp\left(-\frac{t}{\tau_B}\right)\\ &+ \left.\left(\sigma_{BGS} - \frac{\tau_{CV}\sigma_{CV}}{2\tau_B} - \frac{k_B\mathrm{D}_{KL}}{\tau_B}\right)\right|_{t=0} \exp\left(-\frac{t}{\tau_B}\right) + \frac{k_B\mathrm{D}_{KL}}{\tau_B},\end{aligned} \tag{27b}$$

$$\begin{aligned}\sigma_{CV} =& \frac{2\tau_B}{\tau_{CV}}\sigma_{BGS} + \frac{2}{\tau_{CV}}\left[\left(1 - \frac{2\tau_B}{\tau_{CV}}\right)\sigma_{BGS} - \frac{2k_B\mathrm{D}_{KL}}{\tau_{CV}}\right] * \exp\left(-\frac{2t}{\tau_{CV}}\right)\\ &+ \left.\left(\sigma_{CV} - \frac{2\tau_B\sigma_{BGS}}{\tau_{CV}} - \frac{2k_B\mathrm{D}_{KL}}{\tau_{CV}}\right)\right|_{t=0} \exp\left(-\frac{2t}{\tau_{CV}}\right) + \frac{2k_B\mathrm{D}_{KL}}{\tau_{CV}}.\end{aligned} \tag{27c}$$

From the above equations, it is found that the effects of the global non-equilibrium degree D_{KL} are consisted of three parts: memory dependency, initial value and linear term. Similar to the first-order cases, the memory behaviors of D_{KL} are also expressed in convolution forms with exponential memory kernels determined by the relaxation times, whose initial effects are exponentially decaying either. Although $k_B\mathrm{D}_{KL}$ is one-order smaller than $\tau_B\sigma_{BGS}$, $k_B\left|\frac{\partial\mathrm{D}_{KL}}{\partial t}\right|$ might not be much smaller than $\tau_B\left|\frac{\partial\sigma_{BGS}}{\partial t}\right|$. A simple case is taken as an example, where $\tau_B\sigma_{BGS} = C_1\ k_B\mathrm{D}_{KL} = C_2 \sin\omega t$ ($\frac{C_2}{C_1} \ll 1$, ω, C_1 and C_2 are constants). Obviously, $k_B\mathrm{D}_{KL} \ll \tau_B\sigma_{BGS}$ but $k_B\left|\frac{\partial\mathrm{D}_{KL}}{\partial t}\right| > \tau_B\left|\frac{\partial\sigma_{BGS}}{\partial t}\right|$, and for sufficiently large ω, $k_B\frac{\partial\mathrm{D}_{KL}}{\partial t}$ could even play a dominant role in Eq. (26). Therefore, the second-order term could also result in negative σ_{CIT} as D_{KL} increases fast enough, which gives another limitation for the theoretical applicability of classical irreversible thermodynamics. Analogously, $\tau_{CV} = 2\tau_B$ is also a special case which can simplify the Eq. (27b) into:

$$\sigma_{BGS} - \sigma_{CV} - \frac{k_B \mathrm{D}_{KL}}{\tau_B} = \left.\left(\sigma_{BGS} - \sigma_{CV} - \frac{k_B \mathrm{D}_{KL}}{\tau_B}\right)\right|_{t=0} \exp\left(-\frac{t}{\tau_B}\right) - \frac{k_B \mathrm{D}_{KL}}{\tau_B^2} * \exp\left(-\frac{t}{\tau_B}\right). \tag{28}$$

In this case, the entropic memory behaviors are eliminated but the memory of the global non-equilibrium degree still exists.

In the above discussion, $\tau_{CV} = 2\tau_B$ is found as a special relation and we will try to explain this particularity in the following discussion. For the microscopic relaxation time approximation, a well-known exponential decay can be derived from the Boltzmann equation under the condition of $\nabla f = \mathbf{0}$ $(|f - f_0| \ll f_0)$

$$\frac{f - f_0}{(f - f_0)|_{t=0}} = \exp\left(-\frac{t}{\tau_B}\right). \tag{29}$$

Consider the two following functions of χ

$$\phi(\chi) = (f_0 + \chi)\ln(f_0 + \chi), \tag{30a}$$

$$\varphi(\chi) = \left(f_0 + \mathrm{e}^{-\frac{t}{\tau_B}}\chi\right)\ln\left(f_0 + \mathrm{e}^{-\frac{t}{\tau_B}}\chi\right), \tag{30b}$$

and by setting $\chi = (f - f_0)|_{t=0}$, we have

$$\frac{(f_0 \ln f_0 - f\ln f)}{(f_0 \ln f_0 - f\ln f)|_{t=0}} = \frac{\varphi(0) - \varphi(\chi)}{\phi(0) - \phi(\chi)}. \tag{31}$$

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

$$\frac{\varphi(0) - \varphi(\chi)}{\phi(0) - \phi(\chi)} = \frac{g'(\varepsilon)}{h'(\varepsilon)} = \mathrm{e}^{-\frac{t}{\tau_B}} \frac{\left[1 + \ln\left(f_0 + \mathrm{e}^{-\frac{t}{\tau_B}}\varepsilon\right)\right]}{1 + \ln(f_0 + \varepsilon)} \cong \exp\left(-\frac{t}{\tau_B}\right). \tag{32}$$

Then, an exponential decay for the deviation between the BGS and CIT entropies can be obtained as follows

$$\frac{S_{BGS} - S_{CIT}}{(S_{BGS} - S_{CIT})|_{t=0}} = \frac{\sum(f_0 \ln f_0 - f\ln f)}{\sum(f_0 \ln f_0 - f\ln f)|_{t=0}} \cong \exp\left(-\frac{t}{\tau_B}\right). \tag{33}$$

Similarly, at the macroscopic level, the deviation between the EIT and CIT entropies also decays exponentially under the condition of $\nabla T = \mathbf{0}$

$$\frac{S_{CV} - S_{CIT}}{(S_{CV} - S_{CIT})|_{t=0}} = \exp\left(-\frac{2t}{\tau_{CV}}\right). \tag{34}$$

By comparing the two exponential decays, we find that the BGS and EIT entropies predict a same decaying behavior of the deviation from the CIT entropy. Thus, when the macroscopic and microscopic relaxation times satisfy $\tau_{CV} = 2\tau_B$, extended irreversible thermodynamics and BGS statistical mechanics will give similar temporal behaviors. However, it should be noted that this similarity of temporal behaviors only exists for entropy and entropy generation, which respectively correspond to the zero-order and first-order terms. This is because Eq. (28) shows that the memory dependence of D_{KL} is not eliminated when $\tau_{CV} = 2\tau_B$, and therefore, the similarity no longer holds for the global non-equilibrium degree.

4. Conclusions

Based on the relaxation time approximation and first-order expansion, unidirectional memory dependences on the integrated history of the CIT entropy production rate are established for the BGS entropy production rate. Similar memory behaviors are also found between the BGS and EIT entropy production rates, which are bidirectional and coexist with the linear terms. The entropic memory kernels decay exponentially and when $\tau_{CV} = 2\tau_B$, the memory relation between σ_{CV} and σ_{BGS} will disappear. It means that the memory modification in EIT can give more accurate macroscopic estimations of the statistical entropic definitions. The memory behaviors provide an understanding of the EIT entropic structure, an improvement of the CIT entropy by eliminating partial memory dependence. Similar to the non-Fourier constitutive models between the temperature gradient and heat flux, the memory dependence between the CIT entropy production rate and its macroscopic phenomenological generalization could also be summarized as $\sigma_G = Q_e * \sigma_{CIT}$, and different generalizations can be given through different choices of the entropic memory kernels. In this work, the entropic memory kernels are found as an exponential type, which will result in integer-order derivatives. Recently, fractional-order derivatives are also introduced for modeling the long memory behaviors in heat conduction [34,35], which arise from the power-law memory kernels. It seems that the entropic memory kernel could also be chosen as power-law functions, which provides a new perspective for modeling phenomenological entropy.

The initial effects of the entropy production rates, which correspond to the first-order term, also decay exponentially. The second-order term can be understood as the global non-equilibrium degree. The effects of the global non-equilibrium degree are consisted of three parts: memory dependency, initial value and linear term. The memory behaviors of D_{KL} are also expressed in the convolution form with exponential memory kernels determined by the relaxation times, and its initial effects decay exponentially either. $\tau_{CV} = 2\tau_B$ is found as a special case, where extended irreversible thermodynamics and BGS statistical mechanics predict similar temporal behaviors for entropy and entropy generation. This similarity of temporal behaviors will not exist for the global non-equilibrium degree because the memory dependence of the second-order term is not eliminated.

The Cattaneo–Vernotte (CV) model and Fourier's law are phenomenological models on the macroscopic level [36], while the Boltzmann equation is a universal law on the microscopic level, which corresponds to the BGS entropy. Through appropriate assumptions, i.e., the relaxation time approximation and mathematical form of the distribution function, the two phenomenological models can be derived from the Boltzmann equation. In practical engineering, solving the Boltzmann equation would usually be complicated and difficult. Thus, we need phenomenological models to give approximate estimations for heat conduction. The phenomenological heat conduction models may correspond to entropies on the different levels, which would predict different entropic memory (or relaxation) behaviors. This work may provide a perspective to reflect the deviations between the Boltzmann equation and phenomenological models by comparing their entropic memory (or relaxation) behaviors. For Fourier heat conduction, where the CIT entropy are usually applied, the constitutive relation between the heat flux and temperature gradient is instantaneous. The Boltzmann equation and CV model, which respectively correspond to the BGS and EIT entropies, predict memory dependency on the relation between the heat flux and temperature gradient. BGS statistical mechanics shows an entropic memory dependency on the CIT entropy, and the CV model paired with the EIT entropy will also give arise to similar memory behaviors. It exhibits that heat conduction with relaxation will be paired with entropic memory, and different memory kernels would reflect different relaxation behaviors in heat conduction. Then, the heat conduction modeling through introducing relaxation between the heat flux and temperature gradient can also be considered as an approximate description for the entropic memory in BGS statistical mechanics. If a phenomenological heat conduction model predicts an accurate approximation of the entropic memory, this model might be considered as an accurate approximation of heat conduction obeying the Boltzmann equation. It should be emphasized that the above relations between relaxations on the three levels only hold in the near-equilibrium region $|f_0 - f| \ll f_0$, otherwise the similarity in entropic relaxation may not exist.

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References

[1] H.A. Buchdahl, The concepts of classical thermodynamics, Am. J. Phys. 28 (1960) 196–201.
[2] J.L.B. Cooper, The foundations of thermodynamics, J. Math. Anal. Appl. 17 (1967) 172–193.
[3] C. Dafermos, The second law of thermodynamics and stability, Arch. Rat. Mech. Anal. 70 (1979) 167–179.
[4] H.J. Borchers, Some remarks on the second law of thermodynamics, Rep. Math. Phys. 22 (1981) 29–48.
[5] R. Arens, An axiomatic basis for classical thermodynamics, J. Math. Anal. Appl. 6 (1963) 207–229.
[6] L. Onsager, Reciprocal relations in irreversible processes. I, Phys. Rev. 37 (1931) 405–426.
[7] L. Onsager, Reciprocal relations in irreversible processes. II, Phys. Rev. 38 (1931) 2265–2279.
[8] D. Jou, J. Casas-Vazquez, G. Lebon, Extended Irreversible Thermodynamics, Springer, Heidelberg, 2010.
[9] L. Onsager, Reciprocal relations in irreversible processes, Phys. Rev. 37 (1931) 405–426.
[10] C. Cattaneo, Sur une forme de léquation de lachaleur éliminant le paradoxe d'une propagation instantanée, Comptes Rendus 247 (1958) 431–433.
[11] P. Vernotte, Les paradoxes de la théorie continue de l'équation de la chaleur, Comptes Rendus 246 (1958) 3154–3155.
[12] P. Rosenau, Fast and superfast diffusion processes, Phys. Rev. Lett. 74 (1995) 1056–1059.
[13] S. Giordano, F. Manca, Analysis of heterogeneous structures described by the two-temperature model, Int. J. Heat Mass Transfer 78 (2014) 189–202.
[14] D.Y. Tzou, The generalized lagging response in small-scale and high-rate heating, Int. J. Heat Mass Transfer 33 (1990) 877–885.
[15] A. Sellitto, V.A. Cimmelli, D. Jou, Analysis of three nonlinear effects in a continuum approach to heat transport in nanosystems, Physica D 241 (2012) 1344–1350.
[16] R.A. Guyer, J.A. Krumhansl, Solution of the linearized phonon Boltzmann equation, Phys. Rev. 148 (1966) 766–778.
[17] D.D. Joseph, L. Preziosi, Heat waves, Rev. Modern Phys. 61 (1989) 41–73.
[18] D.D. Joseph, L. Preziosi, Addendum to the paper heat waves, Rev. Modern Phys. 62 (1990) 375–391.
[19] J. Hristov, Transient heat diffusion with a non-singular fading memory: From the Cattaneo constitutive equation with Jeffrey's Kernel to the Caputo–Fabrizio time-fractional derivative, Therm. Sci. 20 (2016) 757–762.
[20] Y. Taitel, On the parabolic, hyperbolic and discrete formulation of the heat conduction equation, Int. J. Heat Mass Transfer 15 (1972) 369–371.
[21] A. Barletta, E. Zanchini, Unsteady heat conduction by internal-energy waves in solids, Phys. Rev. B 55 (1997) 14208–14213.
[22] E. Zanchini, Hyperbolic heat-conduction theories and nondecreasing entropy, Phys. Rev. B 60 (1999) 991–997.
[23] G. Lebon, P. Dauby, Heat transport in dielectric crystals at low temperature: A variational formulation based on extended irreversible thermodynamics, Phys. Rev. A 42 (1990) 4710–4715.
[24] D. Jou, G. Lebon, M. Criado-Sancho, Variational principles for thermal transport in nanosystems with heat slip flow, Phys. Rev. E 82 (2010) 031128.
[25] G. Lebon, D. Jou, J. Casas-Vazquez, W. Muschik, Weakly nonlocal and nonlinear heat transport in rigid solids, J. Non-Equilib. Thermodyn. 23 (1998) 176–191.
[26] A. Wehrl, General properties of entropy, Rev. Mod. Phys. 50 (1978) 221–260.
[27] E.T. Jaynes, Information theory and statistical mechanics, Phys. Rev. 106 (1957) 620–630.
[28] C. Tsallis, Possible generalization of Boltzmann–Gibbs statistics, J. Stat. Phys. 52 (1988) 479–487.
[29] R. Thapliyal, H.C. Taneja, V. Kumar, Characterization results based on non-additive entropy of order statistics, Physica A 417 (2015) 297–303.

[30] V. Kumar, Some results on Tsallis entropy measure and k-record values, Physica A 462 (2016) 667–673.
[31] P.L. Bhatnagar, E.P. Gross, M. Krook, A model for collision processes in gases. I. Small amplitude in charged and neutral one-component systems, Phys. Rev. 94 (1954) 511–525.
[32] J. Callaway, Model for lattice thermal conductivity at low temperatures, Phys. Rev. 113 (1959) 1046–1051.
[33] S. Kullback, R.A. Leibler, On information and sufficiency, Ann. Math. Statist. 22 (1951) 79–86.
[34] J. Hristov, Steady-state heat conduction in a medium with spatial non-singular fading memory: Derivation of Caputo–Fabrizio space-fractional derivative with Jeffrey's kernel and analytical solutions, Therm. Sci. 21 (2017) 827–839.
[35] J. Hristov, Derivatives with non-singular kernels from the caputo–fabrizio definition and beyond: appraising analysis with emphasis on diffusion models, in: Frontiers in Fractional Calculus, Bentham Science, Sharjah, 2017.
[36] M. Grmela, Thermodynamics implied by reducing the phonon and the Cattaneo heat conduction theories to the Fourier theory, in: 13th Int. Conf. HEFA 606–610, Portoroz, 2017.