Thermodynamic Extremum Principles for Nonequilibrium Stationary State in Heat Conduction

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

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

Moran Wang[1]
Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Engineering Mechanics and CNMM, Tsinghua University, Beijing 100084, China
e-mail: mrwang@tsinghua.edu.cn

Minimum entropy production principle (MEPP) is an important variational principle for the evolution of systems to nonequilibrium stationary state. However, its restricted validity in the domain of Onsager's linear theory requires an inverse temperature square-dependent thermal conductivity for heat conduction problems. A previous derivative principle of MEPP still limits to constant thermal conductivity case. Therefore, the present work aims to generalize the MEPP to remove these nonphysical limitations. A new dissipation potential is proposed, the minimum of which thus corresponds to the stationary state with no restriction on thermal conductivity. We give both rigorous theoretical verification of the new extremum principle and systematic numerical demonstration through 1D transient heat conduction with different kinds of temperature dependence of the thermal conductivity. The results show that the new principle remains always valid while MEPP and its derivative principle fail beyond their scopes of validity. The present work promotes a clear understanding of the existing thermodynamic extremum principles and proposes a new one for stationary state in nonlinear heat transport.
[DOI: 10.1115/1.4036086]

Keywords: minimum entropy production principle, nonequilibrium stationary state, variational principle, nonlinear heat conduction

1 Introduction

Thermodynamics plays an important role in determining the dynamic behaviors of systems in nature and engineering [1–8]. In classical thermodynamics, the concept of "entropy" introduced by Clausius provides a criterion of the evolution of isolated systems to equilibrium state, known as the entropy increase principle. The monotonic increase of entropy was later proved by Boltzmann from microscopic perspective, and constitutes the cornerstone of second law of thermodynamics [9]. An extension of the thermodynamic extremum criterion from equilibrium systems to nonequilibrium ones was represented by Onsager's principle of the least dissipation of energy [10,11]. Prigogine then proposed the minimum entropy production principle (MEPP) in the domain of Onsager's linear classical irreversible thermodynamics [12,13]. The original MEPP was developed for discrete systems [13,14], and later generalized for continuous ones, stating that a nonequilibrium stationary state is characterized by the minimum of entropy production compatible with external constraints [15]. MEPP has achieved huge success with extensive applications in many fields [15–19], and also fosters the development of various thermodynamic extremum principles [20–23] for transport processes, such as the widely spread entropy generation minimization principle [24,25] and maximum entropy production principle [26]. In recent years, the MEPP has also been generalized to account for nonequilibrium transport with nonlocal effects which becomes pertinent in cryogenic or nanoscale systems [27,28].

Heat conduction is one of the most common transport processes [29] and acts as a typical example for the application of MEPP since the beginning of this principle [15]. In spite of its huge success, there have been still lots of debates on MEPP for characterizing a nonequilibrium stationary state in heat conduction over the past dozens of years. The diverse debates mainly include three aspects: theoretical analysis [30–34], numerical demonstration [35], and experimental verification [36–38], as to be summarized below.

The first theoretical query of MEPP may be due to Ref. [30], where a simple heat conduction through an infinite plate with constant thermal conductivity was explored under two isothermal ends. The derived temperature profile from MEPP was found to contradict the well-known linear profile from a steady-state heat equation. Later, more rigorous analysis [31,33] showed that the Euler–Lagrange equation obtained from the variational problem of MEPP was incompatible with the steady-state energy balance equation except in a very special case. Similar results were obtained in heat conduction with the temperature power-dependent thermal conductivity [32], where the temperature field through the extremalization of entropy production was generally different from that deduced from the steady-state heat equation except for a power "−2." On the other hand, the temporal evolution of entropy production was analytically [34] and numerically [35] studied when the heat conduction process approaches the stationary state. For the considered cases except an inverse temperature square-dependent thermal conductivity, the minimum of entropy production was reached before the stationary state was arrived [35]. For some special case, the entropy production may be even an increasing function of time [34]. These theoretical and numerical works clearly demonstrate the limited validity of MEPP for heat conduction. Some experimental try was also made to verify the MEPP by heat conduction through a rod with constant thermal conductivity [36]. But more serious analysis indicated that the observed stationary state with linear temperature profile along the rod was not the state with minimum entropy production [37,38]. To sum up, MEPP is only valid in the domain of Onsager's linear theory which requires constant phenomenological coefficient or an inverse temperature square-dependent thermal conductivity. Such a requirement is too restrictive for most of the materials in nature [29].

[1]Corresponding author.
Contributed by the Heat Transfer Division of ASME for publication in the Journal of Heat Transfer. Manuscript received May 26, 2016; final manuscript received February 21, 2017; published online April 4, 2017. Assoc. Editor: Robert D. Tzou.

To remove or release such nonphysical constraints on the thermal conductivity, many efforts have been paid to generalize the MEPP. An early progress was actually made by Prigogine himself based on a weighted entropy production, with the temperature square as the weight function [16]. A minimum of the weighted entropy production corresponds rigorously to the stationary state in heat conduction with constant thermal conductivity [16,34]. The limitation of MEPP is thus relieved to some extent since constant thermal conductivity is an appreciably reasonable approximation for some engineering applications. Nevertheless, from both theoretical and practical viewpoints, an arbitrarily temperature-dependent medium thermal conductivity is more realistic and intrinsic. Therefore, a thermodynamic extremum principle without the restrictions on the thermal conductivity is desirable, which becomes the main aim of the present work. The second try was also made by the group of Prigogine through a linearization of the temperature profiles [18], which extends the validity of the minimum principle of entropy production or a local potential [39] by an average system temperature. However, the assumption of small temperature gradient becomes the main limitation [32]. The integral principle based on picture representation [40] provides another search of generalized MEPP for heat conduction. Three classical pictures have been given: entropy picture, energy picture, and Fourier picture, with different forms of thermodynamic forces and fluxes. The dissipation potentials in entropy picture and Fourier picture are actually equivalent to entropy production and weighted entropy production, respectively. A general Γ-picture was thereafter proposed for treating the nonlinear heat conduction [40–42]. Despite the unified framework of general Γ-picture, an explicit expression of the dissipation potential has to be determined case by case and is still not convenient for actual use. Last, a recent effort rooted in nonequilibrium statistical mechanics is worth mentioning [43], which proposed a minimum principle of integrated entropy production instead of the usual instantaneous one. It indeed supplies a way to generalize MEPP for nonlinear transport processes. However, the complicated expression of integrated entropy production and the nontrivial solution of inverse problem of calculus of variation may make it impractical for actual application.

In a word, there still lacks a simple and efficient thermodynamic extremum principle for characterizing nonequilibrium stationary state in heat conduction with the arbitrarily temperature-dependent thermal conductivity. Therefore, the present work represents such an attempt to provide a credible solution to this problem. A new dissipation potential is proposed after a careful revisit of MEPP and its current derivative principle, as the main content of Sec. 2. In Secs. 3 and 4, a systematical numerical demonstration of the new extremum principle and existing ones will be then conducted based on the classical 1D transient heat conduction with three types of temperature dependence of the thermal conductivity. The concluding remarks of the present work are finally given in Sec. 5.

2 Thermodynamic Extremum Principles

In this section, first an overview is given on the principles of minimum entropy production and minimum weighted entropy production, with both their validity and limitations elucidated. Then a minimum principle of a new dissipation potential is proposed, supplemented with the rigorous theoretical verification of its effectiveness in characterizing the nonequilibrium stationary state in heat conduction. It will be shown that the new extremum principle removes the limitations and generalizes the validity of MEPP and its derivative principle.

2.1 Principle of Minimum Entropy Production. In classical irreversible thermodynamics, the local entropy production for heat conduction is derived from the entropy balance equation and written as the product of thermodynamic flux and force [15]

$$\sigma^s = \mathbf{q} \cdot \nabla\left(\frac{1}{T}\right) \tag{1}$$

Combined with the linear transport law $\mathbf{q} = L_{qq}\nabla(1/T)$, Eq. (1) becomes

$$\sigma^s = L_{qq}\nabla\left(\frac{1}{T}\right) \cdot \nabla\left(\frac{1}{T}\right) = \frac{k}{T^2}\nabla T \cdot \nabla T \tag{2}$$

where L_{qq} is the phenomenological coefficient related to the thermal conductivity k by $kT^2 = L_{qq}$. For a transient heat conduction process, the stationary state is reached at the minimum entropy production $P = \int \sigma^s dV$ in the whole system, as the main content of MEPP. The MEPP is based on three vital assumptions within the domain of Onsager's linear theory [15,40]: (a) linear phenomenological transport law (Fourier's law here); (b) constant phenomenological coefficient (L_{qq}); (c) the Onsager reciprocal relation for cross transport processes (necessary for multitransport processes such as thermal diffusion). The mathematical tenets of MEPP for heat conduction include twofold: (i) the extremum of the entropy production in the whole system

$$\delta P = \delta \int \sigma^s dV \tag{3}$$

gives rise to the stationary state heat equation and (ii) the temporal derivative of entropy production is negative

$$\frac{dP}{dt} \le 0 \tag{4}$$

The second condition (ii) ensures the stability of the stationary state. The details of the rigorous proof of the two tenets can be found in many classical monographs of nonequilibrium thermodynamics [15,40] and will not be repeated here anymore. In general, the entropy production of the system decreases in time when it approaches a stationary state, and will achieve a minimum value when the system reaches the stationary state. Once the system is deviated from the stationary state from external thermal perturbation, Eq. (4) continuously decreases the entropy production with time until the stable stationary state is returned. The substantial limitation of MEPP comes from the assumption (b): constant L_{qq} infers an inverse temperature square-dependent thermal conductivity ($k \propto 1/T^2$ from $kT^2 = L_{qq}$), which is often too restrictive and nonrealistic for most materials.

2.2 Principle of Minimum Weighted Entropy Production. To release the limitation of MEPP, a weighted entropy production was instead considered as [16]

$$P_1 = \int T^2\sigma^s dV = \int k\nabla T \cdot \nabla T dV \tag{5}$$

where Eq. (2) has been substituted in the derivation of Eq. (5). The stationary state of heat conduction with constant thermal conductivity can thus be characterized by the minimum of the weighted entropy production, Eq. (5) [16] (note a similar extremum principle based on half of the weighted entropy production has also been formulated [44]). On the other hand, the stability condition of extremum principle $dP_1/dt \le 0$ can be also proved to ensure a stable stationary state [34]. A constant thermal conductivity k is a more reasonable approximation in some engineering applications than $k \propto 1/T^2$ in MEPP, but not yet sufficient for many materials with highly temperature-dependent thermal conductivity as displayed in the classical textbook of heat transfer [29].

2.3 Minimum Principle of a New Dissipation Potential. The new dissipation potential is proposed as an integral of the product of a weight function kT^2 and the local entropy production

$$P_2 = \int kT^2\sigma^s dV \tag{6}$$

Substituting Eq. (2) into Eq. (6) gives the full expression of the new dissipation potential

$$P_2 = \int k^2 \nabla T \cdot \nabla T dV \tag{7}$$

The two mathematical tenets (Eqs. (3) and (4)) given in Sec. 2.1 are rigorously verified below for the minimum principle of the new dissipation potential. The heat conduction with the arbitrarily temperature-dependent thermal conductivity is taken into account.

The extremum of Eq. (7) is obtained by conducting a variational computation

$$\delta P_2 = \delta \int [k(T)]^2 \nabla T \cdot \nabla T dV = 0 \tag{8}$$

which leads to

$$\delta P_2 = \int \left[2k \frac{dk}{dT} (\nabla T)^2 - \nabla \cdot \left(2k^2 \nabla T\right) \right] \delta T dV + \int_{\partial V} 2k^2 \nabla T \delta T \cdot \mathbf{n} dS \tag{9}$$

In Eq. (9), ∂V denotes the boundary surface of the system volume V, with $\mathbf{n}$ being the unit vector along the surface external normal direction. As in the principles of minimum entropy production and minimum weighted entropy production, the fixed temperature condition at the boundary of system is assumed such that

$$(\delta T)_{\partial V} = 0 \tag{10}$$

Substituting Eq. (10) into Eq. (9), we obtain the Euler–Lagrange equation for the variational problem, Eq. (8)

$$2k \frac{dk}{dT} (\nabla T)^2 - \nabla \cdot \left(2k^2 \nabla T\right) = 0 \tag{11}$$

After a slight transform, Eq. (11) results in the steady-state heat equation

$$\nabla \cdot [k(T) \nabla T] = 0 \tag{12}$$

Thus, the extremum of the new dissipation potential, Eq. (7), exactly corresponds to the stationary state. Next, the stability of the stationary state will be verified as well.

The temporal derivative of P_2 is obtained as

$$\frac{dP_2}{dt} = \int \frac{\partial \left(k^2 \nabla T \cdot \nabla T\right)}{\partial t} dV \tag{13}$$

With the aid of partial integration and Gauss theorem [15], Eq. (13) is rewritten as

$$\frac{dP_2}{dt} = \int_{\partial V} 2k^2 \nabla T \frac{\partial T}{\partial t} \cdot \mathbf{n} dS - \int 2 \frac{\partial T}{\partial t} k \nabla \cdot (k \nabla T) dV \tag{14}$$

The heat equation for the transient conduction process is

$$C_V \frac{\partial T}{\partial t} = \nabla \cdot [k(T) \nabla T] \tag{15}$$

Combined with Eqs. (10) and (15), Eq. (14) becomes

$$\frac{dP_2}{dt} = -\int 2 C_V k \left(\frac{\partial T}{\partial t}\right)^2 dV \tag{16}$$

Based on the thermodynamic stability of equilibrium system ($C_V > 0$) and positive thermal conductivity ($k \geq 0$), Eq. (16) signifies

$$\frac{dP_2}{dt} \leq 0 \tag{17}$$

Therefore, the minimum principle of the new dissipation potential is obtained: for a transient heat conduction process with the arbitrarily temperature-dependent thermal conductivity, the total dissipation potential P_2 in the whole system decreases with time and achieves a minimum value when the system reaches the stationary state. After obtaining such an extremum principle, we came across a similar thermodynamic treatment in biophysical field [45] by using the integral of the square of metabolic matter flow (termed as dissipative flow elsewhere [46]). Although the present new dissipation potential can be reformulated as a similar form, $P_2 = \int \mathbf{q}^2 dV$, with the help of linear transport law $\mathbf{q} = -k \nabla T$, we prefer the expression, Eq. (7), as a quadratic function of the temperature gradient since temperature is a quantity more easily measured than the heat flux in actual application. On the other hand, the present formalism for pure heat conduction in a homogeneous medium remains to be generalized to heat transport in a heterogeneous medium such as the graded systems [47] and heat convection processes [31,33] in future work. In the following Secs. 3 and 4, the new extremum principle will be demonstrated through the classical one-dimensional (1D) transient heat conduction, with also a systematic comparison to principles of minimum entropy production and minimum weighted entropy production.

3 Physical Models and Mathematical Descriptions

The classical 1D transient heat conduction across an infinite plate with a thickness L is taken for the illustration of the thermodynamic extremum principles in Sec. 2. For generality, the thermal conductivity and volumetric heat capacity of the medium are assumed dependent on temperature in arbitrary forms $k(T)$ and $C_V(T)$, respectively. As assumed in MEPP, its derivative principle, and the new extremum principle, fixed temperature boundary conditions are considered for the plate, with its leftside and rightside ends keeping at T_L and T_R, respectively. A uniform initial temperature T_0 is assumed in the medium. The governing heat equation of this problem is

$$C_V(T) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[k(T) \frac{\partial T}{\partial x} \right] \tag{18}$$

with the boundary conditions

$$x = 0,\ T = T_L;\ x = L,\ T = T_R,\ t > 0 \tag{19}$$

and the initial condition

$$t = 0,\ T = T_0,\ 0 \leq x \leq L \tag{20}$$

To demonstrate the validity of the new extremum principle and the limitation of the principles of minimum entropy production and minimum weighted entropy production, three different kinds of temperature dependences of the plate thermal conductivity are designed

$$k = \frac{C_1}{T^2} \tag{21}$$

$$k = C_2 \tag{22}$$

$$k = C_3 T^2 \tag{23}$$

with the constants C_1, C_2, and C_3 to be specified soon. Hereafter, the heat conduction with Eq. (21), Eq. (22), and Eq. (23) are referred as case I, case II, and case III, respectively. For all the cases, $T_L = 500\,\mathrm{K}$, $T_R = 100\,\mathrm{K}$, with an average temperature of about 300 K throughout the plate. Therefore, the properties of

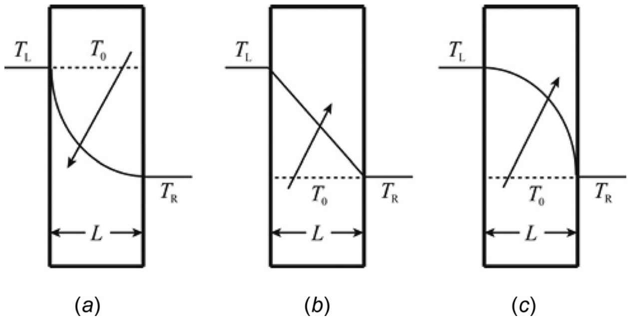

Fig. 1 Schematic of 1D transient heat conduction across an infinite plate with thickness *L*: (*a*) case I, (*b*) case II, and (*c*) case III. The dashed and solid lines denote the initial and final temperature distributions, respectively. The arrow line means the direction of temporal evolution.

silicon at a reference temperature $T_r = (T_L + T_R)/2 = 300$ K are taken: the thermal conductivity $k_r = 148$ W/m K, the volumetric heat capacity $C_{Vr} = 1.66 \times 10^6$ J/m^3 K, and the heat carrier mean free path $l = 41.79$ nm [48]. The thickness of the plate is assumed $L = 41.79\,\mu$m with an average Knudsen number $\mathrm{Kn} = 0.001$ (defined as the ratio of mean free path l to system length L) such that Fourier's law is valid to describe the heat conduction. In case II, the constant properties of silicon are used, i.e., $k = C_2 = k_r$, $C_V = C_{Vr}$. In case I and case III, the thermal conductivity of silicon at T_r acts as the reference data such that the coefficient constants C_1 and C_3 are calibrated as $C_1 = k_r T_r^2$ and $C_3 = k_r / T_r^2$. The volumetric heat capacities are chosen to have the same temperature dependence as that of thermal conductivities, i.e.,

$$C_V = \frac{C_{Vr} T_r^2}{T^2} \tag{24}$$

$$C_V = \frac{C_{Vr} T^2}{T_r^2} \tag{25}$$

for cases I and III, respectively. The reason why we choose the forms of Eqs. (24) and (25) for volumetric heat capacity will be elaborated later. In terms of the initial conditions, $T_0 = T_L$ for case I, $T_0 = T_R$ for cases II and III. Here, the initial condition $T_0 = T_L$ rather than $T_0 = T_R$ is considered for case I since one has

$$\frac{dP_1}{dt} = -2k_r T_r^2 \int \frac{\partial T}{\partial t}\left[\frac{1}{\alpha_r T^2}\frac{\partial T}{\partial t} + \frac{(\nabla T)^2}{T^3}\right] dV \tag{26}$$

An artifact of decreasing weighted entropy production of the system along the time will be obtained from Eq. (26) attributed to $\partial T/\partial t > 0$ thereafter when $T_0 = T_R$ is initialized for case I. To avoid an erroneous conclusion about the validity of the principle of minimum weighted entropy production for case I due to the initial condition, we thus consider $T_0 = T_L$ instead. The same logic is established for the other two cases. For clarity, the schematic and parameter details of the three cases are shown in Fig. 1 and Table 1, respectively.

For case II, the analytical solution of Eq. (18) can be directly obtained with the method of variable separation [49]

$$(\Theta)_{\mathrm{II}} \equiv \frac{T - T_R}{T_L - T_R} = 1 - \mathrm{X} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin(n\pi \mathrm{X})\exp(-n^2\pi^2\mathrm{Fo}) \tag{27}$$

where the dimensionless spatial and temporal coordinates are defined, respectively, as $\mathrm{X} = x/L$ and $\mathrm{Fo} = \alpha_r t/L^2$, with $\alpha_r = k_r/C_{Vr}$ being the thermal diffusivity. For cases I and III, a direct analytical solution of Eq. (18) is difficult due to the nonlinear properties. To eliminate the nonlinearity of heat equation, the following Kirchhoff transformation is introduced [50]:

$$\theta = \int_{T_r}^{T} \frac{k(T)}{k_r} dT \tag{28}$$

Substitution of Eq. (28) into Eq. (18) results in the following differential equation for θ:

$$\frac{\partial \theta}{\partial t} = \frac{k(T)}{C_V(T)}\frac{\partial^2 \theta}{\partial x^2} \tag{29}$$

Attributed to the same temperature dependence of volumetric heat capacity as that of the thermal conductivity, Eq. (29) reduces to a linear partial differential equation

$$\frac{\partial \theta}{\partial t} = \alpha_r \frac{\partial^2 \theta}{\partial x^2} \tag{30}$$

Analytical solution of Eq. (30) becomes feasible when the boundary conditions (θ_L and θ_R) and initial conditions (θ_0) are acquired from the correlation between θ and T. For case I, we get this correlation by substituting Eq. (21) into Eq. (28)

$$\theta = \frac{T_r(T - T_r)}{T} \tag{31}$$

whereas for case III we get by substituting Eq. (23) into Eq. (28)

$$\theta = \frac{T^3 - T_r^3}{3T_r^2} \tag{32}$$

In this way, the analytical solution of θ distribution in case I is obtained as

$$(\Theta)_{\mathrm{I}} \equiv \frac{\theta_L - \theta}{\theta_L - \theta_R} = \mathrm{X} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin[n\pi(1 - \mathrm{X})]\exp(-n^2\pi^2\mathrm{Fo}) \tag{33}$$

Table 1 Parameters in three cases of 1D transient heat conduction

Cases	Boundary conditions T_L (K)	Boundary conditions T_R (K)	Initial condition, T_0 (K)	Thermal conductivity	Volumetric heat capacity
I	500	100	500	$k = \frac{k_r T_r^2}{T^2}$	$C_V = \frac{C_{Vr} T_r^2}{T^2}$
II	500	100	100	$k = k_r$	$C_V = C_{Vr}$
III	500	100	100	$k = \frac{k_r T^2}{T_r^2}$	$C_V = \frac{C_{Vr} T^2}{T_r^2}$

The analytical solution of θ distribution in case III is obtained as

$$(\Theta)_{\mathrm{III}} \equiv \frac{\theta - \theta_{\mathrm{R}}}{\theta_{\mathrm{L}} - \theta_{\mathrm{R}}} = 1 - \mathrm{X} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin(n\pi\mathrm{X})\exp\left(-n^2\pi^2\mathrm{Fo}\right) \tag{34}$$

The nonlinear temperature distributions are then calculated inversely from Eqs. (33) and (34) via Eqs. (31) and (32).

Once the temperature fields are obtained, the entropy production and weighted entropy production as well as the present new dissipation potential are computed as

$$P = \int_0^L \frac{k}{T^2}\frac{dT}{dx}\frac{dT}{dx}dx \tag{35}$$

$$P_1 = \int_0^L k\frac{dT}{dx}\frac{dT}{dx}dx \tag{36}$$

$$P_2 = \int_0^L k^2\frac{dT}{dx}\frac{dT}{dx}dx \tag{37}$$

For a convenient comparison between different thermodynamic extremum principles, the dimensionless dissipation potentials are introduced as

$$P^* = \frac{P}{P(\mathrm{Fo} = 0.1)} \tag{38}$$

where P stands shortly for all the P, P_1, and P_2 in Eqs. (35)–(37).

4 Results and Discussion

4.1 Evolution of Temperature Distributions. For the 1D transient heat conduction discussed in Sec. 3 with different kinds of temperature-dependent thermal conductivities, the results of temporal evolutions of temperature distributions across the plate are shown in Fig. 2. When the stationary state is finally reached, the temperature distribution in case II with constant thermal conductivity becomes the classical linear profile shown in Fig. 2(*b*). In contrast, a convex and a concave temperature profiles are obtained for case I and case III with thermal conductivities inversely and directly proportional to the square of temperature separately, as is shown in Figs. 2(*a*) and 2(*c*), respectively.

4.2 Demonstration of Thermodynamic Extremum Principles. As is explained in Sec. 2, when a thermodynamic extremum principle is available, the corresponding dissipation potential (entropy production for MEPP) will decrease with time when the system approaches the stationary state and achieve the minimum value once the stationary state is finally reached. In Fig. 3, a thorough comparison is made between the three extremum principles in Sec. 2 for the three cases of 1D transient heat conduction in Sec. 3. For case I with the inverse temperature square-dependent thermal conductivity, the MEPP is valid as expected (cf. Sec. 2.1), as is shown in Fig. 3(*a*); for case II with constant thermal conductivity, the principle of minimum weighted entropy production is valid as expected (cf. Sec. 2.2), as is shown in Fig. 3(*b*). For case III with a temperature square-dependent thermal conductivity, both the principles of minimum entropy production and minimum weighted entropy productions fail, since their minimum values have been achieved before the final stationary state is reached, as is shown in Fig. 3(*c*). In addition, the principle of minimum weighted entropy production is invalid for case I whereas the MEPP is invalid for case II. In strong contrast, for all the three cases, the present new extremum principle is always valid as the new dissipation potential, Eq. (37), decreases with time till the final stationary state when its minimum value is achieved. The results indicate that the limitations of MEPP and its derivative

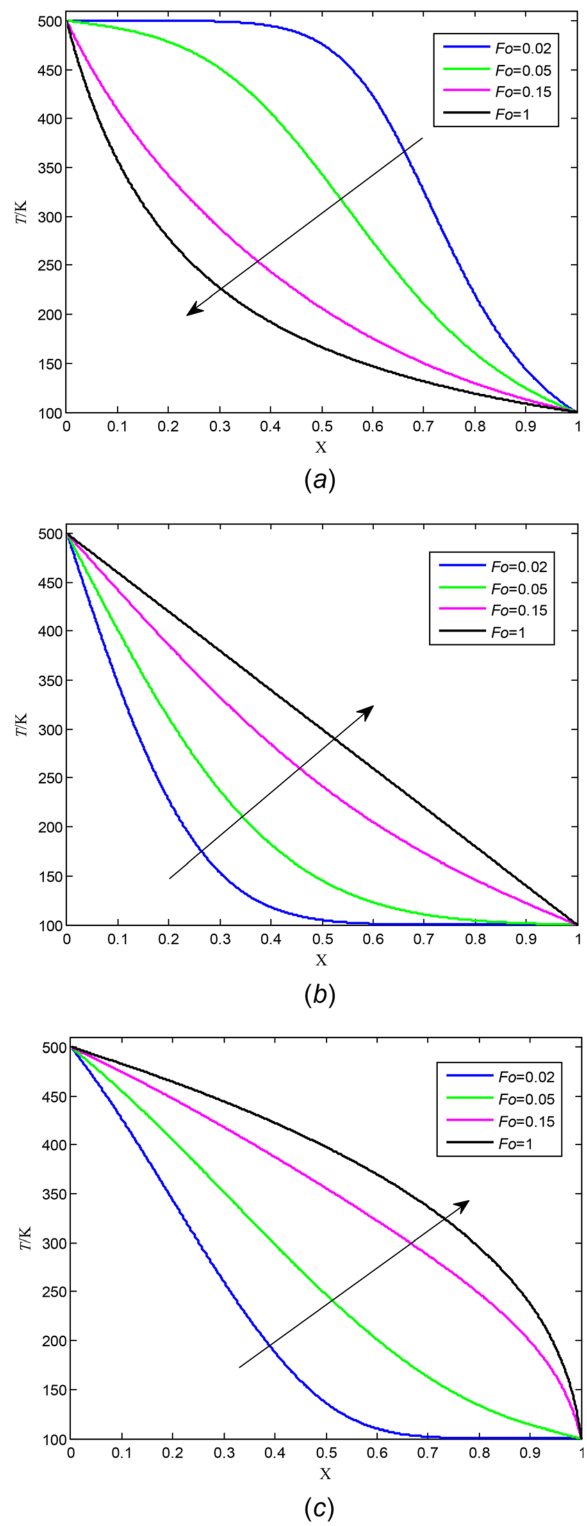

Fig. 2 Temporal evolution of temperature distributions in 1D transient heat conduction: (*a*) case I, an inverse temperature square-dependent thermal conductivity $k = k_r T_r^2/T^2$ and volumetric heat capacity $C_V = C_{Vr} T_r^2/T^2$; (*b*) case II, constant thermal conductivity $k = k_r$ and volumetric heat capacity $C_V = C_{Vr}$; and (*c*) case III, the temperature square-dependent thermal conductivity $k = k_r T^2/T_r^2$ and volumetric heat capacity $C_V = C_{Vr} T^2/T_r^2$. For all the three cases, the Fourier number (Fo) is defined based on the thermal diffusivity at the reference temperature ($T_r = 300$ K): $\alpha_r = k_r/C_{Vr}$. Temperature distributions at four sequential (Fo) have been displayed: Fo = 0.02, 0.05, 0.15, and 1. The arrow lines signify the direction of temporal evolution.

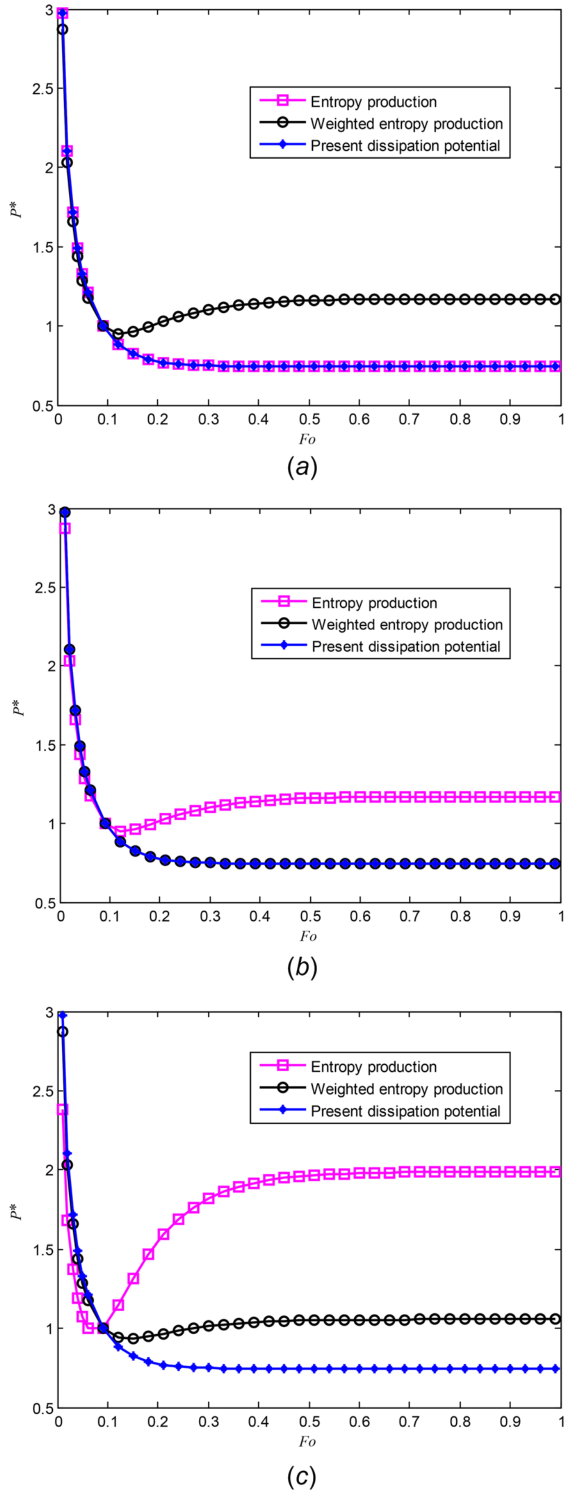

Fig. 3 Dimensionless dissipation potential versus time in 1D transient heat conduction: (*a*) case I, the inverse temperature square-dependent thermal conductivity $k = k_r T_r^2/T^2$ and volumetric heat capacity $C_V = C_{Vr} T_r^2/T^2$; (*b*) case II, constant thermal conductivity $k = k_r$ and volumetric heat capacity $C_V = C_{Vr}$; (*c*) case III, the temperature square-dependent thermal conductivity $k = k_r T^2/T_r^2$ and volumetric heat capacity $C_V = C_{Vr} T^2/T_r^2$. For all the three cases, the Fourier number (Fo) is defined based on the thermal diffusivity at the reference temperature ($T_r = 300$ K): $\alpha_r = k_r/C_{Vr}$. Solid line-square represents entropy production, Eq. (35), and solid line-circle represents weighted entropy production, Eq. (36), whereas the solid line-star represents the present new dissipation potential, Eq. (37).

principle have been successfully removed. The minimum principle of the new dissipation potential is capable of characterizing the nonequilibrium stationary state in heat conduction without any restrictions on the medium thermal conductivity.

5 Conclusions

In the present work, a systematic study is performed on the thermodynamic extremum principles for nonequilibrium stationary state in heat conduction. Aiming at eliminating the nonphysical restrictions on the medium thermal conductivity of minimum entropy production principle (MEPP) and its current derivative principle, we propose a novel extremum principle based on a new dissipation potential. A rigorous theoretical verification shows that the new extremum principle satisfies both the extremum condition and stability condition as required in original MEPP. The new dissipation potential will decrease with time and achieve its minimum value when the heat conduction approaches the final stationary state. A thorough demonstration of the new extremum principle and existing ones is also conducted through the classical 1D transient heat conduction with different temperature-dependent thermal conductivities. The results indicate that the new extremum principle remains always available while MEPP and its derivative principle fail once beyond their domain of validity. The present work would contribute to a clarified understanding of the thermodynamic variational principles for nonequilibrium states, and a generalization of the classical MEPP to nonlinear heat conduction. Moreover, the new dissipation potential may provide a promising avenue for thermodynamic optimization of nonlinear transport problems.

Acknowledgment

The authors appreciate helpful discussions with Professor N. Pan, Professor S. Y. Chen, and Dr. H. C. Zhang. This work was financially supported by the Key Basic Scientific Research Program (Grant No. 2013CB228301), the NSF grant of China (Grant No. 51321002), and the Tsinghua University Initiative Scientific Research Program.

Nomenclature

C = constants
C_V = volumetric heat capacity at constant volume (J/m^3 K)
Fo = Fourier number
k = thermal conductivity (W/m K)
Kn = Knudsen number
l = mean free path of heat carrier (m)
L = length of the conducting medium (m)
L_{qq} = phenomenological coefficient in heat conduction
P = entropy production in the whole system (W/K)
P_1 = weighted entropy production in the whole system (W K)
P_2 = new dissipation potential in the whole system (W^2/m)
$\mathbf{q}$ = heat flux (W/m^2)
t = time (s)
T = thermodynamic temperature (K)
V = volume of the conducting region (m^3)
x = x component of Cartesian coordinates (m)
X = dimensionless x-coordinate

Greek Symbols

θ = temperature after Kirchhoff transformation (K)
Θ = dimensionless temperature
σ^s = local entropy production (W/K m^3)

Subscripts

L = leftside
r = reference state
R = rightside
0 = initial state

References

[1] Prigogine, I., 1980, *From Being to Becoming Time and Complexity in the Physical Sciences*, W. H. Freeman, San Francisco, CA.

[2] Jou, D., Casas-Vázquez, J., and Criado-Sancho, M., 2011, *Thermodynamics of Fluids Under Flow*, 2nd ed., Springer, New York.

[3] Grmela, M., and Öttinger, H. C., 1997, "Dynamics and Thermodynamics of Complex Fluids. I. Development of a General Formalism," Phys. Rev. E, **56**(6), pp. 6620–6632.

[4] Liu, L. H., and Chu, S. X., 2006, "On the Entropy Generation Formula of Radiation Heat Transfer Processes," ASME J. Heat Transfer, **128**(5), pp. 504–506.

[5] Cimmelli, V. A., Sellitto, A., and Jou, D., 2010, "Nonlinear Evolution and Stability of the Heat Flow in Nanosystems: Beyond Linear Phonon Hydrodynamics," Phys. Rev. B, **82**(18), p. 184302.

[6] Sellitto, A., and Cimmelli, V. A., 2012, "A Continuum Approach to Thermomass Theory," ASME J. Heat Transfer, **134**(11), p. 112402.

[7] Guo, Y., and Wang, M., 2015, "Phonon Hydrodynamics and Its Applications in Nanoscale Heat Transport," Phys. Rep., **595**, pp. 1–44.

[8] Guo, Y., and Wang, M., 2016, "Thermodynamic Analysis of Gas Flow and Heat Transfer in Microchannels," Int. J. Heat Mass Transfer, **103**, pp. 773–782.

[9] Müller, I., 2007, *A History of Thermodynamics* (The Doctrine of Energy and Entropy), Springer, Heidelberg.

[10] Onsager, L., 1931, "Reciprocal Relations in Irreversible Thermodynamics I," Phys. Rev., **37**(4), pp. 405–426.

[11] Onsager, L., 1931, "Reciprocal Relations in Irreversible Thermodynamics II," Phys. Rev., **38**(12), pp. 2265–2279.

[12] Prigogine, I., 1947, *Etude Thermodynamique des Processus Irréversibles*, Desoer, Paris, France.

[13] Prigogine, I., 1955, *Thermodynamics of Irreversible Processes*, Charles C Thomas, Springfield, IL.

[14] Klein, M. J., and Meijer, P. H., 1954, "Principle of Minimum Entropy Production," Phys. Rev., **96**(2), p. 250.

[15] De Groot, S. R., and Mazur, P., 1962, *Non-Equilibrium Thermodynamics*, Dover Publications, New York.

[16] Glansdorff, P., and Prigogine, I., 1971, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, London.

[17] Jaynes, E. T., 1980, "The Minimum Entropy Production Principle," Annu. Rev. Phys. Chem., **31**(1), pp. 579–601.

[18] Kondepudi, D., and Prigogine, I., 1998, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, Wiley, New York.

[19] Fischer, F., Svoboda, J., and Petryk, H., 2014, "Thermodynamic Extremal Principles for Irreversible Processes in Materials Science," Acta Mater., **67**, pp. 1–20.

[20] Vujanovic, B., and Djukic, D., 1972, "On One Variational Principle of Hamilton's Type for Nonlinear Heat Transfer Problem," Int. J. Heat Mass Transfer, **15**(5), pp. 1111–1123.

[21] Ván, P., and Muschik, W., 1995, "Structure of Variational Principles in Nonequilibrium Thermodynamics," Phys. Rev. E, **52**(4), pp. 3584–3590.

[22] Lucia, U., 2013, "Stationary Open Systems: A Brief Review on Contemporary Theories on Irreversibility," Physica A, **392**(5), pp. 1051–1062.

[23] Cimmelli, V. A., Jou, D., Ruggeri, T., and Ván, P., 2014, "Entropy Principle and Recent Results in Non-Equilibrium Theories," Entropy, **16**(3), pp. 1756–1807.

[24] Bejan, A., 1979, "A Study of Entropy Generation in Fundamental Convective Heat Transfer," ASME J. Heat Transfer, **101**(4), pp. 718–725.

[25] Herwig, H., 2012, "The Role of Entropy Generation in Momentum and Heat Transfer," ASME J. Heat Transfer, **134**(3), p. 031003.

[26] Martyushev, L., and Seleznev, V., 2006, "Maximum Entropy Production Principle in Physics, Chemistry and Biology," Phys. Rep., **426**(1), pp. 1–45.

[27] Lebon, G., and Dauby, P., 1990, "Heat Transport in Dielectric Crystals at Low Temperature: A Variational Formulation Based on Extended Irreversible Thermodynamics," Phys. Rev. A, **42**(8), pp. 4710–4715.

[28] Jou, D., Lebon, G., and Criado-Sancho, M., 2010, "Variational Principles for Thermal Transport in Nanosystems With Heat Slip Flow," Phys. Rev. E, **82**(3), p. 031128.

[29] Bergman, T., Lavine, A., Incorpera, F., and DeWitt, D., 2011, *Fundamentals of Heat and Mass Transfer*, Wiley, Hoboken, NJ.

[30] Lampinen, M., 1990, "A Problem of the Principle of Minimum Entropy Production," J. Non-Equilib. Thermodyn., **15**(4), pp. 397–402.

[31] Barbera, E., 1999, "On the Principle of Minimal Entropy Production for Navier–Stokes-Fourier Fluids," Continuum Mech. Thermodyn., **11**(5), pp. 327–330.

[32] Martyushev, L., Nazarova, A., and Seleznev, V., 2007, "On the Problem of the Minimum Entropy Production in the Nonequilibrium Stationary State," J. Phys. A: Math. Theor., **40**(3), pp. 371–380.

[33] Bertola, V., and Cafaro, E., 2008, "A Critical Analysis of the Minimum Entropy Production Theorem and Its Application to Heat and Fluid Flow," Int. J. Heat Mass Transfer, **51**(7–8), pp. 1907–1912.

[34] Zullo, F., 2016, "Entropy Production in the Theory of Heat Conduction in Solids," Entropy, **18**(3), p. 87.

[35] Semenov, A. M., 2002, "Numerical Simulation of the Dynamics of Entropy Production in a One-Dimensional Unsteady, Thermally Inhomogeneous System," High Temp., **40**(2), pp. 320–321.

[36] Danielewicz-Ferchmin, I., and Ferchmin, A. R., 2000, "A Check of Prigogine's Theorem of Minimum Entropy Production in a Rod in a Nonequilibrium Stationary State," Am. J. Phys., **68**(10), pp. 962–965.

[37] Palffy-Muhoray, P., 2001, "Comment on 'A Check of Prigogine's Theorem of Minimum Entropy Production in a Rod in a Nonequilibrium Stationary State' by Irena Danielewicz-Ferchmin and A. Ryszard Ferchmin [Am. J. Phys., 68(10), pp. 962–965 (2000)]," Am. J. Phys., **69**(7), pp. 825–826.

[38] Hoover, W. G., 2002, "Note on 'Comment on "A Check of Prigogine's Theorem of Minimum Entropy Production in a Rod in a Nonequilibrium Stationary State," by Irena Danielewicz-Ferchmin and A. Ryszard Ferchmin [Am. J. Phys., 68(10), 962–965 (2000)],' by Peter Palffy-Muhoray [Am. J. Phys., 69(7), 825–826 (2001)]," Am. J. Phys., **70**(4), pp. 452–454.

[39] Glansdorff, P., and Prigogine, I., 1964, "On a General Evolution Criterion in Macroscopic Physics," Physica, **30**(2), pp. 351–374.

[40] Gyarmati, I., 1970, *Non-Equilibrium Thermodynamics* (Field Theory and Variational Principles), Springer-Verlag, Berlin.

[41] Kiss, E., 1994, "On the Validity of the Principle of Minimum Entropy Production," Period. Polytech. Chem. Eng., **38**(3–4), pp. 183–197.

[42] Kiss, E., 1997, "On the Principle of Minimum Entropy Production in Quasilinear Case and Its Connection to Statistical Mechanics," Period. Polytech. Chem. Eng., **41**(2), pp. 205–211.

[43] Suzuki, M., 2013, "Irreversibility and Entropy Production in Transport Phenomena, III—Principle of Minimum Integrated Entropy Production Including Nonlinear Responses," Physica A, **392**(2), pp. 314–325.

[44] Rosen, P., 1953, "On Variational Principles for Irreversible Processes," J. Chem. Phys., **21**(7), pp. 1220–1221.

[45] Richardson, I. W., 1969, "On the Principle of Minimum Entropy Production," Biophys. J., **9**(2), pp. 265–267.

[46] Pleshanov, A., 2001, "On the Extremal Principles in the Theory of Irreversible Processes," Doklady Phys., **46**(11), pp. 765–769.

[47] Jou, D., Carlomagno, I., and Cimmelli, V., 2015, "A Thermodynamic Model for Heat Transport and Thermal Wave Propagation in Graded Systems," Physica E, **73**, pp. 242–249.

[48] Guo, Y., and Wang, M., 2016, "Lattice Boltzmann Modeling of Phonon Transport," J. Comput. Phys., **315**, pp. 1–15.

[49] Hahn, D. W., and Özisik, M. N., 2012, *Heat Conduction*, 3rd ed., Wiley, Hoboken, NJ.

[50] Vadasz, P., 2010, "Analytical Solution to Nonlinear Thermal Diffusion: Kirchhoff Versus Cole–Hopf Transformations," ASME J. Heat Transfer, **132**(12), p. 121302.