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Local formulation of the first law and the second law of thermodynamics for a nonequilibrium system

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In this paper we construct a local formulation of the first law and the second law of thermodynamics for a nonequilibrium system such that their global forms are equivalent to Kelvin's principle and Clausius's principle. We also study the relationship between the entropy balance equation and the calotropy balance equation obtained by Eu [Phys. Rev. E **51**, 768 (1995)] by examining the model equations of the nonconserved variables proposed by Jou, Casse-Vazquez, and Lebon [Rep. Prog. Phys. **51**, 1105 (1988); *Extended Irreversibie Thermodynamics* (Springer, Heidelberg, 1993)] in extended irreversible thermodynamics.

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I. INTRODUCTION

Irreversible thermodynamics is a subject with many different sects. Since the publication of the celebrated book on nonequilibrium thermodynamics by De Groot and Mazur in 1962 [1], there has been a great amount of research done on this subject in the past, especially in extended irreversible thermodynamics (EIT). Notably there are two schools of theories in EIT. The first school of EIT is due to Jou, Casse-Vazquez, and Lebon [2] and Müller and Ruggeri, respectively [3]. In this school of EIT entropy is considered as a state function which satisfies the entropy balance equation, where the entropy production is semipositive definite. Its kinetic foundation is based on the linearization of ln(f) in terms of Grad's moment method [4], where f is the one-particle distribution function. The second school of EIT is due to Eu, where the calotropy (compensation function) ψ is considered as a state function which satisfies the calotropy balance equation [5]. Its kinetic foundation is based on the expansion of f in exponential form in terms of tensor Hermite polynomials. This series expansion is also closely related to Grad's method. Recently Eu has rederived the calotropy balance equation from the Carnot theorem and Clausius's inequality [6]. The main objective of this paper is to reexamine the main features of these theories of EIT in an alternative approach which is independent of kinetic theory in terms of the Boltzmann equation. Since dissipative fluxes are considered as independent variables in addition to the conserved variables in EIT, the traditional balance equation for the internal energy density must be modified so that contributions due to the dissipative fluxes are taken into consideration. Thus we construct a local formulation of the first law and the second law of thermodynamics accordingly, such that their global forms are equivalent to Kelvin's principle [7] and Clausius's principle [8]. We then show that our formulation gives rise to a generalized entropy balance equation and a generalized Gibbs relation, which reduce to the results obtained by Jou, Casse-Vazquez, and Lebon under appropriate conditions.

Consider a system of molecules in r components contained in a region $\Omega\subset\mathbb{R}^3$ with volume V, where no chemical reactions take place. Let ϵ be the internal energy density, $\nu=\rho^{-1}$ the specific volume, c_i the molar fraction of species i, p the hydrostatic pressure, and ϕ_i^α the generalized fluxes. For example, $\phi_i^{(1)}=\vec{J}_i^{(1)}$ is the mass flux, $\phi_i^{(2)}=\overleftrightarrow{\pi}_i$ is the traceless symmetric part of the pressure tensor $\overleftrightarrow{P}_i$, $\phi_i^{(3)}=\vec{Q}_i$ is the heat flux, etc. Here the index i refers to the ith molecular species and the superscript α represents the various kinds of fluxes. Except for α=1,3, in general ϕ_i^α is a tensor function of order α ($\vec{Q}_i$ is the contraction of the third order tensor). From a physical point of view, we may include sufficiently many fluxes for an appropriate description of irreversible processes. Let $x=(x^1,x^2,\ldots,x^n)=(\epsilon,\nu,\{c_i\},\{\hat{\phi}_i^\alpha=\rho^{-1}\phi_i^\alpha\},i=1,2,\ldots,r,\alpha=1,2,\ldots,k)$ be the set of thermodynamic variables. Let $\theta\in[a,b]$ be an empirical temperature in an arbitrary scale which can be employed to measure the hotness or the coldness of a nonequilibrium system at a local point $(\vec{r},t)$. At the moment it is difficult to describe the relationship between θ and x. However, in the Appendix we show that θ is a differentiable and monotonically increasing function of the local thermodynamic function T, which in turn becomes a C^1 function of x via the constitutive relation. The state of a nonequilibrium local system is then specified by x, where $x^i:\mathbb{R}^3\times\mathbb{R}^+\to\mathbb{R}^1$ is assumed to be a function of class C^1 in Ω, and satisfies the following set of dynamical equations:

$$d_t\rho=-\rho\vec{\nabla}\cdot\vec{u},\tag{1}$$

$$\rho d_t c_i=-\vec{\nabla}\cdot\vec{J}_i,\quad 1\leqslant i\leqslant r\tag{2}$$

$$\rho d_t\vec{u}=-\vec{\nabla}\cdot\overleftrightarrow{P},\quad \overleftrightarrow{P}=\overleftrightarrow{\pi}+p_b\hat{I}+p\hat{I}\tag{3}$$

$$\rho d_t\epsilon=-\vec{\nabla}\cdot\vec{Q}-\overleftrightarrow{P}:\vec{\nabla}\vec{u},\tag{4}$$

$$\rho d_t\hat{\phi}_i^\alpha=Z_i^\alpha+\Lambda_i^\alpha,\quad 1\leqslant i\leqslant r,\quad 1\leqslant\alpha\leqslant k\tag{5}$$

where $d_t=\partial_t+\vec{u}\cdot\vec{\nabla}$ is the substantial differential operator, $\vec{u}$ the hydrodynamic velocity, p_b the bulk viscous pressure (the excess normal stress), and $\hat{I}$ a unit second rank tensor. Furthermore, Z_i^α is a kinematic term depending on $\hat{\phi}_i^\alpha$ as

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well as the gradients of ϵ, ν, c_i, etc., while Λ_i^α is a dissipative term which does not involve the gradients of x. In general Λ_i^α is a nonlinear function of x such that the decomposition of Z_i^α and Λ_i^α in Eq. (5) is unique. The detailed expressions of Z_i^α and Λ_i^α depend on the specific model under consideration. For example, Jou, Casse-Vazquez, and Lebon considered the following set of equations for Eq. (5):

$$\rho d_t p_b = -\tau_0^{-1}\rho\zeta\vec{\nabla}\cdot\vec{u} + \tau_0^{-1}\rho\beta'\zeta g\vec{\nabla}\cdot\vec{Q} - \tau_0^{-1}\rho p_b = Z^b + \Lambda^b, \tag{6a}$$

$$\begin{aligned}\rho d_t\vec{Q} &= -\tau_1^{-1}\rho\lambda\vec{\nabla} g + \tau_1^{-1}\rho\beta\lambda g^2\vec{\nabla}\cdot\overleftrightarrow{\pi}\\ &\quad + \tau_1^{-1}\rho\beta'\lambda g\vec{\nabla} p_b - \tau_1^{-1}\rho\vec{Q}\\ &= Z^h + \Lambda^h,\end{aligned} \tag{6b}$$

$$\begin{aligned}\rho d_t\overleftrightarrow{\pi} &= -\tau_2^{-1}2\rho\eta[\vec{\nabla}\vec{u}]^{(2)} + \tau_2^{-1}2\rho\beta\eta g[\vec{\nabla}\vec{Q}]^{(2)} - \tau_2^{-1}\rho\overleftrightarrow{\pi}\\ &= Z^t + \Lambda^t,\end{aligned} \tag{6c}$$

where $\Lambda^b = -\tau_0^{-1}\rho p_b$, $\Lambda^h = -\tau_1^{-1}\rho\vec{Q}$, $\Lambda^t = -\tau_2^{-1}\rho\overleftrightarrow{\pi}$, ζ, λ, and η are the bulk viscosity, thermal conductivity, and shear viscosity, respectively, τ_0, τ_1, τ_2 are the relaxation times for the fluxes p_b, $\vec{Q}$, and $\overleftrightarrow{\pi}$, respectively, β' and β are constants, and g is a positive, monotonically increasing function of θ of class C^1 on $[a,b]$. Later it will be identified with the local thermodynamic temperature T in absolute temperature scale. Furthermore, $[\vec{\nabla}\vec{u}]^{(2)}$ represents the traceless symmetric part of $\vec{\nabla}\vec{u}$.

In the next section we discuss the local formulation of the first law and the second law of thermodynamics for a nonequilibrium system.

II. LOCAL FORMULATION OF THE FIRST LAW AND THE SECOND LAW OF THERMODYNAMICS

In the following discussions work will be considered positive if it is done on the system and negative if it is performed by the system. On the other hand, heat is considered positive if it is absorbed by the system, while it is negative if it is liberated by the system.

In order to consider the local formulation of the first law and the second law of thermodynamics we first divide the material system into a sufficiently large number of subsystems. Consider an arbitrary local system centered at $\vec{r}$ with volume element $d\vec{r}$ at time t. The thermodynamic state of the local system is specified by $x = (x^1,\ldots,x^n)$ with volume element dx and satisfies the dynamical equations (1)–(5).

In equilibrium thermodynamics the static pressure p is considered as the force for the volume change, and the chemical potentials μ_i as the generalized forces for the change of matter. Thus in the absence of external forces the work 1-form dw is given by $dw = -p d\nu + \Sigma\mu_i dc_i$. However, the work $\Sigma\mu_i dc_i$ is not included in the balance equation for the internal energy density ϵ given by Eq. (4). Hence Eq. (4) must be generalized in an appropriate manner.

A. Linear irreversible thermodynamics (LIT)

Multiplying Eq. (1) by p, Eq. (2) by $-\mu_i$ and summing over i, then adding these results to Eq. (4) we obtain

$$\begin{aligned}\rho\{d_t\epsilon + p d_t\nu - \Sigma_i\mu_i d_t c_i\} &= -\vec{\nabla}\cdot\vec{Q} - [\overleftrightarrow{\pi} + p_b\hat{I}]:\vec{\nabla}\vec{u}\\ &\quad + \Sigma_i\mu_i\vec{\nabla}\cdot\vec{J}_i\\ &= -\vec{\nabla}\cdot(\vec{Q} - \Sigma_i\mu_i\vec{J}_i)\\ &\quad - \{(\overleftrightarrow{\pi} + p_b\hat{I}):\vec{\nabla}\vec{u} + \Sigma_i\vec{J}_i\cdot\vec{\nabla}\mu_i\},\end{aligned} \tag{7}$$

where ‘‘:’’ denotes contraction of tensors.

Let $\vec{Q}_c = \vec{Q} - \Sigma_i\mu_i\vec{J}_i$ be the net heat flux, and set

$$\Sigma_d = -\{(\overleftrightarrow{\pi} + p_b\hat{I}):\vec{\nabla}\vec{u} + \Sigma_i\vec{J}_i\cdot\vec{\nabla}\mu_i\}. \tag{8}$$

It is well known that $[\vec{\nabla}\vec{u}]^{(2)}$, $\vec{\nabla}\cdot\vec{u}$, and $\vec{\nabla}\mu_i$ are the thermodynamic forces for the viscous flows and diffusion, respectively. Thus Σ_d is an internal work. The energy associated with Σ_d is a dissipative energy which cannot be converted to other useful work.

Since mass flux can also contribute to the heat flux, we define $\rho dq/dt = -\vec{\nabla}\cdot\vec{Q}_c$, where dq is the heat added to the local system per unit mass. On the other hand, it is evident that Eq. (4) is equivalent to Eq. (7), which can be rewritten as

$$d\epsilon = dq + dw + dq_d, \tag{9}$$

where $dq_d = \rho^{-1}\Sigma_d dt$. Therefore Eq. (9) is the local formulation of the first law.

Let $\xi = d\epsilon - dw = d\epsilon + p dv - \Sigma_i\mu_i dc_i$. The local formulation of the second law can be expressed as

$$\xi\wedge d\xi = 0, \tag{10a}$$

$$\Sigma_d \geqslant 0, \quad \Sigma_d = 0 \text{ only at thermodynamic equilibrium,} \tag{10b}$$

where ‘‘$\wedge$’’ represents the exterior product of differential forms.

Denote $\hat{x} = (\nu, c_1,\ldots,c_r) = (x^2,\ldots,x^n)$, and assume that p, μ_i, are C^1 functions of $\hat{x}$ and θ. In the Appendix we show that by Eq. (10a) there exist a positive function $g(\theta)$ and a scalar-valued function ψ such that g and ψ are functionally independent, and furthermore, $\xi = g d\psi$ [9]. This implies that g^{-1} is an integrating factor of ξ. Once an integrating factor is obtained, we can construct infinitely many integrating factors. We can therefore choose g as a positive, monotonically increasing function of θ such that $g(\theta)$ can be identified with the local thermodynamic temperature T in absolute temperature scale [10]. Thus

$$T d\psi = d\epsilon - dw = d\epsilon + p d\nu - \Sigma_i\mu_i dc_i. \tag{11}$$

With Eqs. (7) and (11) we can obtain the following balance equation for ψ:

$$\rho d_t\psi + \vec{\nabla}\cdot(\vec{Q}_c T^{-1}) = \Xi_c, \tag{12}$$

where

$$\Xi_c = T^{-1}(\Sigma_d - \vec{Q}_c \cdot \vec{\nabla} \ln T)$$

$$= -T^{-1}\{\vec{Q}_c \cdot \vec{\nabla} \ln T + (\overleftrightarrow{\pi} + p_b \hat{I}):\vec{\nabla}\vec{u} + \Sigma_i \vec{J}_i \cdot \vec{\nabla}\mu_i\}.$$

In view of the expressions of $\vec{Q}_c T^{-1}$ and Ξ_c given above, we notice that these quantities are identical to the entropy current $\vec{J}_s$ and entropy production σ, respectively, in linear irreversible thermodynamics. Furthermore, by Eqs. (11) and (12), ψ can be identified as the entropy density s. Thus Eq. (11) is the Gibbs relation, while Eq. (12) is the entropy balance equation. It should be emphasized that Eq. (11) is a consequence of the (Frobenius) condition $\xi \wedge d\xi = 0$, where T^{-1} is an integrating factor of the 1-form $\xi = d\epsilon - dw$. Traditionally, Gibbs relation (11) is obtained via local equilibrium assumption. However, this assumption is not required in our approach.

B. Model equations of Jou, Casse-Vazquez, and Lebon in EIT

In the theory of EIT proposed by Jou, Casse-Vazquez, and Lebon, p_b, $\vec{Q}$, and $\overleftrightarrow{\pi}$ are considered as independent variables in addition to ϵ, ν, and c_i. By examining Eqs. (6a)–(6c), we multiply Eq. (1) by p, Eq. (6a) by $(-\zeta^{-1}\rho\tau_0)p_b$, Eq. (6b) by $(-\lambda g)^{-1}\rho\tau_1\vec{Q}$, Eq. (6c) by $(-2\eta)^{-1}\rho\tau_2\overleftrightarrow{\pi}$, and add these results together to Eq. (4). We then obtain

$$\rho\{d_t\epsilon + p d_t\nu - [\tau_0\zeta^{-1}p_b d_t p_b + \tau_1(\lambda g)^{-1}\vec{Q}\cdot d_t\vec{Q} + \tau_2(2\eta)^{-1}\overleftrightarrow{\pi}:d_t\overleftrightarrow{\pi}]\} = -\vec{\nabla}\vec{Q}_c + \Sigma_d, \tag{13}$$

with

$$\vec{Q}_c = \vec{Q} + (\beta' p_b\vec{Q} + \beta\vec{Q}\cdot\overleftrightarrow{\pi})g, \tag{14}$$

$$\Sigma_d = \vec{Q}_c \cdot \vec{\nabla} \ln g + \{\zeta^{-1}\cdot p_b^2 + (\lambda g)^{-1}\vec{Q}\cdot\vec{Q} + (2\eta)^{-1}\overleftrightarrow{\pi}:\overleftrightarrow{\pi}\}. \tag{15}$$

In view of Eq. (13) we define the generalized work 1-form dw by

$$dw = -p d\nu + X_b dp_b + \vec{X}_h \cdot d\vec{Q} + \vec{X}_t : d\overleftrightarrow{\pi}, \tag{16}$$

where

$$X_b = -\tau_0(\rho\zeta)^{-1}p_b, \quad \vec{X}_h = -\tau_1(\rho\lambda g)^{-1}\vec{Q},$$

$$X_t = -\tau_2(\rho 2\eta)^{-1}\overleftrightarrow{\pi}$$

are the generalized potentials conjugate to p_b, $\vec{Q}$, and $\overleftrightarrow{\pi}$, respectively. Thus, except for the first term on the right hand side of Eqs. (14) and (16), the remaining terms are the contributions to the work 1-form and the net heat flux, respectively, due to the additional independent variables p_b, $\vec{Q}$, and $\overleftrightarrow{\pi}$. Again set $\rho dq/dt = -\vec{\nabla}\cdot\vec{Q}_c$ and $\xi = d\epsilon - dw$. By Eq. (13), the local formulation of the first law can be written as

$$d\epsilon = dq + dw + dq_d, \quad dq_d = \rho^{-1}\Sigma_d dt,$$

while the local formulation of the second law can be written as

$$\xi \wedge d\xi = 0,$$

$$\Sigma_d \geqslant 0, \quad \Sigma_d = 0 \text{ only at thermodynamic equilibrium.}$$

Hence by the integrability condition (10a) there exist a local thermodynamic temperature $g(\theta) = T$ in absolute temperature scale and a scalar-valued function ψ, such that

$$T d\psi = d\epsilon + p d\nu - \{\tau_0\zeta^{-1}p_b dp_b + \tau_1(\lambda T)^{-1}\vec{Q}\cdot d\vec{Q} + \tau_2(2\eta)^{-1}\overleftrightarrow{\pi}:d\overleftrightarrow{\pi}\} \tag{17}$$

is the generalized Gibbs relation. Furthermore, Eq. (13) yields

$$\rho d_t\psi + \vec{\nabla}\cdot(\vec{Q}_c T^{-1}) = T^{-1}(\Sigma_d - \vec{Q}_c\cdot\vec{\nabla} \ln T) = \Xi_c, \tag{18}$$

with

$$\Xi_c = (\zeta T)^{-1}p_b^2 + (\lambda T^2)^{-1}\vec{Q}\cdot\vec{Q} + (2\eta T)^{-1}\overleftrightarrow{\pi}:\overleftrightarrow{\pi}. \tag{19}$$

Notice that $\vec{Q}_c T^{-1} = \vec{J}_s$ is the entropy current, $\Xi_c = \sigma$ is the entropy production, and $\psi = s$ is the entropy density that satisfy the entropy balance equation (18).

C. General case

From the discussions above we notice that a generalized entropy balance equation can be obtained if the internal energy balance equation (4) is modified such that contributions due to the dissipative fluxes $\hat{\phi}_i^\alpha$ are taken into account. To this end, we multiply Eq. (1) by p, Eq. (2) by $-\mu_i$ and sum over i, Eq. (5) by X_i^α and sum over i and α, respectively. Adding these results to Eq. (4) yields the following equation equivalent to Eq. (4):

$$\rho\{d_t\epsilon + p d_t\nu - \Sigma_i\mu_i d_t c_i + \Sigma_{i,\alpha}X_i^\alpha : d_t\hat{\phi}_i^\alpha\} = -\vec{\nabla}\cdot\vec{Q} - (\overleftrightarrow{\pi} + p_b\hat{I}):\vec{\nabla}\vec{u} + \Sigma_i\mu_i\vec{\nabla}\cdot\vec{J}_i + \Sigma_{i,\alpha}X_i^\alpha : [Z_i^\alpha + \Lambda_i^\alpha]$$

$$= -\vec{\nabla}\cdot\vec{Q}_c - \{(\overleftrightarrow{\pi} + p_b I):\vec{\nabla}\vec{u} + \Sigma_i\vec{J}_i\cdot\vec{\nabla}\mu_i - \Sigma_{i,\alpha}\Psi_i^\alpha : (\vec{\nabla}\cdot X_i^\alpha)\} + \Sigma_{i,\alpha}X_i^\alpha : (Z_i^\alpha + \vec{\nabla}\cdot\Psi_i^\alpha + \Lambda_i^\alpha). \tag{20}$$

where Ψ_i^α is the flux of $\hat{\phi}_i^\alpha$ [11], X_i^α (the conjugate variable of $\hat{\phi}_i^\alpha$) is the generalized potential, and $\vec{Q}_c$ is the net heat flux given by

$$\vec{Q}_c = \vec{Q} - \Sigma_i \mu_i \vec{J}_i + \Sigma_{i,\alpha} X_i^\alpha : \Psi_i^\alpha . \tag{21}$$

Denote

$$\Sigma_d = -\{(\overleftrightarrow{\pi} + p_b \hat{I}) : \vec{\nabla}\vec{u} + \Sigma_i \vec{J}_i \cdot \vec{\nabla}\mu_i - \Sigma_{i,\alpha}\Psi_i^\alpha : (\vec{\nabla}\cdot X_i^\alpha)\}$$
$$+ \Sigma_{i,\alpha} X_i^\alpha : (Z_i^\alpha + \vec{\nabla}\cdot\Psi_i^\alpha + \Lambda_i^\alpha). \tag{22}$$

Similar to $\vec{\nabla}\vec{u}$ and $\vec{\nabla}\mu_i$, $\vec{\nabla}\cdot X_i^\alpha$ can also be considered as a generalized thermodynamic force attributable to the tensorial flows Ψ_i^α. Thus the first term of Eq. (22) represents a dissipative internal work. We call Σ_d the dissipative energy which cannot be converted to other useful work.

Next we define the generalized work 1-form dw for a nonequilibrium local system by

$$dw = -p\,d\nu + \Sigma_i \mu_i dc_i - \Sigma_{i,\alpha} X_i^\alpha : d\hat{\phi}_i^\alpha .$$

Since mass flows and other tensorial flows can also contribute to the heat flux, we define the local rate of change of heat per unit mass dq/dt by

$$\rho\,\frac{dq}{dt} = -\vec{\nabla}\cdot\vec{Q}_c .$$

Hence Eq. (20) can be rewritten as

$$d\epsilon = dq + dw + dq_d, \quad dq_d = \rho^{-1}\Sigma_d dt, \tag{23}$$

where $dx^i = (\vec{\nabla}x^i)\cdot d\vec{r} + (\partial_t x^i)dt$ is the substantial differential.

Equation (23) is the local formulation of the first law. On the other hand, if we set $\xi = d\epsilon - dw$, then the local formulation of the second law can be expressed as

$$\xi \wedge d\xi = 0, \tag{24a}$$

$$\Sigma_d \geqslant 0, \quad \Sigma_d = 0 \ \text{only at thermodynamic equilibrium.} \tag{24b}$$

Therefore there exist a local thermodynamic temperature T in absolute temperature scale and a state function ψ which is additive under composition of subsystems [10], such that

$$\xi = T d\psi = d\epsilon + p\,d\nu - \Sigma_i \mu_i dc_i + \Sigma_{i,\alpha} X_i^\alpha : d\hat{\phi}_i^\alpha \tag{25}$$

is the generalized Gibbs formula. Further, Eq. (20) yields the equation

$$\rho d_t \psi + \vec{\nabla}\cdot(\vec{Q}_c T^{-1}) = \Xi_c , \tag{25$'$}$$

where $\Xi_c = T^{-1}[\Sigma_d - \vec{Q}_c \cdot \vec{\nabla} \ln T]$.

Therefore by considering $\hat{\phi}_i^\alpha$ as the additional independent variables and by generalizing Eq. (14) appropriately to take into consideration the contributions due to $\hat{\phi}_i^\alpha$, we can obtain a generalized entropy balance equation (25′). In Eq. (25′), $\Xi_c \geqslant 0$ is the generalized entropy production. It contains the dissipative energy Σ_d and the dissipative internal work due to the net heat flux with thermodynamic force $-\vec{\nabla}\ln T$.

Based on the notion of uncompensated heat introduced by Clausius, Eu has recently obtained Eq. (25′) from Carnot theorem and Clausius inequality [6]. He called Ξ_c the calotropy production, $\vec{Q}_c T^{-1}$ the calotropy current, and ψ the calotropy density. So far the results in Eqs. (25) and (25′) do not depend on the specific expressions of Z_i^α and Λ_i^α. Thus Eqs. (25) and (25′) are general equations in irreversible thermodynamics that are not restricted to the framework of the Boltzmann equation, although kinetic theory can be helpful in the construction of Z_i^α and Λ_i^α. As a matter of fact, Z_i^α and Λ_i^α can be obtained from phenomenological theory such as the model equations (6a)–(6c) considered by Jou, Casse-Vazquez, and Lebon.

In the school of EIT by Jou, Casse-Vazquez, and Lebon and by Müller and Ruggeri, respectively, entropy density s is a state function which satisfies the entropy balance equation, while in the school of EIT by Eu, calotropy density ψ is a state function which satisfies the calotropy balance equation (25′). We devote the remaining section to investigating the relationship between these two approaches in terms of Eqs. (5) and (6a)–(6c).

In view of Eqs. (6a)–(6c) and (22), Ξ_c can be rewritten as

$$\begin{aligned}\Xi_c = {} & -T^{-1}(\vec{\nabla}\cdot\vec{u})[p_b + \rho\zeta\tau_0^{-1}X_b] \\ & -T^{-1}[\vec{\nabla}\vec{u}]^{(2)} : [\overleftrightarrow{\pi} + 2\rho\eta\tau_2^{-1}X_t] \\ & -T^{-1}\vec{\nabla}T\cdot[T^{-1}\vec{Q} + \rho\lambda\tau_1^{-1}X_h] \\ & +\vec{\nabla}\cdot\{T^{-1}[X_b\Psi_b + X_h : \Psi_h + X_t : \Psi_t]\} \\ & +\rho\{\beta'[\zeta\tau_0^{-1}X_b\vec{\nabla}\cdot\vec{Q} + \lambda T\tau_1^{-1}X_h\cdot\vec{\nabla}p_b] \\ & +\beta[\lambda T\tau_1^{-1}X_h : \vec{\nabla}\cdot\overleftrightarrow{\pi} + 2\eta\tau_1 X_t : [\vec{\nabla}\vec{Q}]^{(2)}]\} \\ & -T^{-1}\{\rho\tau_0^{-1}X_b p_b + \rho\tau_0^{-1}X_h\cdot\vec{Q} + \rho\tau_2^{-1}X_t : \overleftrightarrow{\pi}\}.\end{aligned} \tag{26}$$

We must determine X_b, X_h, X_t, Ψ_b, Ψ_h, and Ψ_t such that Eq. (26) becomes the entropy production σ given by Eq. (19). Since $\vec{\nabla}\cdot\vec{u}$, $[\vec{\nabla}\vec{u}]^{(2)}$, and $\vec{\nabla}T$ are functionally independent, we set the first three terms of Eq. (26) to zero. Then

$$X_b = -\tau_0(\rho\zeta)^{-1}p_b, \quad X_h = -\tau_1(\rho\lambda T)^{-1}\vec{Q},$$
$$X_t = -\tau_2(\rho 2\eta)^{-1}\overleftrightarrow{\pi}, \tag{27a}$$

and the last term of Eq. (26) becomes

$$\sigma = (\zeta T)^{-1}p_b^2 + (\lambda T^2)^{-1}\vec{Q}\cdot\vec{Q} + (2\eta T)^{-1}\overleftrightarrow{\pi} : \overleftrightarrow{\pi},$$

which is the same as Eq. (19). Thus Eq. (26) reduces to

$$\Xi_c = \sigma + \vec{\nabla}\cdot\{T^{-1}(X_b\Psi_b + X_h\Psi_h + X_t\Psi_t)$$
$$-(\beta p_b\vec{Q} + \beta\vec{Q}\cdot\overleftrightarrow{\pi})\}.$$

It is evident that $\Xi_c \equiv \sigma$ if and only if the divergence term vanishes. Consequently,

$$\Psi_b = -\tau_0^{-1}\rho\beta\zeta T\vec{Q}, \quad \Psi_h = -\tau_1^{-1}\rho\beta\lambda T^2\overleftrightarrow{\pi}, \quad \Psi_t \equiv 0, \tag{27b}$$

and

$$\begin{aligned}\vec{Q}_c T^{-1} &= T^{-1}(\vec{Q} + X_b\Psi_b + X_h\Psi_h + X_t\Psi_t)\\ &= T^{-1}\vec{Q} + \beta' p_b\vec{Q} + \beta\vec{Q}\cdot\overleftrightarrow{\pi}.\end{aligned}$$

Hence $\vec{Q}_c T^{-1} \equiv \vec{J}_s$, $\Xi_c \equiv \sigma$, and $\psi \equiv s$ if Eq. (27a) and (27b) are satisfied.

Therefore, under the approximations of Eqs. (27a) and (27b) in conjunction with the specific expressions of Z_i^α and Λ_i^α as given in Eqs. (6a)–(6c), Ξ_c, $\vec{Q}_c T^{-1}$, and ψ reduce to the entropy production σ, entropy current $\vec{J}_s$, and entropy density s, respectively. For this reason, it appears more appropriate to call ψ the generalized entropy density, $\vec{Q}_c T^{-1}$ the generalized entropy current, Ξ_c the generalized entropy production, and Eq. (25′) the generalized entropy balance equation. Finally it should be emphasized that the parameters T, p, μ_i, and X_i^α are constitutive parameters that are determined by phenomenological considerations.

III. GLOBAL FORMULATION OF THE FIRST LAW AND THE SECOND LAW

So far the first law and the second law of thermodynamics for a nonequilibrium system have been formulated in terms of the local thermodynamic variables x that satisfy the dynamical equations (1)–(5). Thus the state of the local subsystem centered at $\vec{r}$ with volume element $d\vec{r}$ is described by x with volume element dx in the thermodynamic space. When the global system undergoes an irreversible process, the local system correspondingly also undergoes a similar irreversible process at a microscopic scale which is mapped to a path in the thermodynamic space. However, it is difficult to describe precisely what this microscopic irreversible process is. For this reason we next consider the global formulation of the first law and the second law. It should be remarked that the global formulation is quite different from the local formulation. If the boundary of the material system is impermeable to the flows of Ψ_i^α, then the thermodynamic variables of the global system would be reduced to E, V, and $\{C_i\}$, where E, V, $\{C_i\}$ can be obtained by integrating ϵ, ν, $\{c_i\}$ over the volume of the material system. Let

$$\frac{dE}{dt} = \int \rho d_t\epsilon, \quad \frac{dQ}{dt} = -\int \vec{\nabla}\cdot\vec{Q}_c, \quad \frac{dQ_d}{dt} = \int \Sigma_d,$$

and

$$\frac{dW}{dt} = \int -\rho\{p d_t\nu - \Sigma_i\mu_i d_t c_i + \Sigma_{i,\alpha}X_i^\alpha d_t\hat{\phi}_i^\alpha\}.$$

By Eq. (20) we obtain the first law of thermodynamics in global form as

$$dE = dQ + dW + dQ_d. \tag{28}$$

Let $\hat{\Omega}(t) = dE - dW$. Notice that $\hat{\Omega} = dQ$ when the system is at thermal equilibrium. The global form of the second law can be expressed as

$$\hat{\Omega}\wedge d\hat{\Omega} = 0, \tag{29a}$$

$$Q_d \geqslant 0, \quad Q_d = 0 \text{ only at thermodynamic equilibrium.} \tag{29b}$$

Equation (29a) is the inaccessibility condition of Caratheodory [12]. The Caratheodory principle states that from an arbitrary initial point (state) there is a finite region (set of states of finite measure in the thermodynamic space) that cannot be reached by an adiabatic process, reversible or irreversible. This region may be taken arbitrarily close to the initial state.

As a consequence of Eq. (29a) there exist a global thermodynamic temperature $\hat{T}(t)$ and a global calotropy function $\Psi(t)$ such that

$$\hat{\Omega} = dE - dW = \hat{T}d\Psi.$$

Therefore the generalized Gibbs formula in global form can be written as [13]

$$\hat{T}d\Psi = dE + \hat{p}dV - \Sigma_i\hat{\mu}_i dC_i + \Sigma_{i,\alpha}\hat{X}_i^\alpha : d\Phi_i^\alpha. \tag{30}$$

In Eq. (30), $\hat{p}$, $\hat{\mu}_i$, $\hat{X}_i^\alpha$ are the global intensive thermodynamic variables. For example, $\hat{p}$ is defined as follows:

$$\hat{p}\,\frac{dV}{dt} = \int (p\rho d_t\nu)d\vec{r}.$$

The other intensive global thermodynamic variables are defined in a similar manner. Thus

$$\hat{T}\,\frac{d\Psi}{dt} = \int T(\rho d_t\psi)d\vec{r},$$

and Eq. (30) can be obtained from Eq. (25) by integrating over the volume of the material system.

We now prove that Eq. (29) is equivalent to Kelvin's principle and Clausius's principle. These principles are stated as follows.

(i) Kelvin's principle: In a cycle of processes, it is impossible to transfer heat from a heat reservoir and convert it all into work, without at the same time transferring a certain amount of heat from a hotter to a colder body.

(ii) Clausius's principle: It is impossible that at the end of a cycle of processes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.

The proof given below is patterned after the proof by Kirkwood and Oppenheim for equilibrium thermodynamics [8]. (1) Let $\hat{T}_i = \text{const}$, $i = 1,2$ be two hypersurfaces of constant temperatures, $\hat{T}_1 > \hat{T}_2$, in the thermodynamic space with coordinates $z = (z_1, z_2, \ldots, z_n)$ given by the global thermodynamic variables E, V, $C_i, \ldots$. Let γ_i be a reversible isotherm on the $\hat{T}_i = \text{const}$ surface. We assume that heat absorbed or liberated by the system along any reversible isotherm outside the phase transition region is a continuous function of z. Consider an arbitrary initial state z_1 on γ_1. Let states z_1' and z_1'' be further to the left of z_1 such that the heat absorbed by the system from z_1'' to z_1' and from z_1' to z_1 along γ_1, respectively, is positive (V is increasing from z_1'' to z_1' and from z_1' to z_1). Through states z_1' and z_1'' we draw reversible adiabatic paths ($\Delta Q=0$) that intersect isotherm γ_2 at z_2' and z_2'', respectively. Notice that both $\hat{\Phi}_i^\alpha$ and Σ_d vanish along a reversible path. We now prove that no points along the adiabatic paths $z_1'-z_2'$ and $z_1''-z_2''$ are accessible from state z_1 by an adiabatic path, with $\hat{\Omega}=0$, reversible or irreversible.

Suppose an adiabatic path exists between z_1 and z_2' where $\hat{\Omega}=0$. Consider the cycle $z_1-z_2'-z_1'-z_1$. The net heat absorbed by the system in this cycle is $\Delta Q_{1'1}=-\Delta Q_{11'}>0$, where we have used the abbreviation $\Delta Q_{1'1}$ to denote the heat absorbed from state z_1' to state z_1. On the other hand, by Eq. (28) we have $\Delta E=\Delta Q_{1'1}+\Delta W=0$ in the cycle. Hence $-\Delta W=\Delta Q_{1'1}$. This is impossible since the net heat absorbed would be converted completely into work done by the system ($\Delta W<0$). Similarly no adiabatic path exists between z_1 and z_2''. By the same reasoning no reversible adiabatic paths can cross each other. Hence $z_2'\neq z_2''$. This implies that no points between z_2' and z_2'' along γ_2 can be reached from z_1 by adiabatic path with $\hat{\Omega}=0$, reversible or irreversible. Next, let γ be an isotherm on the $\hat{T}=\text{const}$ surface, $\hat{T}_1>\hat{T}>\hat{T}_2$, such that it intersects the reversible adiabatic paths $z_1'-z_2'$ and $z_1''-z_2''$ at z_c and z_d, respectively. By the same reasoning no points along z_c-z_d can be reached from z_1 by adiabatic paths (reversible or irreversible). As $\hat{T}$ is arbitrary, a region of finite volume between the two surfaces $\hat{T}_1$ and $\hat{T}_2$ can be generated which is inaccessible from state z_1 by adiabatic paths with $\hat{\Omega}=0$. This region can be taken arbitrarily close to z_1. This proves the equivalence of Eq. (29) and Kelvin's principle for a nonequilibrium system.

(2) Let $\hat{T}_i=\text{const}$, $i=1,2,3$, be hypersurfaces of constant temperatures in the thermodynamic space with $\hat{T}_1>\hat{T}_2>\hat{T}_3$. Let γ_i, $i=1,2,3$ be reversible isotherms on the $\hat{T}_i=\text{const}$ hypersurface. Consider an initial state z_1 on γ_1. Let z_1' and z_1'' be located further to the right of z_1 such that the heat $\Delta Q_{11'}$ absorbed by the system along γ_1 from z_1 to z_1' is positive. Similarly $\Delta Q_{1'1''}$ is also positive. Through z_1' and z_1'' we draw reversible adiabatic paths that intersect γ_2 at z_2' and z_2'', respectively, and intersect γ_3 at z_3' and z_3'', respectively. Locate points z_3 and $\overline{z_3}$ on γ_3 such that $\Delta Q_{33'}=\Delta Q_{11'}$ and $\Delta Q_{\overline{3}3''}=\Delta Q_{11''}$. We now prove the assertion that no adiabatic path, reversible or irreversible, connects states z_1 and z_3. Furthermore, $z_3\neq\overline{z_3}$.

Suppose there exists an adiabatic path ($\hat{\Omega}=0$) connecting z_1 and z_3. Consider the cycle $z_1-z_3-z_3'-z_1'-z_1$. The net heat absorbed by the cycle is $\Delta Q=\Delta Q_{33'}+\Delta Q_{1'1}=\Delta Q_{33'}-\Delta Q_{11'}=0$. On the other hand, by Eq. (28) we have $\Delta W=0$. But this is impossible for $\Delta W=0$ implies that the net result of the cycle is to transfer heat $\Delta Q_{33'}$ at $\hat{T}_3$ to heat $\Delta Q_{11'}$ at $\hat{T}_1>\hat{T}_3$ without converting a certain amount of work into heat at the same time. This is against Clausius's principle. Hence no adiabatic path, reversible or irreversible, connects z_1 and z_3. By the same reasoning we can show that $\Delta Q_{1'1''}\neq\Delta Q_{3'3''}$. Since $\Delta Q_{\overline{3}3''}-\Delta Q_{33''}=\Delta Q_{11''}-\Delta Q_{33''}=\Delta Q_{1'1''}-\Delta Q_{3'3''}\neq 0$, $z_3\neq\overline{z_3}$. Therefore any point along γ_3 between z_3 and $\overline{z_3}$ is inaccessible from z_1 by an adiabatic path with $\hat{\Omega}=0$. Next we locate z_2 and $\overline{z_2}$ on γ_2 such that $\Delta Q_{22'}=\Delta Q_{11'}$ and $\Delta Q_{\overline{2}2''}=\Delta Q_{11''}$. Similarly any point along γ_2 between z_2 and $\overline{z_2}$ is inaccessible from z_1 by adiabatic paths. In fact, let $\hat{T}=\text{const}$ be an arbitrary temperature hypersurface between $\hat{T}_1=\text{const}$ and $\hat{T}_3=\text{const}$. Let γ be an isotherm on the $\hat{T}=\text{const}$ hypersurface which intersects the reversible adiabatic path between z_1' and z_3' at z_c, and intersects the reversible adiabatic path between z_1'' and z_3'' at z_d. Locate z_a and z_b on γ by the condition $\Delta Q_{ac}=\Delta Q_{11'}$ and $\Delta Q_{bd}=\Delta Q_{11''}$. Then any point along γ between z_a and z_b is adiabatically inaccessible from z_1. Indeed a region generated in this manner cannot be connected from z_1 by adiabatic paths with $\hat{\Omega}=0$, reversible or irreversible. Again we have proven the equivalence of Eq. (29) and Clausius's principle.

In conclusion, we have considered the dissipative fluxes $\hat{\phi}_i^\alpha$ as independent variables in addition to the conserved variables ϵ, ν, and c_i. We then reformulate the local forms of the first law and the second law accordingly by taking into consideration the contributions of the dissipative fluxes. As a consequence of this approach, a generalized entropy balance equation as well as a generalized Gibbs relation can be obtained. The method discussed in this paper is very different from the traditional approach in LIT, where the Gibbs relation is assumed in order to obtain the entropy balance equation. Finally we show that the global formulation of the second law given by Eq. (29) in conjunction with the first law (28) is equivalent to Kelvin's principle and Clausius's principle. We have also investigated the conditions such that the generalized entropy balance equation (25′) reduces to the entropy balance equation (18) by examining the dynamical equations (6a)–(6c) for the dissipative fluxes proposed by Jou, Casse-Vazquez, and Lebon in EIT.

APPENDIX

In this appendix we consider the integrability condition (10a) of the 1-form ξ. For simplicity we denote $\hat{x}=(x^2,\ldots,x^n)=(\nu,c_1,\ldots,c_r)$ and $(p,-\mu_1,\ldots,-\mu_r)=(w_2,\ldots,w_n)$. Assume that p, μ_i are C^1 functions of $(\hat{x},\theta)$. We then rewrite ξ in terms of w_j's as

$$\xi=dx^1+p\,d\nu-\sum_i \mu_i dc_i=dx^1+\sum_{j\geqslant 2} w_j(\hat{x},\theta)dx^j. \tag{A1}$$

It can easily be proved that $\xi\wedge d\xi=0$ if and only if $d\xi=0$ for $\xi=0$ [14]. This in turn implies

$$\partial_j w_k=\partial_k w_j \quad \text{for all} \quad \theta\in[a,b] \quad \text{and } j,k\geqslant 2. \tag{A2}$$

Here $\partial_j=\partial/\partial x^j$. Notice that Eq. (A2) is similar to Maxwell's relations at constant temperature. By Eq. (A2) there exists a C^1 function $V(\hat{x},\theta)$ such that $w_j(\hat{x},\theta)=-\partial_j V(\hat{x},\theta)$. Thus

$$dV=-\sum_{j\geqslant 2} w_j(\hat{x},\theta)dx^j-u(\hat{x},\theta)d\theta,$$

where $u(\hat{x},\theta)=-\partial_\theta V(\hat{x},\theta)$. Consequently,

$$\xi=d(x^1-V)-ud\theta.$$

By Eq. (10a); $\xi\wedge d\xi=-d(x^1-V)\wedge du\wedge d\theta=0$ implies

$$x^1-V=h[u(\hat{x},\theta),\theta]$$

for some h, and thus

$$\xi=dh(u,\theta)-ud\theta. \tag{A3}$$

Now we prove the existence of a local thermodynamic temperature T such that T^{-1} is an integrating factor for ξ. The local temperature can be measured by inserting a thermodynamic probe into a portion of the system in a manner described by Muschik as the contact temperature [15]. Let U be a neighborhood of an arbitrary local point $(\vec{r},t)$ of the system. Let $\theta\in[a,b]$ be the empirical temperature in U. Consider two subsystems in contact with each other. Each subsystem is described by $(\hat{x}_i,\theta_i)$, $i=1,2$ and satisfies Eq. (A3), respectively. Within a short period of time, both subsystems and the combined system have the same temperature θ. The combined system is then described by $(\hat{x}_1,\hat{x}_2,\theta)$ and also satisfies Eq. (A3). Suppose there is no interaction between the two subsystems. Then $\xi=\xi_1+\xi_2$. Hence,

$$dh(u,\theta)-ud\theta=d[h(u_1,\theta)+h(u_2,\theta)]-(u_1+u_2)d\theta.$$

This equation can be solved by setting

$$u=u_1+u_2 \quad \text{and} \quad h(u_1+u_2,\theta)=h(u_1,\theta)+h(u_2,\theta).$$

Consequently

$$h(u,\theta)=z(\theta)u,$$

where z is an arbitrary function of θ on $[a,b]$. We can choose z such that $z(\theta)>0$. Thus

$$\xi=d(zu)-ud\theta. \tag{A4}$$

The Pfaffian equation $\xi=0$ has an integral curve given by

$$u=cz^{-1}\exp\left(\int z^{-1}d\theta\right)=ct(\theta),$$

where c is a constant. In order to find the integral surfaces of Eq. (A4) we consider c as a new independent variable and denote it by ψ. Then $u=\psi t$ and

$$\xi=d(zu-ud\theta)=d(zt\psi)-\psi td\theta=\psi d(zt)+ztd\psi-\psi td\theta.$$

But $d(zt)=td\theta$. Thus

$$\xi=(zt)d\psi=\left(\exp\int z^{-1}d\theta\right)d\psi=g(\theta)d\psi.$$

Since we have chosen $z(\theta)>0$ for all $\theta\in[a,b]$, we now identify

$$T=g(\theta)=\exp\left(\int z^{-1}d\theta\right)$$

as the local thermodynamic temperature. As $dT/d\theta=Tz^{-1}>0$, g can be inverted to yield θ as a function of T. Next we consider the significance of V. Since $x^1-V(\hat{x},\theta)=h(u(\hat{x},\theta),\theta)$ and $h(u(\hat{x},\theta),\theta)=z(\theta)u$, we have

$$\epsilon=V+zu. \tag{A5}$$

This shows that ϵ is a function of $\hat{x}$ and θ. Denote

$$V(\hat{x},\theta)=V(\hat{x},\theta(T))=\overline{V}\hat{x},T),$$

$$\epsilon(\hat{x},\theta)=\overline{\epsilon}(\hat{x},T).$$

By definition, $u=-\partial_\theta V(\hat{x},\theta)=-\partial_T\overline{V}(\hat{x},T)dT/d\theta=\overline{u}Tz^{-1}$, where $\overline{u}=-\partial_T V$. Hence

$$T\overline{u}=zu \tag{A6}$$

and

$$\overline{\epsilon}=\overline{V}+T\overline{u}. \tag{A7}$$

The differential of Eq. (A7) in conjunction with Gibbs relation (12) yields $\overline{u}=s$, and

$$d\overline{V}=-pd\nu+\sum_i \mu_i dc_i-sdT. \tag{A8}$$

By Eqs. (A7) and (A8) we can conclude that $\overline{V}$ is the Helmholtz potential.

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