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Reversible reciprocal relation of thermoelectricity

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The first Kelvin relation, which states the Peltier coefficient should be equal to the product of temperature and Seebeck coefficient, is a fundamental principle in thermoelectricity. It has been regarded as an important application and direct experimental verification of the Onsager reciprocal relation (ORR) that is a cornerstone of irreversible thermodynamics. However, some critical questions still remain: (a) why Kelvin's proof—which omits all irreversibility within a thermoelectric transport process—can reach the correct result, (b) how to properly select the generalized-force-flux pairs for deriving the first Kelvin relation from the ORR, and (c) whether the first Kelvin relation is restricted by the requirement of the linear transport regime. The aim of the present work is to answer these questions based on the fundamental thermodynamic principles. Since the thermoelectric effects are reversible, we can redefine the Seebeck and Peltier coefficients using the quantities in reversible processes with no time derivative involved; these are renamed "reversible Seebeck and Peltier coefficients." The relation between them (called "the reversible reciprocal relation of thermoelectricity") is derived from the Maxwell relations, which can be reduced to the conventional Kelvin relation, when the local equilibrium assumption (LEA) is adopted. In this sense, the validity of the first Kelvin relation is guaranteed by the reversible thermodynamic principles and the LEA, without the requirement of the linear transport process. Additionally, the generalized force-flux pairs to obtain the first Kelvin relation from the ORR can be proper both mathematically and thermodynamically, only when they correspond to the conjugate-variable pairs of which Maxwell relations can yield the reversible reciprocal relation. The present theoretical framework can be further extended to other coupled phenomena.

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I. INTRODUCTION

Thermoelectric effects refer to the direct conversion of heat to electric energy and vice versa, which encompasses three separately identified phenomena [1]: the Seebeck effect, Peltier effect, and Thomson effect, with three corresponding coefficients. The Seebeck coefficient (α) is the ratio between the induced thermoelectric voltage in response to a temperature difference across a particular material, the Peltier coefficient (Π) is defined as the ratio between the electric-current-induced heat flow and the electric current, and the Thomson coefficient (χ) is the ratio between the heat production rate per unit volume and the product of electric current and temperature gradient. Note that the thermoelectric effects are thermodynamically reversible, and strong evidence for this point is that the efficiency of a thermoelectric module can approach the Carnot efficiency with the increasing *ZT* coefficient [2,3], which implies the heat-electricity conversion should be totally reversible in the limiting case excluding the irreversible factors including heat conduction and Joule heating. Nevertheless, the thermoelectric coefficients are conventionally defined using the quantities of irreversible transport processes (such as electric current and heat flux) with time derivatives involved.

Early in 1851, Lord Kelvin (also known as William Thomson) [4] identified that these three effects are not independent from each other, and proposed the Kelvin relations (also known as Thomson relations) that correlate the Seebeck, Peltier, and Thomson coefficients on the basis of fundamental reversible thermodynamics [5]. The first Kelvin relation is $\alpha T = \Pi$ with temperature T, while the second Kelvin relation gives $\chi = T d\alpha/dT$. In 1893, the Kelvin relations were first verified experimentally, and from then on they have been widely accepted and utilized [6,7]. It is noted that the second Kelvin relation can be readily derived from the first Kelvin relation, energy conservation law, and local equilibrium assumption [1]; in this sense, the first Kelvin relation should be the core of the relations among the three thermoelectric effects.

To derive the relations, Lord Kelvin assumed an electrical short circuit comprising two kinds of materials. There are two contact junctions within that device, and they are in contact with heat reservoirs of different temperatures. All irreversible factors, including Joule heating and heat conduction, are neglected. The conservation of energy and the balance of entropy flows will yield the required results. A detailed introduction about Kelvin's proof can be found in Ref. [8] (Sec. 2.1.4). Note that Kelvin's proof is questionable indeed [9], since these irreversible factors should not be neglected in the electrical short circuit with a finite temperature difference. As stated by Onsager in his famous

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paper in 1931 [9], "*Thomson's relation has not been derived entirely from recognized fundamental principles, nor is it known exactly which general laws of molecular mechanics might be responsible for the success of Thomson's peculiar hypothesis.*" Even now, the question remains as to why Kelvin's proof that omits all irreversible factors within a thermoelectric transport process, i.e., "Thomson's peculiar hypothesis" as called by Onsager, can reach the correct result.

In 1931, Onsager [9,10] developed the Onsager reciprocal relations (ORRs) on the basis of statistical thermodynamics and microscopic reversibility. The first Kelvin relation can be readily derived from the ORRs when the generalized-force-flux pairs are chosen properly [11,12]. Afterwards, the Kelvin relation was put on a solid physical basis, and reciprocally its experiments have been regarded as an important experimental verification of the ORR [6,13]. However, when taking a close look at the derivation from the ORR to the first Kelvin relation, one critical issue exists, which is how to properly select the generalized-force-flux pairs to construct the linear phenomenological relations. Some researchers summarized two requirements [12] on the selection of generalized fluxes $\boldsymbol{J}$ and forces $\boldsymbol{X}$: (i) The product of $\boldsymbol{J}$ and $\boldsymbol{X}$ is equal to the local entropy production rate σ_S, that is, $\sigma_S = \boldsymbol{J} \cdot \boldsymbol{X}$ (R1); and (ii) $\boldsymbol{J}$ is the time derivative of a *state variable*, and $\boldsymbol{X}$ is the derivative of the entropy deviation with respect to the state variable (R2). However, counterexamples do exist. For instance, in Miller's paper [6], the generalized flux and force are heat flux $\boldsymbol{q}_{\mathrm{h}}$ and $-\nabla T/T$ for heat conduction, while the charge transport's generalized flux and force are electric current $\boldsymbol{I}_e$ and the negative voltage gradient $-\nabla V_e$; the products of generalized force and flux are $T\sigma_S$ rather than σ_S.

Additionally, the linear hypothesis to derive the ORR has been stressed among many papers in the literature [14–17]. This actually indicates that the first Kelvin relation should be valid merely in the regimes of linear transport, since the ORR has been regarded as the physical basis of the Kelvin relation [1]. However, in practice the first Kelvin relation is generally employed to handle the problems with large temperature difference where the linearity of constitutive relations may be violated [18]. Therefore, it is also needed to clarify whether the first Kelvin relation is restricted by the requirement of linearity.

The present work is trying to answer the questions above on the basis of fundamental thermodynamic principles. Firstly, we will introduce the concepts of reversible Seebeck and Peltier coefficients with no time derivative involved, and clarify their relations with the conventional thermoelectric coefficients. Then, the relation between reversible Seebeck and Peltier coefficients will be derived from the Maxwell relations. Based on it, the selection of generalized-flux-force pairs and the requirement of linearity are clarified.

II. REVERSIBLE SEEBECK AND PELTIER COEFFICIENTS

The thermoelectric effects are reversible; thus, they can be analyzed in terms of the fundamental reversible thermodynamics. To do this, we redefine the thermoelectric coefficients using the quantities in the reversible processes with no time derivative involved, and for convenience we call them "reversible Seebeck and Peltier coefficients." Note that we here focus on the thermoelectric effects in solids with volume kept constant.

Figure 1 shows an electrically insulated subsystem embedded in an outer system with infinite thermal and electric capacitances. The initial equilibrium state is characterized by $\{S_0, N_{e0}, T_0, \mu_{e0}\}$ with entropy S_0, number of charge particles N_{e0}, temperature T_0, and electrochemical potential μ_{e0}. Then, the outer system is replaced by a new one with an infinitesimal change ΔT to its temperature and its electrochemical potential staying unchanged; a quasistatic reversible process occurs, during which heat is transferred from the outer system to the subsystem until the new equilibrium state of the subsystem is reached. At this new equilibrium state, the subsystem's quantity of charge is unchanged due to its electrically insulated boundaries, and instead the thermoelectric effect will cause a change of electrochemical potential, $\Delta\mu_e = e\Delta V_e$, with ΔV_e the voltage change and e the elementary charge. In this case, a reversible Seebeck coefficient can be defined as

$$\alpha_r = -\frac{\Delta V_e}{\Delta T} = -\frac{\Delta\mu_e}{e\Delta T}. \tag{1}$$

Apparently, the process depicted above should be reversible. To further demonstrate this point, its corresponding reverse process is depicted. For the subsystem with new equilibrium state $\{S_0 + \Delta S, N_{e0},\ T_0 + \Delta T,\ \mu_{e0} + \Delta\mu_e\}$, the outer system is changed to the original one with the initial temperature T_0; a reverse quasistatic process occurs, where heat is transferred from the subsystem to the outer system until the subsystem return its initial state, as illustrated in Fig. 1.

Similarly, a reversible Peltier coefficient is defined by constructing a quasistatic process shown in Fig. 2. A subsystem with open boundaries is embedded in the outer system. Figure 2(a) illustrates the initial equilibrium state. Then, the outer system is replaced by a new one with an infinitesimal change $\Delta\mu_e$ to its electrochemical potential and its temperature remains unchanged; $\Delta\mu_e$ drives both heat and charge quantity to transfer from the outer system to the subsystem until the new equilibrium state of subsystem is reached. Finally, for the subsystem, the changes of entropy S and charge quantity Q_e are denoted by ΔS and ΔQ_e, respectively. The change of heat ΔQ_h is equal to $T_0\Delta S$ with T_0 the temperature kept constant during the quasistatic process. The change of charge quantity ΔQ_e should be equal to $e\Delta N_e$ where N_e is the number of charge particles. Thus, the reversible Peltier coefficient is given by

$$\Pi_r = \frac{\Delta Q_h}{\Delta Q_e} = \frac{T_0\Delta S}{e\Delta N_e}, \tag{2}$$

which is "heat per carrier" in the quasistatic reversible process. Furthermore, the corresponding reverse process can also be designed by resetting the outer system to the initial one, as shown in Fig. 2.

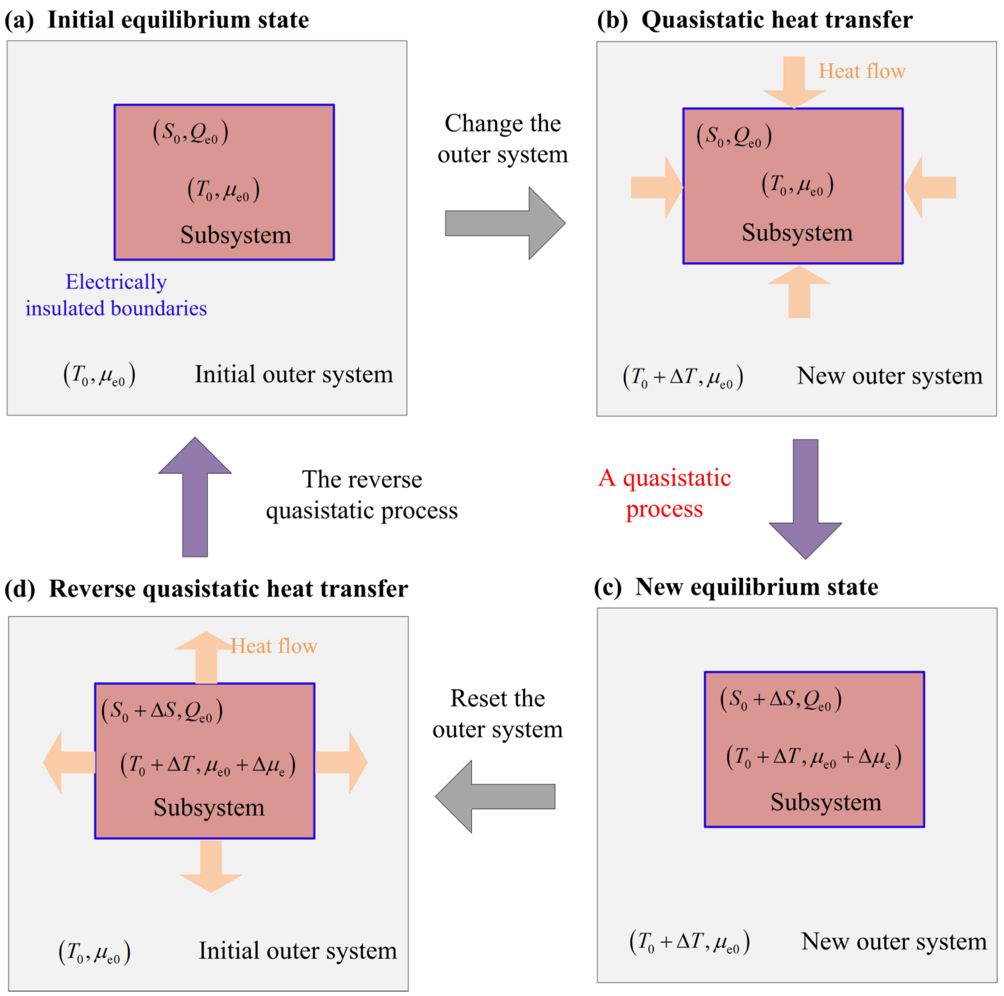

FIG. 1. Schematics for the definition of reversible Seebeck coefficient: (a) initial equilibrium state; (b) quasistatic heat transfer; (c) new equilibrium state; (d) reverse quasistatic heat transfer.

III. MAXWELL RELATIONS AND THE FIRST KELVIN RELATION

A. Derivation of the reversible reciprocal relation of thermoelectricity from Maxwell relations

We start from the basic equations in reversible thermodynamics [19].

First law of thermodynamics:

$$TdS = dU + \sum_i -\mu_i dN_i + pdV, \tag{3}$$

Euler integration:

$$ST = U + \sum_i -\mu_i N_i + pV, \tag{4}$$

and the Gibbs-Duhem equation:

$$SdT = \sum_i -N_i d\mu_i + Vdp. \tag{5}$$

Setting $V = V_0 = \text{const.}$ for solids, we have

$$dU = TdS + \sum_i \mu_i dN_i, \tag{6}$$

$$d(V_0 p) = V_0 dp = SdT + \sum_i N_i d\mu_i. \tag{7}$$

Particularly for thermoelectric systems, Eqs. (6) and (7) become

$$dU = TdS + \mu_e dN_e, \tag{8}$$

$$d(V_0 p) = SdT + N_e d\mu_e. \tag{9}$$

Two pairs of conjugate variables are selected in terms of Eqs. (8) and (9), which are

$$\{S, T\}, \{N_e, \mu_e\}, \tag{10}$$

where S and N_e are extensive variables, while T and μ_e are intensive ones. Two exact differentials are thus given by

$$-dS = \Gamma_{11} dT + \Gamma_{12} d\mu_e, \tag{11}$$

$$-dN_e = \Gamma_{21} dT + \Gamma_{22} d\mu_e. \tag{12}$$

Note that it is not necessary for the parameters, Γ_{11}, Γ_{12}, Γ_{21}, and Γ_{22}, to be constant. The combination of Eqs. (9), (11), and (12) leads to a Maxwell relation [19] of Γ_{12} and Γ_{21}

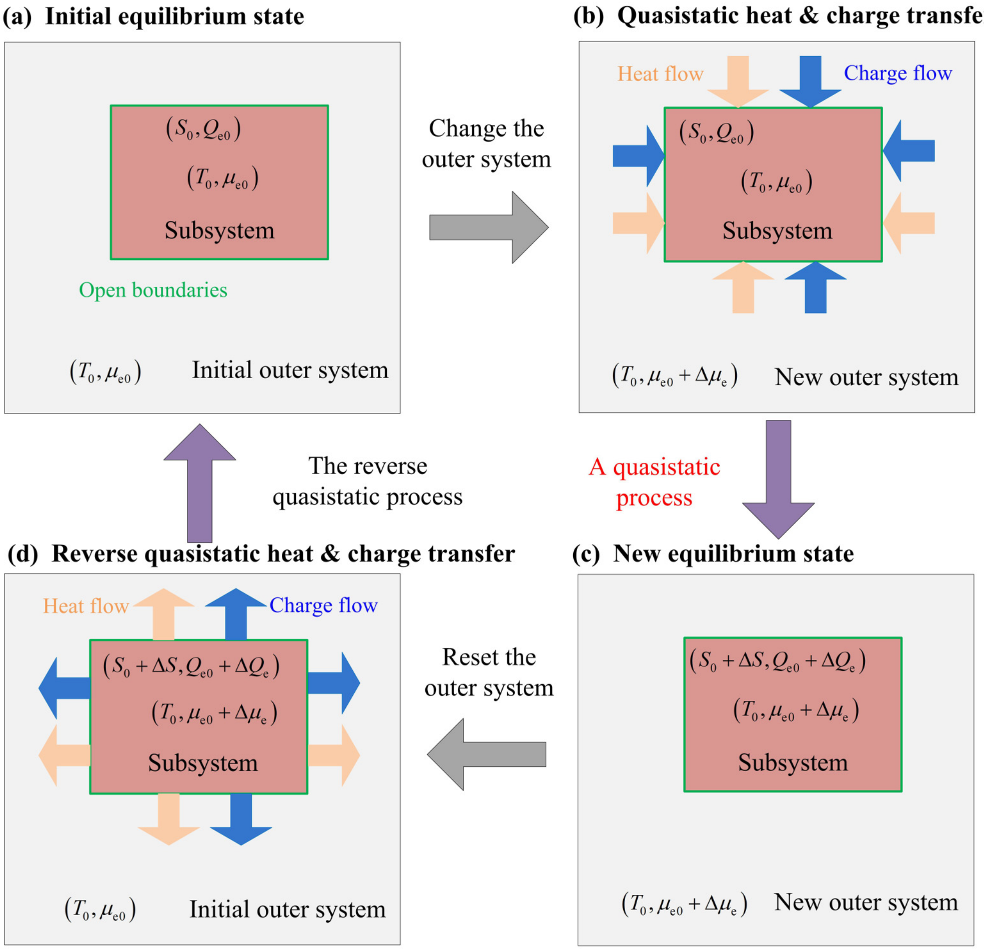

FIG. 2. Schematics for the definition of reversible Peltier coefficient: (a) initial equilibrium state; (b) quasistatic heat and charge transfer; (c) new equilibrium state; (d) reverse quasistatic heat and charge transfer.

(MR1),

$$\Gamma_{12} = \frac{-dS}{d\mu_e}\bigg|_T = -\frac{d^2(V_0 p)}{dT\, d\mu_e} = -\frac{d^2(V_0 p)}{d\mu_e dT} = \frac{-dN_e}{dT}\bigg|_{\mu_e} = \Gamma_{21}. \tag{13}$$

For the quasistatic process shown in Fig. 1 where N_e is unchanged, Eq. (12) becomes

$$dN_e = \Gamma_{21} dT + \Gamma_{22} d\mu_e = 0 \Rightarrow \Gamma_{21}\Delta T + \Gamma_{22}\Delta\mu_e = 0. \tag{14}$$

Referring to Eq. (1), the reversible Seebeck coefficient is given by

$$-\frac{\Delta\mu_e}{e\Delta T} = \alpha_r = \frac{1}{e}\frac{\Gamma_{21}}{\Gamma_{22}}. \tag{15}$$

Furthermore, for the quasistatic process shown in Fig. 2 with dT vanishing, Eqs. (11) and (12) are reduced to

$$-dS = \Gamma_{12} d\mu_e \Rightarrow -\Delta S = \Gamma_{12}\Delta\mu_e, \tag{16}$$

$$-dN_e = \Gamma_{22} d\mu_e \Rightarrow -\Delta N_e = \Gamma_{22}\Delta\mu_e. \tag{17}$$

Thus, according to Eq. (2), the reversible Peltier coefficient is

$$\Pi_r = \frac{\Delta Q_h}{e\Delta N_e} = \frac{T}{e}\frac{\Gamma_{12}}{\Gamma_{22}}. \tag{18}$$

Apparently, in terms of MR1, we have

$$T\alpha_r = \Pi_r. \tag{19}$$

Actually, we can derive two other exact differentials for these conjugate-variable pairs, which are reciprocal to Eqs. (11) and (12),

$$\begin{aligned} -dT &= \mathrm{R}_{11} dS + \mathrm{R}_{12} dN_e, \\ -d\mu_e &= \mathrm{R}_{21} dS + \mathrm{R}_{22} dN_e. \end{aligned} \tag{20}$$

Then, combining Eqs. (8) and (20) yields a Maxwell relation of R_{12} and R_{21} (MR2),

$$\mathrm{R}_{12} = -\frac{dT}{dN_e}\bigg|_S = -\frac{d^2U}{dN_e dS} = -\frac{d^2U}{dS dN_e} = \frac{d\mu_e}{dS}\bigg|_{N_e} = -\mathrm{R}_{21}. \tag{21}$$

Following the identical procedure, the same relation as Eq. (19) can be recovered from MR2.

The derivation above yields a relation that shows the reversible Peltier coefficient is equal to the product of temperature and reversible Seebeck coefficient, which has the same form as the conventional first Kelvin relation. For convenience, we call this relation "the reversible reciprocal relation of thermoelectricity."

B. Relation between the conventional Kelvin relation and the reversible reciprocal relation of thermoelectricity

In order to clarify the relation between the conventional Kelvin relation and the reversible reciprocal relation of thermoelectricity, we need to analyze the relationship between the conventional and reversible thermoelectric coefficients.

The conventional Seebeck and Peltier coefficients are defined in irreversible transport processes, which are given by [1]

$$\alpha = -\frac{\nabla_x V_e}{\nabla_x T}, \tag{22}$$

with the temperature gradient $\nabla_x T$ along a specific direction x and the corresponding temperature-gradient-induced voltage gradient $\nabla_x V_e$, and

$$\Pi = \frac{\boldsymbol{q}_{xh}}{\boldsymbol{I}_{xe}}, \tag{23}$$

with the heat flux $\boldsymbol{q}_{xh}$ along a specific direction x and the corresponding electric current $\boldsymbol{I}_{xe}$. In fact, based on the Kelvin relation, $\alpha T = \Pi$, the conventional Seebeck coefficient can be transformed to [11]

$$\alpha = \frac{\boldsymbol{q}_S}{\boldsymbol{I}_e}, \tag{24}$$

in which $\boldsymbol{q}_S$ is entropy flux. Therefore, in the irreversible thermoelectric transport processes, Π is heat per carrier, and α is "entropy per carrier," according to Eqs. (23) and (24).

Furthermore, according to Eq. (2), the reversible Peltier coefficient is heat per carrier in the reversible process. Importantly, using the reversible reciprocal relation of thermoelectricity, Eq. (19), the reversible Seebeck coefficient can be expressed as

$$\alpha_r = \frac{\Delta S}{\Delta Q_e}, \tag{25}$$

which is entropy per carrier in the reversible process. Therefore, when the local equilibrium assumption (LEA) is valid, the reversible thermoelectric coefficients should be equivalent to the conventional ones, and thus these two relations are also equivalent. We note that LEA is a rather fundamental hypothesis within the present framework of irreversible thermodynamics [16], which assumes that a system involving irreversible processes can be divided into infinitesimal subsystems where the usual thermodynamical variables, including temperature, pressure, and entropy, etc., have the same meaning as in the equilibrium states. In this sense, thermodynamic variables can be functions of position and time. Importantly, LEA further assumes that each subsystem can be considered as if it were in local equilibrium, though the gradients of the thermodynamic variables should give rise to the irreversibility of the whole system, and thus it permits one to apply all the results of equilibrium thermodynamics to a given subsystem [6]. Therefore, under LEA, Eq. (25), a result based on equilibrium thermodynamics, can be equivalent to Eq. (22) which is derived for the subsystems of a system undergoing irreversible processes. It is emphasized that LEA is just a hypothesis without much rigorous justification yet [20], though it has been extensively adopted in irreversible thermodynamics. Some researchers augured that LEA can break down for some far-nonequilibrium or nonlinear systems, the reciprocal relations are violated in this case [21–26].

TABLE I. Generalized force-flux pairs for obtaining the first Kelvin relation from the ORR.

		Force	Flux	Product of forces and fluxes
1	Thermal	$\nabla(1/T)$	Total energy flux $\boldsymbol{q}_U$	σ_S
	Electric	$\nabla(-\mu_e/eT)$	$\boldsymbol{I}_e$	
2	Thermal	$\nabla(1/T)$	$\boldsymbol{q}_h$	
	Electric	$\frac{1}{T}\nabla(-\mu_e/e)$	$\boldsymbol{I}_e$	
3	Thermal	$-\nabla \ln T$	$\boldsymbol{q}_S$	
	Electric	$\frac{1}{T}\nabla(-\mu_e/e)$	$\boldsymbol{I}_e$	
4	Thermal	$-\nabla T/T$	$\boldsymbol{q}_h$	$T\sigma_S$
	Electric	$\nabla(-\mu_e/e)$	$\boldsymbol{I}_e$	
5	Thermal	$-\nabla T$	$\boldsymbol{q}_S$	
	Electric	$\nabla(-\mu_e/e)$	$\boldsymbol{I}_e$	

In the regime where LEA is valid, our derivation above shows that the first Kelvin relation can be strictly derived from the basic equations in reversible thermodynamics, without considering irreversibility, which can explain the success of Kelvin's hypothesis that omits all the irreversible factors.

In addition, the derivation above demonstrates that the Kelvin relations are not restricted by the requirement of linear phenomenological relations. In fact, the Kelvin relations will hold, once the LEA and the fundamental thermodynamic principles are valid.

C. Selection of generalized force-flux pairs in the terms of conjugate-variable pairs

Table I summarizes the generalized force-flux pairs in the literature [1,6,11]. Apparently, referring to Table I, the selection of generalized force-flux pairs to obtain the Kelvin relation from the ORR is neither unique nor arbitrary. The product of generalized forces and fluxes is either σ_S or $T\sigma_S$. Note that heat flux $\boldsymbol{q}_h$ can be regarded as the time derivative of a state variable, merely for pure heat conduction in solids.

As a reasonable inference, the proper generalized force-flux pairs should correspond to the conjugate-variable pairs of which Maxwell relations can yield the reversible reciprocal relation of thermoelectricity. The conjugate-variable pairs, $\{S, T\}$, $\{N_e, \mu_e\}$, correspond to the generalized force-flux pairs, $\{\boldsymbol{q}_S, -\nabla T\}$, $\{\boldsymbol{I}_e, -\nabla \mu_e\}$, and the product of generalized force and flux is equal to $T\sigma_S$. Moreover, the reversible reciprocal relation of thermoelectricity can also be derived from another set of conjugate-variable pairs (the relevant proof is given in the Appendix), and they are

$$\left\{U,\frac{1}{T}\right\},\ \left\{N_e,\frac{-\mu_e}{T}\right\}, \tag{26}$$

which corresponds to the generalized force-flux pairs, $\{\boldsymbol{q}_U,\nabla(1/T)\}$, $\{\boldsymbol{I}_e,\nabla(-\mu_e/eT)\}$ with total energy flux $\boldsymbol{q}_U$. In this case, the product of generalized force and flux becomes σ_S.

In this sense, no conjugate-variable pair can be constructed to correspond to the generalized force-flux pairs involving heat flux, since heat flux is not the time derivative of any state variable in thermodynamics. Thus, we need further clarify why these generalized force-flux pairs involving heat flux can also derive the first Kelvin relation.

Take $\{\boldsymbol{q}_h,-\nabla\ln T\}$, $\{\boldsymbol{I}_e,-\nabla(\mu_e/e)\}$ as an example. This set of generalized force-flux pairs implies such two "exact" differentials,

$$-\delta Q_h=\Gamma_{11}^*\frac{1}{T}dT+\Gamma_{12}^*d\mu_e, \tag{27}$$

$$-dN_e=\Gamma_{21}^*\frac{1}{T}dT+\Gamma_{22}^*d\mu_e. \tag{28}$$

Then, we have

$$\Gamma_{12}^*=-\left.\frac{\delta Q_h}{d\mu_e}\right|_T=-T\left.\frac{dS}{d\mu_e}\right|_T,\quad \Gamma_{21}^*=-T\left.\frac{\delta N_e}{dT}\right|_{\mu_e}. \tag{29}$$

According to MR1, Eq. (13), we still have $\Gamma_{12}^*=\Gamma_{21}^*$, which indicates Eqs. (27) and (28) can also derive the reversible reciprocal relation of thermoelectricity. However, it is emphasized that Eq. (27) is definitely illegal in the sense of thermodynamics, since Q_h is a process variable. Thus, the generalized force-flux pairs involving heat flux may be proper in the view of mathematics, but incorrect in the sense of thermodynamics. In fact, another option to guarantee the consistency of the ORR's application to derive the Kelvin relation is to extend the conventional thermodynamics. As in the extended irreversible thermodynamics (EIT) [16], an extended entropy was introduced, and the heat flux can be taken as its additional variables; through such extended analysis, the ORR can be utilized to derive the Kelvin relation with the generalized force-flux pairs involving heat flux, electric flux, and their corresponding time derivatives.

IV. CONCLUSIONS

(1) To analyze the thermoelectric effects using the fundamental reversible thermodynamics, we redefine the Seebeck and Peltier coefficients using the quantities in reversible processes with no time derivative involved. Based on the Maxwell relation derived from the fundamental principles of equilibrium thermodynamics, we demonstrate that the relation between the reversible Seebeck and Peltier coefficients, i.e., the reversible reciprocal relation of thermoelectricity, has the same from as that between the conventional ones.

(2) When the LEA holds, the reversible thermoelectric coefficients should be equivalent to the conventional ones; in this case, the reversible reciprocal relation of thermoelectricity is reduced to the conventional first Kelvin relation.

(3) The first Kelvin relation should not be restricted by the requirement of linear phenomenological relations, and it will hold once the LEA and the fundamental thermodynamic principles are valid.

(4) Since Lord Kelvin omitted all the irreversible factors in a thermoelectric transport process with finite temperature difference, what he derived from the fundamental balance equations in equilibrium thermodynamics is just the reversible reciprocal relation of thermoelectricity. This explains why the questionable proof by Lord Kelvin can lead to the correct result.

(5) For obtaining the first Kelvin relation from the ORR, the generalized force-flux pairs, which are proper in the sense of both mathematics and thermodynamics, should correspond to the conjugate-variable pairs of which Maxwell relations can yield the reversible reciprocal relation of thermoelectricity.

(6) Although the present theoretical framework is used to analyze the thermoelectric effects, it can be extended to deal with other types of coupled phenomena, such as electrokinetics and heat-moisture-coupled transport.

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APPENDIX

This section provides a proof on how to derive the reversible reciprocal relation of thermoelectricity from the conjugate-variable pairs,

$$\left\{U,\frac{1}{T}\right\},\left\{N_e,\frac{-\mu_e}{T}\right\}.$$

For solid-state thermoelectric systems, we have the following:

First law of thermodynamics:

$$TdS=dU-\mu_e dN_e; \tag{A1}$$

Euler integration:

$$ST=U-\mu_e dN_e+pV_0. \tag{A2}$$

Equation (A1) can be transformed to

$$dS=\frac{1}{T}dU+\left(-\frac{\mu_e}{T}\right)dN_e. \tag{A3}$$

Combining Eqs. (A2) and (A3), we have

$$d\left(\frac{-pV_0}{T}\right)=Ud\left(\frac{1}{T}\right)+N_e d\left(\frac{-\mu_e}{T}\right). \tag{A4}$$

In this case, there are two pairs of conjugate variables:

$$\left\{U, \frac{1}{T}\right\}, \left\{N_e, \frac{-\mu_e}{T}\right\}, \tag{A5}$$

where U and N_e are extensive variables, while $1/T$ and $-\mu_e/T$ are intensive ones. For clarity, we set

$$1/T = \beta, \quad -\mu_e/T = \gamma.$$

Two exact differentials are given by

$$dN_e = L_{11}d\gamma + L_{12}d\beta, \tag{A6}$$

$$dU = L_{21}d\gamma + L_{22}d\beta. \tag{A7}$$

Thus, the combination of Eqs. (A4), (A6), and (A7) leads to a Maxwell relation between L_{12} and L_{21},

$$\Gamma_{21} = \left.\frac{dU}{d\gamma}\right|_{\beta} = \frac{d^2\left(-\frac{pV_0}{T}\right)}{d\beta d\gamma} = \frac{d^2\left(-\frac{pV_0}{T}\right)}{d\gamma d\beta} = \left.\frac{dN_e}{d\beta}\right|_{\gamma} = \Gamma_{12}. \tag{A8}$$

For the quasistatic process where N_e is unchanged, we have

$$L_{11}\Delta\gamma + L_{12}\Delta\beta = 0 \Rightarrow 0 = L_{11}\Delta\left(\frac{-\mu_e}{T}\right) + L_{12}\Delta\left(\frac{1}{T}\right). \tag{A9}$$

Referring to Eq. (1), the irreversible Seebeck coefficient is given by

$$-\frac{\Delta\mu_e}{e\Delta T} = \alpha_r = \frac{1}{eT}\left(\frac{L_{12}}{L_{11}} - \mu_e\right). \tag{A10}$$

Additionally, for the quasistatic process shown with dT vanishing, Eqs. (A6) and (A7) become

$$e\Delta N_e = eL_{11}\Delta\left(\frac{-\mu_e}{T}\right), \tag{A11}$$

$$\Delta U = L_{21}\Delta\gamma \Rightarrow \Delta U = L_{21}\Delta\left(\frac{-\mu_e}{T}\right). \tag{A12}$$

With $\Delta Q_h = \Delta U - \mu_e\Delta N_e$, we have

$$\Delta Q_h = L_{21}\Delta\left(\frac{-\mu_e}{T}\right) - \frac{\mu_e}{e}(e\Delta N_e). \tag{A13}$$

The reversible Peltier coefficient is thus given by

$$\Pi_r = \frac{1}{e}\left(\frac{\Gamma_{21}}{\Gamma_{11}} - \mu_e\right) = \frac{\Delta Q_h}{e\Delta N_e}. \tag{A14}$$

According to Eqs. (A10) and (A14), the reversible reciprocal relation of thermoelectricity is recovered,

$$T\alpha_r = \Pi_r. \tag{A15}$$

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