General expression for entropy production in transport processes based on the thermomass model

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The entropy production in classical irreversible thermodynamics is expressed as a bilinear form of generalized (driving) forces and conjugated (driven) fluxes, which suffers from the arbitrary decomposition of the forces and the fluxes, and the possible negative entropy production in non-Fourier heat conduction problems (heat waves). This paper presents a general form of the entropy production for heat conduction based on the thermomass model, which is the product of the friction force and the drift velocity of the thermomass divided by the temperature; it holds true for both Fourier and non-Fourier heat conduction. Then a generalization of the entropy production is consistent with that given by extended irreversible thermodynamics, where the system entropy depends not only on the classical variables, but also on the dissipative fluxes, for example, the heat flux in heat conduction problems.

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I. INTRODUCTION

The establishment of classical irreversible thermodynamics (CIT) can be traced back to 1931, when Onsager postulated the reciprocal relations in two of his papers [1]. He deduced a "dissipation function" with a bilinear form of the "forces" and "velocities." The theory was further developed by Prigogine [2,3] and de Groot and co-workers [4–9] with the dissipation function clarified to be the entropy production σ^s . The entropy production in CIT is a bilinear product of the thermodynamic (generalized) forces, or driving forces *X*, and the conjugated fluxes, or driven fluxes *J* [4,7]:

$$\sigma^s = \sum_{\alpha} J_{\alpha} X_{\alpha}.$$
 (1)

CIT assumes a linear relationship between the thermodynamic forces and fluxes, so it is also regarded as linear irreversible thermodynamics. CIT has been applied well in many fields. For instance, the reciprocal relations facilitate analyses of the cross effects of various irreversible processes, such as thermoelectric and thermophoresis effects; the least dissipation of energy [1]; the minimum entropy production principle for stationary states [2,3] based on variational principles can be used to derive the transport equations and for thermodynamic optimization of irreversible processes [10–12].

However, CIT is still imperfect. First, the decomposition of the forces and fluxes in the entropy production expression is to some extent arbitrary [4,13,14]. For instance, the thermodynamic force in heat conduction processes can be defined as $-\nabla T$, $-\nabla \ln T$, or $\nabla (T^{-1})$ in Fourier's picture, the energy picture or the entropy picture, respectively [15]. Soon after the establishment of the reciprocal relations, the ambiguity in the selection of these forces and fluxes was found to be harmful to the reciprocity theorem [16]. Therefore, the physical identification of the thermodynamic forces and fluxes is very important and is regarded as one of the fundamental questions about CIT [14,16]. Second, the linear relations between the forces and fluxes are not accurate in some cases, such as for chemical reactions and rheological flows, which are generally characterized by nonlinear constitutive equations [4,13,14]. The linear heat conduction law is applicable only in normal practical conditions. When combined with the energy conservation relation, the linear Fourier law of heat conduction leads to a parabolic evolution function for the state variables, which predicts the nonphysical infinite propagation speed of thermal perturbations. Many efforts have been made to establish more general laws for irreversible processes in extreme conditions. The Cattaneo-Vernotte (CV) model [17–19] [see Eq. (7)] for heat conduction, which contains a heat flux relaxation term, gives a hyperbolic evolution function which removes the paradox of the infinite propagation speed. A similar modification is used to remove the paradox of Fick's law [20-24] and Newton's viscosity law (i.e., the Maxwell model for viscoelasticity) [21,25–27]. Since the heat flux is not proportional to the temperature gradient or the thermodynamic force, the entropy production is no longer positive semidefinite, which seems to violate the second law of thermodynamics [13,28]. This deviation from linearity undermines CIT theories, which motivated the development of extended irreversible thermodynamics (EIT) [13,28-39]. EIT introduces fluxes as independent variables and redefines some concepts, such as temperature and entropy. The definition of entropy production has a new form in EIT, which remains positive semidefinite in extreme conditions, such as heat transport at high frequencies and short wavelengths. However, the physical meanings of the modified generalzed forces have not been clarified up to now.

The thermomass (TM) model [40–44] has been developed in recent years to establish a general relation for heat conduction on the basis of first principles. Based on the Einstein mass-energy equivalence relation, the TM model gives a governing equation for heat conduction including nonlocal and nonlinear effects, which are ascribed to the thermomass inertia. This model is also useful for studying the unusual transport phenomena in nanoscale systems [44]. Comparisons

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of the TM model with EIT and phonon hydrodynamics have revealed the consistency between the constitutive equations for heat transport in different theories [35,45,46]. The entropy production for hyperbolic heat conduction based on the TM model has also been derived and found to be analogous with the EIT results [47]. In the present paper, the physical essences of the forces and fluxes are further examined with the assistance of TM theory to develop a general expression for entropy production in irreversible transport processes, which is applicable to both ordinary and fast transient conditions.

II. GENERALIZED ENTROPY PRODUCTION IN EIT

The entropy production for transport processes in CIT is

$$\sigma^{s} = \boldsymbol{q} \cdot \boldsymbol{\nabla} \left(\frac{1}{T}\right) - \frac{1}{T} \mathbf{P}^{v} : \boldsymbol{\nabla} \boldsymbol{u}_{\mathrm{f}} - \sum_{k=1}^{N} \boldsymbol{J}_{k} \cdot \boldsymbol{\nabla} \left(\frac{\mu_{k}}{T}\right) + \frac{1}{T} \boldsymbol{i} \cdot \boldsymbol{\nabla} \varphi_{e}, \qquad (2)$$

where q is the heat flux vector, T is the temperature, \mathbf{P}^{v} is the stress tensor, $u_{\rm f}$ is the fluid velocity, J_k is the diffusion flux, μ_k is the chemical potential, i is the current density, and φ_e is the electrical potential. Equation (2) characterizes the irreversibility induced by the transport of heat, momentum, mass fraction, and charge and as the sum of products of flow quantities (thermodynamic fluxes) and gradients of intensive state variables (thermodynamic forces). This expression is semipositive definite as long as the linear transport relations hold:

$$q = -\kappa \nabla T$$
 (Fourier's law for heat conduction), (3a)

$$\boldsymbol{J}_{k} = -\sum_{j=1}^{n} \rho D_{kj} \boldsymbol{\nabla} c_{j} \quad \text{(Fick's law for mass diffusion),} \quad (3b)$$

$$\mathbf{i} = -\frac{1}{r_e} \nabla \varphi_e$$
 (Ohm's law for electrical conduction), (3c)

$$\mathbf{P}^{v} = -2\eta \nabla \boldsymbol{u}_{f} \quad \text{(Newton's law for viscous flow)}, \tag{3d}$$

where κ is the thermal conductivity, η is the viscosity, D is the diffusivity, ρ is the density, c_k is the mass ratio defined by ρ_k/ρ , and r_e is the electrical resistance. When they coexist, these processes can cause cross effects, such as the thermoelectric and thermal diffusion effect. In these cases the linear transport relations become

$$\boldsymbol{q} = L_{qq} \nabla(1/T) - \sum_{k=1}^{N} L_{qk} \nabla(\mu_k/T) - L_{qe} \nabla(\varphi_e/T), \quad (4a)$$

$$\boldsymbol{J}_{k} = L_{kq} \boldsymbol{\nabla}(1/T) - \sum_{j=1}^{N} L_{kj} \boldsymbol{\nabla}(\mu_{j}/T) - L_{ke} \boldsymbol{\nabla}(\varphi_{e}/T), \quad (4b)$$

$$\mathbf{i} = L_{eq} \nabla(1/T) - \sum_{k=1}^{N} L_{ek} \nabla(\mu_k/T) - L_{ee} \nabla(\varphi_e/T), \quad (4c)$$

where L are phenomenological coefficients that must be symmetric according to Onsager's reciprocal relations.

However, these linear laws have some inherent theoretical problems. For example, in rigid bodies or fluids at rest, the energy conservation relation

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \boldsymbol{q} \tag{5}$$

combined with Fourier's law of heat conduction leads to a parabolic equation for the temperature evolution:

$$\rho C_V \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T), \qquad (6)$$

where *u* is the internal energy density and C_V is the specific heat. Although this equation is accurate enough for most engineering applications, it predicts an infinite propagation speed of the thermal perturbations and incorrect temperature evolution for fast transient heating problems. The Cattaneo-Vernotte model resolves this problem as [17–19]

$$\tau_{\rm CV} \frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\kappa \nabla T, \qquad (7)$$

where τ_{CV} is the relaxation time in the CV model. The relaxation time is generally very small ($\sim 10^{-12}$ s) for condensed matter. However, this modification results in new problems, since the deviation from linearity breaks the semipositive definiteness of the classical entropy production,

$$\sigma^{s} = \frac{\kappa \nabla T \cdot \nabla T}{T^{2}} + \frac{\tau_{\rm CV}}{T^{2}} \frac{\partial \boldsymbol{q}}{\partial t} \cdot \nabla T.$$
(8)

Equation (7) can be negative because of the second term on the right-hand side, as has been verified numerically [13,28] and seems to violate the second law of thermodynamics. EIT theory assumes the heat flux q to be a new state variable, and changes the entropy definition to

$$s = s_{\rm eq} - \frac{1}{2} \frac{\tau_{\rm CV}}{\rho \kappa T^2} \boldsymbol{q} \cdot \boldsymbol{q}.$$
⁽⁹⁾

Thus, EIT generalizes the entropy production for heat conduction as [13,29]

$$\sigma_{\rm EIT}^{\rm s} = \frac{1}{\kappa T^2} \boldsymbol{q} \cdot \boldsymbol{q}. \tag{10}$$

This is always semipositive definite for heat waves as shown in Fig. 1. The modified entropy production is exactly the same as the classical expression of Eq. (2) if Fourier's law holds. For heat conduction in fluids, Müller and others [21–31] choose the heat flux and the stress tensor as the independent variables, with the transport process then agreeing with the kinetic theory of gases from a derivation based on Grad's 13-moment distributions [21]. In this case the entropy production is positive definite with a quadratic form of the heat flux and stress tensor. The same analyses can be made for other transport processes, with the generalized entropy production in EIT to the lowest order of the flux becoming

$$\sigma^{s} = \frac{1}{\kappa T^{2}} \boldsymbol{q} \cdot \boldsymbol{q} + \frac{1}{2\eta T} \mathbf{P}^{v} : \mathbf{P}^{v} + \frac{1}{T} \sum_{k=1}^{N} \boldsymbol{J}_{k} \cdot \frac{R}{M_{k} \rho_{k}} \mathbf{D}^{-1} \boldsymbol{J}_{k} + \frac{1}{T} r_{e} \boldsymbol{i} \cdot \boldsymbol{i}, \qquad (11)$$

where *D* is the diffusion matrix of Fick's law in Eq. (3c), *R* is the ideal gas constant, and M_k is the molecular mass of species *k*. This expression is semipositive for short wavelengths or high-frequency phenomena since it is quadratic. With a



FIG. 1. The evolutions of the classical equilibrium entropy S_{CIT} and the extended entropy S_{EIT} in an adiabatic system.

similar decomposition as in CIT, the thermodynamic forces are no longer the gradient of the intensive state variables but proportional to the flow quantities. Therefore, the thermodynamic forces in EIT cannot be regarded as driving forces. This difference has been discussed by Llebot and co-workers [13,29] for the thermoelectric effect, with the definitions in EIT shown to be closer to Onsager's original proof of the reciprocal relations. However, the decomposition and physical meaning of thermodynamic forces and fluxes in the generalized entropy production equation have not been clarified.

III. TM-MODEL-BASED GENERAL ENTROPY PRODUCTION IN HEAT TRANSPORT

A. Thermomass model

According to Einstein's mass-energy equivalence relation, the thermal energy divided by the square of the vacuum light speed is part of the "proper mass" of a system. That means "a piece of iron weighs more when red hot than when cool" [48,49]. From this point of view, the mass increase of condensed matter, m_h , due to thermal vibrations is

$$m_h = \frac{mC_V T}{c^2},\tag{12}$$

where *m* is the mass of a body, C_V represents the specific heat capacity at constant volume, and *c* is the speed of light in a vacuum. Thus, the density of the thermomass, ρ_h , in units of kg m⁻³ is

$$\rho_h = \frac{\rho C_V T}{c^2}.$$
(13)

The drift velocity of the thermomass, u_h , can be extracted from the heat flux as

$$\boldsymbol{u}_h = \frac{\boldsymbol{q}}{\rho C_V T}.$$
 (14)

The governing equations of heat conduction have been obtained by analogy with porous hydrodynamics as

$$\frac{\partial \rho_h}{\partial t} + \boldsymbol{\nabla} \cdot (\rho_h \boldsymbol{u}_h) = 0, \qquad (15)$$

$$h_{h} \frac{\partial \boldsymbol{u}_{h}}{\partial t} + (\rho_{h} \boldsymbol{u}_{h} \cdot \boldsymbol{\nabla}) \boldsymbol{u}_{h} + \boldsymbol{\nabla} p_{h} = \boldsymbol{f}_{h}, \qquad (16)$$

where the first and second terms in Eq. (16) represent the inertia effects, f_h is the friction force, and p_h is the thermomass pressure. The thermal pressure can be derived from the Debye state equation for dielectric solids as

 ρ

$$p_h = \gamma \rho_h C_V T = \frac{\gamma \rho \left(C_V T \right)^2}{c^2}, \qquad (17)$$

where γ is the Grüneisen parameter. Substituting Eqs. (13) and (14) in Eq. (15) gives the thermomass (energy) conservation relation. Equation (16) represents the governing equation for heat transport. For bulk materials, the heat conduction process is analogous to fluid flow in porous media where the friction force is proportional to the flow rate:

$$\boldsymbol{f}_h = -\beta \rho_h \boldsymbol{u}_h. \tag{18}$$

The momentum equation (16) reduces to Fourier's conduction law for conditions with negligible thermomass inertia, which means a balance between the driving and friction forces,

$$\nabla p_h = \boldsymbol{f}_h. \tag{19}$$

Inserting Eq. (17) into Eq. (19) and comparing with Fourier's law gives the friction coefficient β as

$$\beta = \frac{2\gamma\rho C_V^2 T}{\kappa},\tag{20}$$

where κ is the thermal conductivity. Thus, the general heat conduction equation can be written as

$$\tau_{\rm TM} \frac{\partial \boldsymbol{q}}{\partial t} + 2\boldsymbol{l} \cdot \frac{\partial \boldsymbol{q}}{\partial x} - b\kappa \nabla T + \kappa \nabla T + \boldsymbol{q} = 0, \qquad (21)$$

with

$$\tau_{\rm TM} = \frac{\kappa}{2\gamma\rho C_V^2 T},\tag{22a}$$

$$\boldsymbol{l} = \frac{\boldsymbol{q}\kappa}{2\gamma C_V \left(\rho C_V T\right)^2} = \boldsymbol{u}_h \tau_{\rm TM}, \qquad (22b)$$

$$b = \frac{q^2}{2\gamma\rho^2 C_V^3 T^3} = Ma_h^2,$$
 (22c)

where τ_{TM} is the lag time between the temperature gradient and the heat flux, l is the characteristic length of heat conduction [44], which is a measure of the spatial inertia effects, where steady-state non-Fourier heat conduction occurs and boundary slip should be considered, and Ma_h is the thermal Mach number defined as the ratio of the drift velocity u_h to the thermal wave speed in the phonon gas u_{hs} . The first three terms on the left-hand side of Eq. (21) come from the inertia effects. The fourth term represents the effect of the pressure gradient (driving force) and the last term is proportional to the resistance force. Equation (21) reduces to the CV model when the second and third inertia terms are neglected, which predicts the heat waves for fast transient perturbation. The third inertia term implies that the effective thermal conductivity will decrease when the heat flux is very high, which agrees with experimental results for nanotubes and nanowires with slip boundary conditions [44]. Cimmelli et al. [35] obtained a similar equation to Eq. (21) based on the concept of a dynamical nonequilibrium temperature, with the nonlocal effect obtained by a nonlinear solution of the phonon Boltzmann equation which was consistent with the phonon hydrodynamics theory [46]. Thermomass theory is limited to conduction in rigid bodies at rest. When dealing with heat conduction in fluids or moving media, more terms are needed to describe the time derivative of the heat flux. Christov and Jordan [50] proposed a material derivative to remove the paradox in second-sound propagation in moving rigid media in inertial frames. More generally, Müller and Ruggeri [21] established the constitutive equations for heat and momentum transfer in fluids in a noninertial frame using extended thermodynamics and kinetic theory. They replaced the time derivative of the heat flux by $\partial q_i / \partial t + q_k (\partial v_i / \partial x_k) - 2q_k W_{ik}$, where v is the fluid velocity and W is the angular velocity matrix, which has two additional terms. The first additional term $q_k(\partial v_i/\partial x_k)$ is from the requirement of objectivity, the so-called Jaumann derivative. The second additional term $-2q_k W_{ik}$ can be rewritten as $-2c^2(\rho_h u_h)_k W_{ik}$ using Eqs. (13) and (14) and regarded as a Coriolis inertia term due to the effects of the noninertial frame.

B. General expression for entropy production during heat transport

The entropy production expression for heat transport can be established based on the thermomass model. Aiming to evaluate the dissipation in the system, in the thermomass model the entropy production is expressed as a product of the friction force and the velocity just like the viscous dissipation in hydrodynamics [47],

$$\sigma_{\rm TM}^s = -\frac{1}{T} \boldsymbol{F}_h \cdot \boldsymbol{u}_h = \frac{1}{\kappa T^2} \boldsymbol{q} \cdot \boldsymbol{q}, \qquad (23)$$

with

$$\boldsymbol{F}_{h} = -\frac{\rho C_{V} \boldsymbol{q}}{\kappa} = f_{h} \bigg/ \bigg(\frac{2\gamma C_{V} T}{c^{2}} \bigg) = f_{h} / \xi. \quad (24)$$

The dimensionless coefficient ξ relating F_h to f_h comes from the ratio of the mechanical energy of the thermomass, E_h , to the internal energy u,

$$\xi = \frac{dE_h}{du} = \frac{dp_h + \rho_h u_h du_h}{du}.$$
 (25)

 E_h consists of a potential part and a kinetic part. In ordinary cases, the potential part corresponding to the internal energy is dominant. The kinetic part is significant only in extreme conditions such as high-frequency heating or very large heat fluxes, when the temperature profile alone is not enough to characterize the transport process. Equation (24) indicates that F_h , with units of Nm⁻³, is the dissipative force per unit volume, i.e., the friction force per unit volume. Equation (23) gives a semipositive definite expression that agrees with the solid curve in Fig. 1.

In EIT, the generalized force in the expression of the generalized entropy production is [13]

$$X = \nabla \theta^{-1} - \frac{\tau}{\kappa \theta^2} \frac{\partial q}{\partial t},$$
(26)

where θ is the nonequilibrium temperature, which reduces to *T* when higher-order terms are negligible. If the relaxation time τ is selected as Eq. (22a), the generalized force appears as

$$-X = \frac{\nabla T}{T^2} + \frac{1}{2\gamma\rho C^2 T^3} \frac{\partial q}{\partial t} = \frac{c^2}{2\gamma\rho C^2 T^3} \left[\nabla p_h + \frac{\partial \left(\rho_h \boldsymbol{u}_h\right)}{\partial t} \right]$$
$$= \frac{1}{\rho C_V T^2 \xi} \boldsymbol{f}_h. \tag{27}$$

Hence, the generalized force in EIT is actually the friction force in the thermomass model. The first term on the right-hand side of Eq. (26) represents the driving force, while the second term is the inertia effect. If the partial differential operator in Eq. (26) is replaced by the material time derivative [35], Eq. (22) exactly reduces to Eq. (16).

In CIT, the thermodynamic forces in Eq. (2) are called "driving forces," which drive the fluxes [5,8]. From thermomass theory, these forces are friction (dissipative) forces, with the same units as body forces in continuum mechanics. Hence, the inapplicability of the traditional expression of Eq. (2) in extreme conditions is because the friction forces, rather than the driving forces, determine the dissipation or irreversibility of the transport processes.

IV. GENERAL EXPRESSION FOR THE ENTROPY PRODUCTION IN OTHER TRANSPORT PROCESSES

A. Mass diffusion

For mass diffusion processes in chemically inert mixtures, the mass conservation relation is

$$\rho \frac{\partial c_k}{\partial t} = -\nabla \cdot \boldsymbol{J}_k. \tag{28}$$

Here, the barycentric motion is omitted for systems enclosed in reservoirs. Fick's law states that at constant temperature and pressure, J_k is proportional to the gradient of c_k as in Eq. (3c). In binary solutions or dilute systems, D_{kj} can be simplified to D_k [51]. In CIT, the entropy production for mass diffusion of an *N*-component system is [4]

$$\sigma^{s} = -\sum_{k=1}^{N} \boldsymbol{J}_{k} \cdot \boldsymbol{\nabla} \left(\frac{\mu_{k}}{T} \right), \tag{29}$$

where μ_k can be related to the mass ratio as [52]

$$\mu_k = \frac{RT}{M_k} \ln \alpha_k c_k + \text{const}, \qquad (30)$$

with *R* the gas constant, M_k the molecular mass of species *k*, and α_k the activity coefficient of species *k*. For ideal solutions such as isomer/isotopic mixtures and dilute systems, α_k will be almost unity and the entropy production can be written as

$$\sigma^{s} = -\sum_{k} \boldsymbol{J}_{k} \cdot \frac{R}{M_{k}c_{k}} \boldsymbol{\nabla} c_{k}, \qquad (31)$$

which is semipositive definite by Fick's law.

The diffusion flux J_k can give the velocity of component u_k by neglecting the barycentric motion of the system,

$$\boldsymbol{J}_k = \rho_k \boldsymbol{u}_k. \tag{32}$$

Substituting this into Eq. (33) gives

$$\sigma^{s} = -\sum_{k} \rho_{k} \boldsymbol{u}_{k} \cdot \frac{R}{M_{k} c_{k}} \boldsymbol{\nabla} c_{k} = -\sum_{k} \boldsymbol{u}_{k} \cdot \frac{R}{M_{k}} \boldsymbol{\nabla} \rho_{k}. \quad (33)$$

For isothermal systems, this can be rewritten as

$$\sigma^{s} = -\sum_{k} \frac{1}{T} \boldsymbol{u}_{k} \cdot \boldsymbol{\nabla} \frac{\rho_{k} RT}{M_{k}} = -\frac{1}{T} \sum_{k} \boldsymbol{u}_{k} \cdot \boldsymbol{\nabla} p_{k}, \quad (34)$$

where p_k is the partial pressure of the ideal gas or the vapor pressure of the component in the solution. Hence, the classical entropy production for mass diffusion can be defined as the product of the driving forces (gradient of p_k) and the diffusive velocities of the components divided by T. The driving forces are identical to external forces acting on the system and a similar expression to Eq. (34) is given by Gallavotti (see Eq. (5.11) in Ref. [53]) for calculating the microscopic entropy production of a deterministic dynamic system.

The friction force for diffusion can be defined in the same manner as in Eq. (19) in ordinary situations for dilute diffusion, i.e., when balanced with the driving force,

$$\boldsymbol{f}_{k} = \boldsymbol{\nabla} \boldsymbol{p}_{k} = \frac{\rho RT}{M_{k}} \boldsymbol{\nabla} \boldsymbol{c}_{k}, \qquad (35)$$

This equation is simply Fick's law of mass diffusion; thus

$$\boldsymbol{f}_{k} = -\rho_{k} \frac{RT}{D_{k}M_{k}} \boldsymbol{u}_{k} = -\frac{p_{k}}{D_{k}} \boldsymbol{u}_{k}.$$
(36)

This is quite similar to the friction force in the thermomass model,

$$\boldsymbol{f}_{h} = -\frac{2\gamma\rho^{2}C_{V}^{3}T^{2}}{\kappa c^{2}}\boldsymbol{u}_{h} = -2p_{h}\frac{\rho C_{V}}{\kappa}\boldsymbol{u}_{h}.$$
 (37)

Note that D_k is defined by Eq. (3c) with the same units of m²/s as has the thermal diffusivity $\kappa/\rho C_V$.

When combined with the conservation relation in Eq. (28), Fick's law gives a parabolic evolution equation for c_k , just as for heat conduction processes,

$$\frac{\partial c_k}{\partial t} = -D_k \nabla^2 c_k, \tag{38}$$

which implies the paradox of an infinite propagation speed of concentration perturbations [21]. Within the framework of rational thermodynamics [21–24], the momentum balance equation for each constituent predicts that an acceleration term should be added into Fick's law under the assumption that each constituent obeys the same balance law as a single fluid. In this way, the time derivative of the diffusion flux corresponding to the acceleration can be introduced into Fick's law as in the CV model [20–24],

$$\tau_k \frac{\partial \boldsymbol{J}_k}{\partial t} + \boldsymbol{J}_k = -\rho D_k \boldsymbol{\nabla} c_k, \qquad (39)$$

where τ_k is the relaxation time. Inserting this relation into the expression for the entropy production, Eq. (33), will make the classical entropy production nonpositive definite. Hence, the expression for the entropy production in CIT should be

modified. We have shown in Sec. III that the problem of the traditional expression for the entropy production comes from the incorrect selection of the generalized forces. Therefore, the general entropy production should be defined based on the friction force, rather than the driving force. The general expression for the entropy production in an ideal solution is then

$$\sigma^{s} = -\frac{1}{T} \sum_{k=1}^{N} \boldsymbol{u}_{k} \cdot \boldsymbol{f}_{k} = \frac{1}{T} \sum_{k=1}^{N} \frac{p_{k}}{D_{k}} \boldsymbol{u}_{k} \cdot \boldsymbol{u}_{k}, \qquad (40)$$

which is quadratic and semipositive definite.

In practical multicomponent systems where the cross effects should be taken into account, the driving force in Eq. (34) cannot be expressed simply by the partial pressure or vapor pressure and the friction force is related to all of the fluxes. Equation (40) should then be reformulated as

$$\sigma^{s} = -\frac{1}{T} \sum_{k=1}^{N} \boldsymbol{u}_{k} \cdot \boldsymbol{f}_{k} = \frac{1}{T} \sum_{k=1}^{N} \left(\boldsymbol{u}_{k} \cdot \sum_{j=1}^{N} \Lambda_{kj} \boldsymbol{u}_{j} \right), \quad (41)$$

where the diffusion matrix Λ is symmetric and positive definite according to the reciprocal relation.

B. Electrical conduction

For electrical conduction, the traditional expression is the product of the electrical driving force (the gradient of electric potential φ_e) and the flux (current density *i*),

$$\sigma^{S} = -\frac{1}{T}\boldsymbol{i} \cdot \boldsymbol{\nabla}\varphi_{e}. \tag{42}$$

The current density is related to the drift velocity of the charge carriers

$$\boldsymbol{i} = \rho_e \boldsymbol{u}_e, \tag{43}$$

where ρ_e is the charge density and u_e is the drift velocity of the charge carriers. Then, the friction force is balanced by the driving force at steady state as

$$\boldsymbol{f}_e = \boldsymbol{\nabla}\varphi_e \rho_e = -i\boldsymbol{r}_e \rho_e = -\rho_e^2 \boldsymbol{r}_e \boldsymbol{u}_e, \qquad (44)$$

where f_e is the friction force per volume, which is proportional to the drift velocity with unit of N/m³. Therefore, the entropy production for electrical conduction is

$$\sigma^{S} = -\frac{1}{T} \boldsymbol{f}_{e} \cdot \boldsymbol{u}_{e} = \frac{1}{T} \rho_{e}^{2} \boldsymbol{r}_{e} \boldsymbol{u}_{e} \cdot \boldsymbol{u}_{e} = \frac{1}{T} \boldsymbol{r}_{e} \boldsymbol{i}^{2}.$$
(45)

This agrees with Joule's first law and is equivalent to the original form in CIT if Ohm's law holds. However, Havemann *et al.* [54] pointed out that a nonlinear term derived from the Boltzmann equation should be inserted into Ohm's law at low temperature, which is not surprising since Ohm's law neglects the time needed to accelerate the charge carriers. This relaxation time under normal conditions is rather small because the electrons are very light and the electrical force is quite strong. A more obvious example is the ballistic transport inside a cathode ray tube, where the inertia of electrons overwhelms the friction effects, so Eq. (42) fails while Eq. (45) is still applicable. This observation has also been obtained using the EIT approach by introducing *i* as the independent variable into

		Vectorial			Tensorial
Irreversible processes		Heat conduction	Mass diffusion	Electrical conduction	Viscous flow
Original ^a	σ^{s}	$oldsymbol{q}\cdot oldsymbol{ abla}\left(rac{1}{T} ight)$	$-\sum_{k=1}^{N}oldsymbol{J}_{k}\cdotoldsymbol{ abla}\left(rac{\mu_{k}}{T} ight)$	$-rac{1}{T}oldsymbol{i}\cdot oldsymbol{ abla}_{e}$	$-\frac{1}{T}\mathbf{P}^{v}:\boldsymbol{\nabla}\boldsymbol{v}$
$\sigma^s = \boldsymbol{J} \cdot \boldsymbol{X}$	J	q	$oldsymbol{J}_k$	i	\mathbf{P}^{v}
	X	$\mathbf{\nabla}\left(rac{1}{T} ight)$	$-oldsymbol{ abla}\left(rac{\mu_k}{T} ight)$	$-\frac{1}{T} \nabla \varphi_e$	$-\frac{1}{T} \nabla v$
General	σ^{s}	$rac{1}{\kappa T^2} oldsymbol{q} \cdot oldsymbol{q}$	$\frac{1}{T}\sum_{k=1}^{N}\left(\boldsymbol{u}_{k}\cdot\sum_{j=1}^{N}\Lambda_{kj}\boldsymbol{u}_{j}\right)$	$\frac{1}{T}\rho_e^2 r_e \boldsymbol{u}_e \cdot \boldsymbol{u}_e$	$-\frac{1}{T}\frac{1}{2\eta}\mathbf{P}^{v}:\mathbf{P}^{v}$
$\sigma^s = -\frac{u \cdot f}{T}$	и	$u_h = rac{q}{ ho C_V T}$	$\boldsymbol{u}_k = \boldsymbol{J}_k / ho_k$	$u_e = i/ ho_e$	$u_m = rac{\mathbf{P}^v \cdot \boldsymbol{u}_f}{\rho \boldsymbol{u}_f^2}$
	f	$-\frac{(\rho C_V)^2 T}{\kappa} \boldsymbol{u}_h$	$-\sum_{j=1}^N \Lambda_{kj} \boldsymbol{u}_j$	$-\rho_e^2 r_e \boldsymbol{u}_e$	$\frac{\rho \boldsymbol{u}_f^2}{\eta/\rho} \boldsymbol{u}_m$

TABLE I. Comparison of the original and general expressions of entropy production.

^aWe just show the most common decomposition of forces and fluxes among different approaches.

the Gibbs equation, with results closer to Onsager's proof of the reciprocal relations [13,29].

C. Momentum transport

For momentum transport, the entropy production in CIT is

$$\sigma^{S} = -\frac{1}{T} \mathbf{P}^{v} : \nabla \boldsymbol{u}_{f}.$$
(46)

This expression is based on mechanical laws, but is slightly different from Eqs. (23), (41), and (45), since the retarding forces have units of N/m^2 and are proportional to the relative velocities (velocity gradients) rather than the absolute velocities. However, Newton's viscosity law breaks down for rheological fluids [25–27], where it should be replaced with the relaxational Maxwell model

$$\tau \Im \mathbf{P}^{\nu} + \mathbf{P}^{\nu} = 2\eta \nabla \boldsymbol{u}_f, \tag{47}$$

where τ is the relaxation time, \Im is the objective time derivative, and η is the viscosity. In this case, Eq. (46) is not positive semidefinite and fails to characterize the actual dissipation. In analogy to the analyses for the other transport processes, \mathbf{P}^{v} can be regarded as a momentum flux and proportional to the friction force, while ∇u_f corresponds to the driving force. Therefore, the entropy production should be modified in a similar way as

$$\sigma^{S} = -\frac{1}{T} \frac{1}{2\eta} \mathbf{P}^{v} : \mathbf{P}^{v}, \qquad (48)$$

which has a similar form as in EIT (see Eq. (15.54) in Ref. [13]).

The drift velocity is found from the shear flow without volume variations, where the kinetic energy is simply dissipated into heat rather than converted into other types of mechanical energy. The drift velocity can be defined as

$$\boldsymbol{u}_m = \frac{\mathbf{P}^v \cdot \boldsymbol{u}_f}{\rho \boldsymbol{u}_f^2},\tag{49}$$

where u_m is the momentum transport velocity. Equation (49) is analogous to Eq. (14) since the numerator represents the flux of shear work and the denominator represents the energy density. Actually u_m is the drift velocity of kinetic energy and can characterize the drift velocity of momentum in this special

case. The friction force f_m is proportional to the drift velocity as

$$\boldsymbol{f}_{m} = \frac{\boldsymbol{P}^{v} \cdot \rho \boldsymbol{u}_{f}}{\eta} = \frac{(\rho \boldsymbol{u}_{f})^{2}}{\eta} \boldsymbol{u}_{m} = \frac{\rho \boldsymbol{u}_{f}^{2}}{\eta/\rho} \boldsymbol{u}_{m}.$$
 (50)

Equation (50) is consistent with Eqs. (33) and (34), where μ/ρ is the transport coefficient with unit of m²/s, ρu_f^2 corresponds to p_1 and p_h as the energy density. Of course, for more general flow conditions, the momentum transport changes the static pressure energy or the gravitational energy, so the momentum drift velocity cannot be as easily defined as in Eq. (49).

The original and general expressions for entropy production for transport processes are summarized in Table I. The general entropy production for irreversible processes is the product of the friction forces, rather than driving forces in classical theories, and the drift velocities divided by the temperature. The general entropy production is applicable not only to normal conditions but also to extreme conditions, such as fast transient perturbation and superhigh fluxes in nanoscale systems. The general expression reduces to the original form for ordinary conditions.

V. CONCLUSIONS

(a) The momentum balance equation (16) for heat conduction based on the thermomass model is the balance of the driving force, inertia force, and resistance force. The balance between the driving force and resistance force corresponds to the Fourier law of heat conduction. Since entropy production arises from the irreversibility of transport processes, the entropy production should be the product of the friction force, rather than the driving force, and the velocity divided by the temperature. This general definition of entropy production is applicable not only to Fourier heat conduction but also to non-Fourier phenomena, such as heat waves and nanoscale heat conduction with extremely high heat fluxes.

(b) The analyses based on the themomass theory can be extended to other transport processes, such as mass diffusion, electrical conduction, and momentum transport processes. The physical essence of the linear transport relations is the balance between the driving forces and the friction forces with the inertia forces ignored. The general expression for the entropy production for irreversible processes is the product of the friction forces and the drift velocities divided by the temperature. The decomposition of the forces and fluxes is no longer arbitrary with this physical identification. The general expression is especially useful for nonlinear transport processes (e.g., heat waves, anomalous diffusion) induced by inertia effects where the classical expressions are not semipositive definite.

(c) The general expression for the entropy production based on thermomass theory agrees well with that based on EIT, although from different theoretical frameworks. EIT characterizes irreversible systems with additional flux

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variables, i.e., the drift velocities multiplied by the density of the extensive properties. This is reasonable since the velocities are actually independent variables in dynamic systems. The thermomass model, however, takes the inertia force into account in the conservation equation. The consistency of both theories will deepen the understanding of irreversible thermodynamics.

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