Review Article

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On the different formalisms for the transport equations of thermoelectricity: A review

Abstract: Researchers in thermoelectricity with backgrounds in non-equilibrium thermodynamics, thermoelectric engineering or condensed-matter physics tend to use different choices of flux densities and generalized forces. These choices are seldom justified from either the dissipation function or the entropy production rate. Because thermoelectric phenomena are a primary focus in several emerging fields, particularly in recent energy-oriented developments, a review of the different formalisms employed is judged timely. A systematic classification of the transport equations is presented here. The requirements on valid transport equations imposed by the invariance of the entropy production are clearly explained. The effective Peltier and Seebeck coefficients, and the thermal conductivity, corresponding to the different choices of flux densities and generalized forces, are identified. Emphasis is made on illustrating the compatibility of apparently disparate formalisms. The advantages and drawbacks of these formalisms are discussed, especially from the point of view of the experimental determination of their thermoelectric coefficients.

Keywords: Thermoelectricity, entropy production, Seebeck coefficient, Peltier coefficient, Kelvin formula, thermopower, observable electric potential, heat flux in open systems

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1 Introduction

The Peltier and the Seebeck thermoelectric coefficients are a primary focus in classical and emerging fields such as thermoelectric heat-pumping and power generation [1–5], heat harvesting [6–8], spin caloritronics [9, 10], thermoelectricity in low-dimensional materials [11–13], and fuel cells [14–16]. The thermoelectricity transport equations are linear relations between flux densities and driving forces. Different formalisms have been presented since the pioneering works carried out in the mid-twentieth century. Thermoelectricity is described in specialized monographs [2, 17, 18] as well as in books of irreversible thermodynamics [19–21], solid-state physics [22, 23], engineering [24], and biophysics [25]. While experts in different fields obviously know the formalism they employ, a considerable mixing of thermoelectric concepts exists because of the increasing number of scientists coming from a broad range of disciplines. A classification of the different formalisms available in the literature is still lacking and judged timely. While a few recent works include some fundamentals [2, 26, 27], the presentation of the fundamentals included here is especially suited for the purpose of the above-mentioned classification. The importance of this literature review is that it enables the comparison of the notation used in different areas and helps in the identification of (quite often) not-defined variables. Moreover, since a number of confusing ideas can be found in the literature, it may also be used to point out the (exceptional, but existing) incorrect formulations of transport equations. For instance, it is at times overlooked that the sets of flux densities and forces cannot be chosen arbitrarily. One possible choice of driving forces is $\{-\nabla\phi, -\nabla T\}$, where ϕ is the electrostatic potential [19, 28]. The electric current density $\boldsymbol{j}$ and a "heat flux density" $\boldsymbol{q}$ are their conjugate flux densities. In the pioneering work [29] (see also [17]), it was stated that

linear equations relating $\{\boldsymbol{j}, \boldsymbol{q}\}$ to $\{-\nabla\phi, -\nabla T\}$ are useless because their transport coefficients do not satisfy the Onsager reciprocal relation. When an electric current flows, what is meant by the heat flux density is not quite obvious, and, indeed, the definitions adopted by different authors are not the same [30]. In open systems the heat flux density can only be defined through conventions [19, 20, 31–33], so that it turns necessary to specify the definition of $\boldsymbol{q}$. Only one of these heat flux densities is compatible with the choice of variables $\{-\nabla\phi, -\nabla T, \boldsymbol{j}\}$ and, when it is used, the linear relations between $\{\boldsymbol{j}, \boldsymbol{q}\}$ and $\{-\nabla\phi, -\nabla T\}$ do satisfy the Onsager reciprocal relation. In the reference work [28], the transport equations are written as $\boldsymbol{j} = L_{11}\nabla\phi + L_{12}\nabla T$ and $\boldsymbol{q} = L_{21}\nabla\phi + L_{22}\nabla T$ with $L_{12} = L_{21}$, without realizing that L_{12} and L_{21} have different dimensions, and also as $\boldsymbol{j} = l_{11}(\nabla\tilde{\mu})/(Te) + l_{12}\nabla(1/T)$ and $\boldsymbol{q} = l_{21}(\nabla\tilde{\mu})/(Te) + l_{22}\nabla(1/T)$, with $l_{12} = l_{21}$. These equations are not compatible with $\boldsymbol{j} = L_{11}\nabla\phi + L_{12}\nabla T$ and $\boldsymbol{q} = L_{21}\nabla\phi + L_{22}\nabla T$, for the validity of one set implies that the other set of equations cannot hold unless a different heat flux density is used.

Expressions such as $\boldsymbol{q} = -\kappa\nabla T + \Pi\sigma\boldsymbol{E}$ (see [9]), $\boldsymbol{q} = -\kappa\nabla T + \Pi\boldsymbol{j}$ (see [26]) and $\alpha\nabla T + \boldsymbol{j}/\sigma = \boldsymbol{E} = -\nabla\phi$ (see [2]) are common in modern formalisms of thermoelectric phenomena. However, it is seldom explained that: (i) different conventions are used to define the "heat current density" $\boldsymbol{q}$, (ii) the thermal conductivities in the two above expressions for $\boldsymbol{q}$ are not the same, and (iii) different conventions are also used to define the thermoelectric coefficients. In the thermoelectricity literature the "electric field" $\boldsymbol{E}$ is often used, without declaring, to denote a quantity different from the negative of the electrostatic potential gradient. Though some authors explain the meaning of the symbols ϕ and $\boldsymbol{E}$ (see [27, 34]), others do not (see [2, 18, 26, 35]), and unaware readers may (incorrectly) associate them with their most frequently used meanings in the scientific literature, i.e. the electrostatic potential and the (Maxwell) electric field. Finally, when energy flux densities other than heat are used, the distinction between total and internal energy flux density is rarely made explicit.

The next section reviews the different formalisms employed in thermoelectric engineering, condensed-matter physics and non-equilibrium thermodynamics, and presents a rational explanation for their choices of flux densities and generalized forces. Novel recent approaches to the subject [36–40] are also discussed. The prevalence of the electrochemical formalism is explained. The advantages and drawbacks of the different formalisms are commented. In addition, the validity of the expressions for the Seebeck coefficient in terms of equilibrium properties is discussed.

2 The theory of thermoelectricity

2.1 Fundamentals

The theory of thermoelectricity is based on the general thermodynamic theory of Onsager and Casimir [41]. This theory relates the flux densities of extensive state quantities, such as electric charge, entropy, internal energy, total energy (internal and electrostatic), enthalpy, etc. to generalized forces, which are gradients of intensive state quantities. Heat is not an extensive state quantity and it has no conjugate intensive state variable. Yet, different heat flux densities can be defined through conventions. Any theoretical formalism proposed to describe thermoelectric phenomena must comply the invariance of the entropy production. That is, the entropy production is independent of the choice of fluxes and forces.

Another fundamental aspect of thermodynamic theories, including that of thermoelectricity, is that the best choice for fluxes and forces is dictated by experimental convenience. Thermodynamics is a phenomenological science that is meant to serve us in the measuring situation. Although many thermoelectric coefficients can be defined, those that can be measured become most useful.

For the sake of clarity, conduction by electrons in a homogeneous and isotropic metal with no concentration gradient, in the absence of magnetic field, is considered. Any valid combination of flux densities and driving forces must be derived from the entropy production rate π_s or from the dissipation function $T\pi_s$ (see [42]). As shown in the Appendix, from the entropy, energy and charge balances, the dissipation function is [20, 26, 34]

$$T\pi_s = \frac{\kappa}{T}(\nabla T)^2 + \frac{1}{\sigma}j^2, \tag{1}$$

where σ is the (isothermal) electrical conductivity and κ is the (static or open-circuit) thermal conductivity. Noticeably, the dissipation function involves no thermoelectric coefficients, and hence the thermoelectric effects are thermodynamically reversible [2, 26], as assumed by W. Thomson (Lord Kelvin) in 1854.

Under steady-state conditions, the entropy balance requires that the entropy production rate is equal to the divergence of the entropy flux density, $\pi_s = \nabla \cdot \boldsymbol{J}_s$. The local equilibrium assumption of irreversible thermodynamics and the Gibbs equation imply that the relation between the total energy flux density $\boldsymbol{J}_E$ and entropy flux density is (see Appendix)

$$\boldsymbol{J}_E = T\boldsymbol{J}_s + \tilde{\mu}\boldsymbol{J}_n = \boldsymbol{J}_Q - \frac{\tilde{\mu}}{e}\boldsymbol{j}, \tag{2}$$

where $\boldsymbol{J}_n = -\boldsymbol{j}/e$ is the flux density of electrons, $\boldsymbol{J}_Q \equiv T\boldsymbol{J}_s$ is the heat flux density, $e > 0$ is the elementary charge, and $\tilde{\mu}$ is the electrochemical potential of the electrons; in the literature, the NIST convention $e > 0$ is often not followed and the name chemical potential can also be used for $\tilde{\mu}$ (see [43]). The conservation of energy requires that the divergence of the total energy flux density vanishes, $\nabla \cdot \boldsymbol{J}_E = 0$, i.e., there is no "dissipation of energy". Similarly, the charge conservation requires that $\nabla \cdot \boldsymbol{j} = 0$. Thus, equation (2) implies that [43]

$$\nabla \cdot \boldsymbol{J}_Q = \boldsymbol{j} \cdot \nabla\tilde{\mu}/e. \tag{3}$$

That is, under steady-state conditions, the power input to the system must be dissipated as heat. The product $\boldsymbol{j} \cdot \nabla\tilde{\mu}/e$ is equal to the electrical Joule power j^2/σ plus a term $\alpha\boldsymbol{j} \cdot \nabla T$, where α is the Seebeck coefficient (see (57) in the Appendix), and it can be considered as the (volume density of) heat production rate. The heat flux density $\boldsymbol{J}_Q$ cannot be observed directly, only its divergence, i.e. the local "dissipation of heat" $\nabla \cdot \boldsymbol{J}_Q$ (see [23]).

2.2 General form of the transport equations

The steady-state entropy production rate is $\pi_s = \nabla \cdot \boldsymbol{J}_s = \nabla \cdot (\boldsymbol{J}_Q/T)$, and (3) implies that

$$T\pi_s = -\boldsymbol{J}_Q \cdot \nabla \ln T + \boldsymbol{j} \cdot \nabla\tilde{\mu}/e. \tag{4}$$

Hence, $\{\boldsymbol{J}_Q, \boldsymbol{j}\}$ is a valid pair of flux densities with conjugate driving forces $\{\boldsymbol{X}_T, \boldsymbol{X}_e\} = \{-\nabla \ln T, \nabla\tilde{\mu}/e\}$. The fundamental principle that rules whichever choice of fluxes and forces is that the entropy production must be invariant. The thermoelectricity transport equations invariably include the electric current density $\boldsymbol{j}$ and $\boldsymbol{X}_T = -\nabla \ln T$ as the thermal driving force because these are most easily controlled in experiments [20]. Different formalisms for the transport equations of thermoelectricity correspond to different choices of the "electrical" driving force $\boldsymbol{X}_e$ and of the "thermal" flux density $\boldsymbol{J}_T$ (i.e., the energy flux density). However, all the formalisms cannot be treated on an equal footing. The formalism that uses $\boldsymbol{X}_e = \nabla\tilde{\mu}/e$ and $\boldsymbol{J}_T = \boldsymbol{J}_Q$ not only provides a clear expression of the entropy production, as evidenced by (4), but it is also the only one whose thermoelectric coefficients can be measured.

The dissipation function can be presented as a sum of products of the flux densities and their conjugate driving forces

$$T\pi_s = \boldsymbol{J}_T \cdot \boldsymbol{X}_T + \boldsymbol{j} \cdot \boldsymbol{X}_e. \tag{5}$$

The equivalent expression for the entropy production rate is

$$\pi_s = \boldsymbol{J}_T \cdot \boldsymbol{Y}_T + \boldsymbol{j} \cdot \boldsymbol{Y}_e, \tag{6}$$

where $\boldsymbol{Y}_T \equiv \boldsymbol{X}_T/T = \nabla(1/T)$ and $\boldsymbol{Y}_e = \boldsymbol{X}_e/T$. In the continuous formalisms considered here (i.e. those involving gradients of potentials), equations (5) and (6) lead to the same transport equations, in spite of their different sets of forces. In discontinuous formalisms (i.e. those involving differences of potentials between two points) only (6) should be used [21]; some authors think that the use of (4) and (5) might also lead to wrong conclusions in continuous descriptions of transport processes in non-isothermal systems.

Formalism i	$\boldsymbol{J}_{\mathrm{T},i}$	$\boldsymbol{X}_{\mathrm{e},i}$	$L_{\mathrm{TT},i}$	$L_{\mathrm{Te},i}$	α_i	$e(\alpha_i-\alpha)$
electrochemical	$\boldsymbol{J}_{\mathrm{Q}}$	$-\nabla\tilde{\phi}\equiv\nabla\tilde{\mu}/e$	$T\tilde{\kappa}$	$\Pi\sigma$	$\alpha\equiv -S_{\mathrm{e}}^*/e$	0
Thomson	$\boldsymbol{J}_{\mathrm{E}}$	$T\nabla(\tilde{\mu}/T)/e$	$T\kappa_{\mathrm{E}}$	$\Pi_{\mathrm{E}}\sigma$	$\alpha-\tilde{\mu}/eT$	$-\tilde{\mu}/T$
Ohmic	$\boldsymbol{J}_{\mathrm{Q,cond}}$	$-\nabla\phi_{\mathrm{ohm}}$	$T\kappa$	0	0	S_{e}^*
electrostatic	$\boldsymbol{J}_{\mathrm{Q}}'$	$-\nabla\phi$	$T\kappa_\phi$	$\Pi_\phi\sigma$	$-Q_{\mathrm{e}}^*/eT$	S_{e}
quantum	$\boldsymbol{J}_{\mathrm{u}}$	$-\nabla\phi+T\nabla(\mu/T)/e$	$T\kappa_{\mathrm{u}}$	$\Pi_{\mathrm{u}}\sigma$	$-(H_{\mathrm{e}}+Q_{\mathrm{e}}^*)/eT$	$-\mu/T$
observable	$\boldsymbol{J}_{\mathrm{Q}}-\Pi_{\mathrm{R}}\boldsymbol{j}$	$-\nabla\psi$	$T\kappa_\psi$	$(\Pi-\Pi_{\mathrm{R}})\sigma$	$\alpha-\alpha_{\mathrm{R}}$	$S_{\mathrm{e,R}}^*$

Table 1. "Thermal" flux densities, "electrical" driving forces $\boldsymbol{X}_{\mathrm{e},i}$ and transport coefficients in the different formalisms. The formalisms could have been named after the quantity (i.e., entropy, total energy, heat, enthalpy or internal energy) used to define the "thermal" flux density, but we have preferred to use an adjective that identifies the electric potential, except for the quantum theory and the total energy (Thomson) formalisms.

Crucially, the quantities $\boldsymbol{X}_{\mathrm{e}}$ and $\boldsymbol{J}_{\mathrm{T}}$ are not independent. The choice of either $\boldsymbol{X}_{\mathrm{e}}$ or $\boldsymbol{J}_{\mathrm{T}}$ determines the other because the invariance of the entropy production requires that the right-hand side of (5) is equal to the right-hand side of (4) for any valid choice of $\boldsymbol{X}_{\mathrm{e}}$ and $\boldsymbol{J}_{\mathrm{T}}$, and hence

$$(\boldsymbol{J}_{\mathrm{T}}-\boldsymbol{J}_{\mathrm{Q}})\cdot\nabla\frac{1}{T}=\frac{1}{T}\boldsymbol{j}\cdot(\nabla\tilde{\mu}/e-\boldsymbol{X}_{\mathrm{e}}). \tag{7}$$

The transport equations can be written in any of the following forms:

$$\begin{pmatrix}\boldsymbol{J}_{\mathrm{T}}\\ \boldsymbol{j}\end{pmatrix}=\begin{pmatrix}TL_{\mathrm{TT}} & TL_{\mathrm{Te}}\\ TL_{\mathrm{eT}} & TL_{\mathrm{ee}}\end{pmatrix}\begin{pmatrix}\boldsymbol{Y}_{\mathrm{T}}\\ \boldsymbol{Y}_{\mathrm{e}}\end{pmatrix}, \tag{8}$$

$$\begin{pmatrix}\boldsymbol{J}_{\mathrm{T}}\\ \boldsymbol{j}\end{pmatrix}=\begin{pmatrix}L_{\mathrm{TT}} & L_{\mathrm{Te}}\\ L_{\mathrm{eT}} & L_{\mathrm{ee}}\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{\mathrm{T}}\\ \boldsymbol{X}_{\mathrm{e}}\end{pmatrix}, \tag{9}$$

where $L_{\mathrm{ee}}=\sigma$ is the (isothermal) electrical conductivity and $L_{\mathrm{Te}}=L_{\mathrm{eT}}$.

Table 1 summarizes the different formalisms explained in the following sections. The determinant of the matrix of transport coefficients in (9) is invariant under a transformation of flux densities and forces, and it is equal to $D=T\kappa\sigma$. If the cross coefficient in formalism i is written as the product of the electrical conductivity and the effective Peltier coefficient, $L_{\mathrm{Te},i}=\Pi_i\sigma$, the Onsager reciprocal relation $L_{\mathrm{Te}}=L_{\mathrm{eT}}$ implies the Thomson's second relation $\Pi_i=T\alpha_i$ between the effective Peltier (Π_i) and Seebeck (α_i) coefficients. Moreover, $L_{\mathrm{TT},i}/T\equiv\kappa_i=\kappa+T(\alpha_i)^2\sigma$ from the invariance of the determinant. Equation (9) gives then the "electrical" driving force in formalism i, usually the negative gradient of some "electric" potential, as

$$\boldsymbol{X}_{\mathrm{e},i}=\alpha_i\nabla T+\boldsymbol{j}/\sigma \tag{10}$$

and the corresponding "thermal" flux density as

$$\boldsymbol{J}_{\mathrm{T},i}=-\kappa\nabla T+\Pi_i\boldsymbol{j}. \tag{11}$$

2.3 Seebeck and Peltier coefficients. Electrochemical formalism

Although (10) and (11) show that every formulation leads to different effective Seebeck (α_i) and Peltier coefficients (Π_i), these names (without qualifiers and subscripts) must be restricted to the electrochemical formalism. This formalism chooses $\boldsymbol{X}_{\mathrm{e}}=\nabla\tilde{\mu}/e\equiv\tilde{\boldsymbol{E}}$ and $\boldsymbol{J}_{\mathrm{T}}=\boldsymbol{J}_{\mathrm{Q}}$, and its transport equations are [2, 18, 23, 28, 44]

$$\tilde{\boldsymbol{E}}=\boldsymbol{j}/\sigma+\alpha\nabla T, \tag{12}$$

$$\boldsymbol{J}_{\mathrm{Q}}=-\kappa\nabla T+\Pi\boldsymbol{j}. \tag{13}$$

Equation (13) is often written without explaining the meaning of the symbol $\boldsymbol{J}_{\mathrm{Q}}$. Equation (7) shows that if $\boldsymbol{X}_{\mathrm{e}}=\tilde{\boldsymbol{E}}$ then $T\boldsymbol{J}_{\mathrm{s}}$ is the only value for $\boldsymbol{J}_{\mathrm{Q}}$ in (13) that warrants the required invariance of the entropy production. In the presence of temperature gradients, $\tilde{\boldsymbol{E}}\equiv\nabla\tilde{\mu}/e$ is not equal to the electric field $\boldsymbol{E}=-\nabla\phi$. Yet, Landau

and Lifshitz proposed to name $\nabla\tilde{\mu}/e$ "electric field" with the notation $\boldsymbol{E} = -\nabla\phi$ (see [34]). In modern presentations [27, 45], it is common to use, quite often without declaring it [2, 18, 26, 43], the symbol $\boldsymbol{E}$ and the term electric field to refer to the gradient $\nabla\tilde{\mu}/e$. Other authors state that, since the gradient of the chemical potential $\mu = \tilde{\mu} + e\phi$ cannot be observed in real experiments, it can be considered that $\boldsymbol{E} = -\nabla\phi = (\nabla\tilde{\mu} - \nabla\mu)/e$ is equivalent to $\nabla\tilde{\mu}/e$ (see [46]). To avoid this source of confusion, we propose the notation $\tilde{\boldsymbol{E}} \equiv \nabla\tilde{\mu}/e \equiv -\nabla\tilde{\phi}$ and restrict the use of the traditional symbol $\boldsymbol{E} = -\nabla\phi$ for the Maxwell electric field; the notation $\phi_\mu \equiv -\tilde{\mu}/e$ is an interesting alternative. The existence of different sign criteria is also noticeable. The Seebeck coefficient α is denoted as $-\eta$ in [47] and $-\varepsilon$ in [19]; consistently, their Peltier coefficient is also the negative of our quantity Π.

Since coupling phenomena arise because electrons transport simultaneously charge and energy, relations can be found among the thermoelectric coefficients and electron transport quantities. Although there is no generally accepted terminology, the quantity $\boldsymbol{J}_\mathrm{Q} \equiv T\boldsymbol{J}_\mathrm{s}$ in (13) can be named the total heat flux density because it is a sum of two contributions:

$$\boldsymbol{J}_\mathrm{Q} = -\kappa\nabla T + TS_\mathrm{e}^*\boldsymbol{J}_\mathrm{n}, \tag{14}$$

where $S_\mathrm{e}^* = -e\Pi/T = -e\alpha$ is the transported entropy of the electrons [27, 30, 45]; this transported entropy introduced by J. N. Agar is different from that defined by E. D. Eastman [19]. In [45], the two terms in the right-hand side of (14) are interpreted, respectively, as conductive and convective contributions to the total heat flux density; presumably, because $TS_\mathrm{e}^*\boldsymbol{J}_\mathrm{n}$ is related to the flux of electrons. However, convection refers to macroscopic motion of the volume elements or mass of the system, and not to the relative motion of one of its components [19, 42], and the adjective convective is not recommended for $TS_\mathrm{e}^*\boldsymbol{J}_\mathrm{n}$.

From (9), an alternative heat flux equation is

$$\boldsymbol{J}_\mathrm{Q} = -\tilde{\kappa}\nabla T + \Pi\sigma\tilde{\boldsymbol{E}}, \tag{15}$$

where $\tilde{\kappa} \equiv \kappa + T\alpha^2\sigma$ is the thermal conductivity in the absence of electrochemical potential gradient. This has also been named short-circuit thermal conductivity [27] and (not very fortunately) interpreted as a sum of the conductive, κ, and convective, $T\alpha^2\sigma$, contributions [45]. It is related to the thermoelectric figure of merit Z as

$$\frac{\tilde{\kappa}}{\kappa} = 1 + \frac{\alpha^2\sigma}{\kappa}T = 1 + ZT. \tag{16}$$

The main advantage of the electrochemical formalism is that its thermoelectric coefficients are measurable, at least in relative terms. An electric potential difference can only be measured between two conductors of the same material and at the same temperature (regardless current is flowing or not). The measured electric potential difference is

$$\phi_2 - \phi_1 \equiv -\frac{1}{e}(\tilde{\mu}_2 - \tilde{\mu}_1). \tag{17}$$

Thus, for instance, the integration of (12) along the circuit between the two terminals connected to a voltmeter gives

$$\phi_2 - \phi_1 = -\frac{1}{e}\int_1^2 \mathrm{d}\tilde{\mu} = -\int_1^2 \alpha\mathrm{d}T - \int_1^2 \frac{j}{\sigma}\mathrm{d}x. \tag{18}$$

The last term vanishes under open-circuit conditions. It is important to note, however, that $\nabla\phi \neq -\alpha\nabla T$ inside an electronic conductor under open-circuit conditions. Remarkably, equation (18) shows that the measured electric potential difference $\phi_2 - \phi_1$ is related to the Seebeck coefficient α in the electrochemical formalism. Because voltages are measured more easily than heat generation, the Peltier coefficient is often evaluated from Thomson's relation [9, 39, 40], but its relative value between two conductors can be measured. The first term in the right-hand side of (18) vanishes, regardless of the temperature distribution, if the circuit between points 1 and 2 is made of only one conductor; a statement closely related to the law of homogeneous materials [24]. When the circuit is composed of two conductors, the difference in their (average) Seebeck coefficients can be determined from the measured electric potential difference.

A drawback of the electrochemical formalism is that $\boldsymbol{X}_\mathrm{e} = \nabla\tilde{\mu}/e$ includes a contribution proportional to ∇T due to the temperature dependence of $\tilde{\mu}$. Because the effect of the temperature gradient cannot be associated only with the first term of the dissipation function in (4), some authors prefer other choices of $\boldsymbol{X}_\mathrm{e}$ and $\boldsymbol{J}_\mathrm{T}$.

2.4 Thomson coefficient

W. Thomson predicted and observed a third thermoelectric effect and introduced the corresponding coefficient. The effect is obviously independent of our choice of fluxes and forces, but it can be illustrated with the greatest simplicity in terms of the flux of energy (internal plus electrostatic). The total energy flux density $\boldsymbol{J}_{\mathrm{E}}$ is widely employed as the "thermal" flux density [2, 23, 30, 38–40, 44], and (7) allows us to identify the corresponding "electrical" driving force as $\boldsymbol{X}_{\mathrm{e}} = T\nabla(\tilde{\mu}/T)/e$. Contrarily to $\boldsymbol{X}_{\mathrm{e}}$ in other formalisms, named after their associated electric potential, the driving force $T\nabla(\tilde{\mu}/T)/e$ cannot be interpreted as the negative gradient of an electric potential. Hence, we propose to denote the formalism that uses $\boldsymbol{J}_{\mathrm{E}}$ and $T\nabla(\tilde{\mu}/T)/e$ after Thomson. The driving force in this formalism can be better understood in its entropic form

$$\boldsymbol{Y}_{\mathrm{e}} = \frac{1}{e}\nabla\frac{\tilde{\mu}}{T} \tag{19}$$

because the flowing tendency of the electrons in non-isothermal systems is determined by the gradient of their absolute electrochemical activity $\tilde{\lambda} \equiv \exp(\tilde{\mu}/k_{\mathrm{B}}T)$ (see [48, p. 302]), where k_{B} is Boltzmann's constant, rather than by the gradient of their electrochemical potential or by the electric field. In statistical thermodynamics, quantum fluids like electrons in metals and semiconductors must be described using the grand canonical ensemble and the absolute activity is the variable characteristic of this ensemble.

The combination of (2) and (13) leads to the transport equation

$$\boldsymbol{J}_{\mathrm{E}} = -\kappa\nabla T + \left(\Pi - \frac{\tilde{\mu}}{e}\right)\boldsymbol{j} \tag{20}$$

which implies that $\Pi_{\mathrm{E}} \equiv \Pi - \tilde{\mu}/e$ is the effective Peltier coefficient in this formalism. The transport equations in terms of this choice of flux densities are [28]

$$\begin{pmatrix} \boldsymbol{J}_{\mathrm{E}} \\ \boldsymbol{j} \end{pmatrix} = T^2 \begin{pmatrix} \kappa_{\mathrm{E}} & \alpha_{\mathrm{E}}\sigma \\ \alpha_{\mathrm{E}}\sigma & \sigma/T \end{pmatrix} \begin{pmatrix} \nabla(1/T) \\ \nabla(\tilde{\mu}/T)/e \end{pmatrix}, \tag{21}$$

where $\kappa_{\mathrm{E}} \equiv \kappa + T(\alpha_{\mathrm{E}})^2\sigma$ and $\alpha_{\mathrm{E}} = \Pi_{\mathrm{E}}/T = -(\tilde{\mu} + TS_{\mathrm{e}}^*)/eT$.

The energy conservation requires that $\nabla \cdot \boldsymbol{J}_{\mathrm{E}} = 0$. Taking the divergence of (20), and using (12), it is concluded that [26, 30, 45, 49]

$$0 = -\nabla \cdot \boldsymbol{J}_{\mathrm{E}} = \nabla \cdot (\kappa\nabla T) - \boldsymbol{j} \cdot \nabla\Pi + \boldsymbol{j} \cdot \tilde{\boldsymbol{E}} = \nabla \cdot (\kappa\nabla T) + \frac{1}{\sigma}j^2 - \tau\boldsymbol{j} \cdot \nabla T, \tag{22}$$

where $\tau \equiv T\mathrm{d}\alpha/\mathrm{d}T = \mathrm{d}\Pi/\mathrm{d}T - \alpha$ is the Thomson coefficient and $\tau\boldsymbol{j} \cdot \nabla T$ is the Thomson heat; the Thomson heat should be written as $T\boldsymbol{j} \cdot \nabla\alpha$ when the Seebeck coefficient varies due to changes in the material, such as doping, besides changes in temperature [50].

The Seebeck and Peltier coefficients can be measured for pairs of conductors [19, 23], that is, only their relative values can be measured. On the contrary, the Thomson coefficient τ can be measured in a single conductor, using an integrated form of (22) [38, 40, 49]. Absolute values of the Seebeck coefficient have, nevertheless, been calculated from the temperature dependence of the Thomson coefficient or assigning a zero value to the Seebeck coefficient of a superconductor.

The main advantage of this formalism is that total energy prevails over any other energy quantity because it is the one that is conserved, and therefore $\boldsymbol{J}_{\mathrm{E}}$ is of paramount importance. A minor drawback is that the effective Peltier and Seebeck coefficients, $\Pi_{\mathrm{E}} \equiv \Pi - \tilde{\mu}/e$ and $\alpha_{\mathrm{E}} = \alpha - \tilde{\mu}/eT$, look rather complicated. However, at a junction between two conductors A and B, the difference $\Pi_{\mathrm{E}}^{\mathrm{A}} - \Pi_{\mathrm{E}}^{\mathrm{B}}$ is equal to $\Pi^{\mathrm{A}} - \Pi^{\mathrm{B}}$ because $\tilde{\mu}$ is continuous; and the same applies to the difference in Seebeck coefficients because T is also continuous at the junction. Therefore, the measurable relative values $\alpha^{\mathrm{A}} - \alpha^{\mathrm{B}}$ and $\Pi^{\mathrm{A}} - \Pi^{\mathrm{B}}$ are the same as the relative values of the effective coefficients.

2.5 Thermoelectricity in terms of the Ohmic electric potential

The equations $\boldsymbol{j} = -\sigma\nabla\phi$ and $\boldsymbol{J}_{\mathrm{Q}} = -\kappa\nabla T$ are only valid in the absence of coupling, that is, under isothermal and static (i.e., $j = 0$) conditions, respectively. Coupling phenomena appear also in other fields, such as

electrodiffusion of multicomponent electrolyte systems. A seminal thesis in this field demonstrated the advantages of employing the Ohmic potential gradient as one of the driving forces [51, 52]. This is defined as $\nabla\phi_{\rm ohm} \equiv -\boldsymbol{j}/\sigma$ regardless of the presence of any other flux or force. Thus, for instance, the transport equations for mass and charge in binary electrolyte solutions become decoupled when formulated in terms of $\nabla\phi_{\rm ohm}$ (see [42, 53]). Similarly, the ionic transport equations within the Nernst–Planck approximation are coupled when formulated in terms of concentration and electric potential gradients, but decoupled in terms of the gradients of the electrochemical potentials of the ions [42].

When the negative Ohmic potential gradient is used as a driving force, heat and charge transport are decoupled in the transport equations of thermoelectricity. The "thermal" flux density in this formulation is the conduction heat flux density $\boldsymbol{J}_{\rm Q,cond} \equiv -\kappa\nabla T$ (see [2, 45]); this equation is valid (with the same κ) when $j \neq 0$. The absence of coupling terms, $L_{\rm eT} = 0$, in the transport equations relating the flux densities $\boldsymbol{J}_{\rm Q,cond}$ and $\boldsymbol{j}$ to the driving forces $-\nabla \ln T$ and $-\nabla\phi_{\rm ohm}$ does not invalidate them; on the contrary, their simplicity should be appreciated. Moreover, in the dissipation function

$$T\pi_{\rm s} = -\boldsymbol{J}_{\rm Q,cond} \cdot \nabla \ln T - \boldsymbol{j} \cdot \nabla\phi_{\rm ohm} \tag{23}$$

the first term is due only to thermal conduction and the second one only to electrical conduction. Contrarily to occasional statements [44], each of the two terms in (5) contains contributions from both thermal and electrical conduction in all other formalisms.

The major disadvantage of the Ohmic formalism is that its transport equations describe only the irreversible processes and must be combined with one equation for the reversible thermoelectric phenomena. Such equation is (12), $-\nabla\tilde{\mu}/e = \nabla\phi_{\rm ohm} - \alpha\nabla T$, as required by the equivalence of (4) and (23). An advantage of this formalism is that its thermal phenomenological coefficient $L_{\rm TT}$ is proportional to the Fourier thermal conductivity κ, the one involved in the entropy production (see equation (1)), in contrast to the other formalisms which involve the effective thermal conductivity $\kappa_i = \kappa + T(\alpha_i)^2\sigma$. However, its main advantage is that it clearly states the conditions under which a flux density, thermal or electrical, can be expressed in terms of a single driving force instead of a linear combination of two driving forces.

2.6 Thermoelectricity in terms of the electrostatic potential

If the (Maxwell) electric field is used as driving force, $\boldsymbol{X}_{\rm e} = \boldsymbol{E} = -\nabla\phi$, equation (10) becomes

$$\boldsymbol{j} = -\sigma(\alpha_\phi\nabla T + \nabla\phi), \tag{24}$$

where α_ϕ is the effective Seebeck coefficient in the electrostatic formalism. The sign of this coefficient is negative when electrons move from hot to cold positions in the absence of current (thus making negative the electrostatic potential at cold positions, with respect to the hot ones).

The basic idea behind the different formalisms is that a transformation can be made from one set of driving forces such as $-\nabla \ln T$ and $\nabla\tilde{\mu}/e$ to a different set of driving forces such as $-\nabla \ln T$ and $-\nabla\phi$ provided that these two sets contain the same information. That is, it is implicit in (24) that $\nabla\tilde{\mu}/e$ can be determined from $-\nabla \ln T$ and $-\nabla\phi$. Since $\nabla\tilde{\mu} = \nabla\mu - e\nabla\phi$, the above statement implies that $\nabla\mu$ is completely determined by ∇T, and hence the relation $\nabla\mu = (\partial\mu/\partial T)_x\nabla T$ can be used, where x denotes a constraint that is specified below. The substitution of $\boldsymbol{X}_{\rm e} = -\nabla\phi$ in (7) leads to the conclusion that its compatible "thermal" flux density is the reduced heat flux density

$$\boldsymbol{J}'_{\rm Q} \equiv \boldsymbol{J}_{\rm Q} + T(\partial\mu/\partial T)_x\boldsymbol{J}_{\rm n} \tag{25}$$

which is widely used in irreversible thermodynamics [19–21, 31, 32].

The transport equations in terms of the electrostatic potential are [19] equation (24) and

$$\boldsymbol{J}'_{\rm Q} = -\kappa_\phi\nabla T - \Pi_\phi\sigma\nabla\phi = -\kappa\nabla T + \Pi_\phi\boldsymbol{j}, \tag{26}$$

where $\Pi_\phi = T\alpha_\phi$ is the effective Peltier coefficient and $\kappa_\phi = \kappa + T(\alpha_\phi)^2\sigma$ is the isoelectric thermal conductivity (i.e., in the absence of electric field). The reduced heat flux density can also be presented as

$$\boldsymbol{J}'_{\rm Q} \equiv -\kappa\nabla T + Q^*_{\rm e}\boldsymbol{J}_{\rm n}, \tag{27}$$

where $Q_e^* = -e\Pi_\phi$ is the heat of transport of the electrons [19]. The comparison of (13), (14), (26) and (27) shows that $\Pi_\phi = \Pi - (T/e)(\partial\mu/\partial T)_x$ and $Q_e^* = T[S_e^* + (\partial\mu/\partial T)_x]$. Thus, the open-circuit electrostatic potential gradient is $\nabla\phi = -\alpha_\phi \nabla T = (Q_e^*/eT)\nabla T$.

When the electron concentration n is not uniform in the conductor, the usual thermoelectric equations actually violate Poisson's equation of electrostatics [50]. The combination of Poisson's equation with the transport equations for thermoelectricity taking into account the gradient of n solves this problem. The Poisson's equation cannot be easily incorporated to the other formalisms, and this essential advantage renders useful the electrostatic formalism. The effective Seebeck coefficient α_ϕ is relevant, among other things, to determine the length scale of the electrostatic potential variations in an inhomogeneous conductor [50].

The disadvantage of this formalism is that the effective thermoelectric coefficients cannot be measured. The electrostatic potential is not a continuous variable at the interfaces between conductors. The contact potential (i.e. the electrostatic potential difference at the interface) depends on temperature [19] and, hence, their contributions, e.g., to the electromotive force of a thermocouple, must be accounted for carefully. Under open-circuit conditions, equation (24) reduces to $\mathrm{d}\phi = -\alpha_\phi \mathrm{d}T$, which should be compared to $\mathrm{d}\tilde{\phi} = -\alpha \mathrm{d}T$ for $\tilde{\phi} \equiv -\tilde{\mu}/e$ (see [18]). The electrochemical potential of the electrons is continuous at the interfaces and the evaluation of the electromotive force of a thermocouple is rather simple within the electrochemical formalism. On the contrary, in the electrostatic formalism $\mathrm{d}\phi = -\alpha_\phi \mathrm{d}T$ has to be integrated along the conductors and then the contact potentials must be added [19] to determine the measurable electric potential difference; which is obviously the same in all formalisms.

Although the motivation of this work is to clarify the relations among the different formalisms and not to solve long standing controversies, some reference to them is necessary. An important aspect of this discussion is the choice of independent variables for the chemical potential of the electrons. This chemical potential is the partial (molar or per particle) Gibbs potential of the electrons and, therefore, its natural variables are temperature, pressure and the composition variables [19]. It does not mean, however, that it cannot be expressed also in terms of a different set of independent state variables. In the case of homogeneous metals, the composition variables can be neglected, and the chemical potential of the electrons can be considered to be a function of temperature and pressure or, equivalently, of temperature and the electron concentration.

R. Haase [19] considered that the heat of transport of the electrons is $Q_e^* = T[S_e^* - S_e]$ where $S_e = -(\partial\mu/\partial T)_p$ is the partial entropy of the electrons and p is the pressure. That is, compared to our relation

$$Q_e^* = T[S_e^* + (\partial\mu/\partial T)_x], \tag{28}$$

Haase considered that constant pressure is the appropriate constraint. Consistently, Haase wrote (25) as (in our notation)

$$\boldsymbol{J}'_Q \equiv T(\boldsymbol{J}_s - S_e \boldsymbol{J}_n). \tag{29}$$

Similarly, Domenicali [29] and Rockwood [54] wrote the electrostatic potential gradient under open-circuit conditions as

$$\nabla\phi = -\alpha_\phi \nabla T = \frac{1}{e}\left(S_e^* + \frac{\partial\mu}{\partial T}\right)\nabla T. \tag{30}$$

They indicated no constraint on the partial derivative but Domenicali cited de Groot [20], and hence Domenicali and Rockwood meant $(\partial\mu/\partial T)_p$ as usual in irreversible thermodynamics. In our notation, de Groot wrote (30) as $\nabla\phi = (Q_e^*/eT)\nabla T$; note that de Groot's heat of transfer of the electrons [20] is equal to Q_e^* plus the partial enthalpy H_e of the electrons because of his choice of $\boldsymbol{J}_u$ as heat flux density; in fact, the name reduced heat flux density comes from the relation $\boldsymbol{J}'_Q = \boldsymbol{J}_u - H_e \boldsymbol{J}_n$ (see [19, 20]).

R. D. Barnard [17] considered that, for a given metal, μ is only a function of T and wrote $\nabla\mu = (\partial\mu/\partial T)\nabla T$ without specifying any constraint on the partial derivative. Refereeing to Barnard, G. D. Mahan [50] considered the chemical potential of the electrons to be a function of temperature and the electron concentration n, and used $\nabla\mu = (\partial\mu/\partial T)_n \nabla T$ for systems in which n is homogeneous. Thus, Mahan defined the effective Seebeck coefficient in the electrostatic formalism, $\bar{S}$ in his notation, as $\alpha_\phi = \alpha - (1/e)(\partial\mu/\partial T)_n$. It is interesting to observe that Mahan did not introduce (25)–(27) but discussed the energy flux densities employed by different authors, including Haase, and denoted the reduced heat flux density as an enthalpy flux density $\boldsymbol{J}_H = \boldsymbol{J}'_Q$. Remarkably, Mahan made no connection to his transport equations. It is also noticeable that, when an estimate

of α_ϕ was needed to describe the spatial variations of the electrostatic potential inside an inhomogeneous semiconductor, Mahan [50] used the approximation $\alpha_\phi \approx \alpha$ in spite of his detailed calculations of $(\partial\mu/\partial T)_n$ for both metals and semiconductors.

A. L. Rockwood [54] considered that the partial molar entropy of the electron and the Seebeck coefficient are essentially equivalent. Combining the widely-accepted relation between the entropy of transport of the electron and the Seebeck coefficient, $S_e^* = -e\alpha$, with a proposed relation between the partial entropy of the electrons and the Seebeck coefficient, $S_e = -\partial\mu/\partial T = -e\alpha$, Rockwood concluded from (30) that $\nabla\phi = 0$, i.e., that the electric field vanishes in a homogeneous conductor in the presence of a temperature gradient. Surprisingly, Rockwood did not discuss that the proposal $S_e = -e\alpha$ implies that α_ϕ, Π_ϕ and Q_e^* all vanish, and hence that there would no coupled thermoelectric phenomena in the electrostatic formalism.

M. R. Peterson and S. Shastry [55] presented the Kelvin formula for the Seebeck coefficient:

$$\alpha = \frac{1}{e}\left(\frac{\partial\mu}{\partial T}\right)_{N,V}, \tag{31}$$

where the constraints of constant number of electrons N and constant volume V are equivalent to fixed electron concentration n. This formula has important implications for the heat of transport of the electrons. If the effective Seebeck coefficient is $\alpha_\phi = \alpha - (1/e)(\partial\mu/\partial T)_n$ as suggested by Barnard and Mahan, then the Peterson–Shastry formula implies that α_ϕ, Π_ϕ and Q_e^* vanish. Haase considered that $\alpha_\phi = \alpha - (1/e)(\partial\mu/\partial T)_p$ where p denotes the thermodynamic or external pressure [19]. In a metal, the conduction electrons have a pressure $p_e > 0$ which is four or five orders of magnitude higher than p and is compensated by a negative contribution from the lattice, $p_i = p - p_e < 0$. The evaluation of the derivatives at constant external pressure in (30) are usually considered to be equivalent to derivatives at constant n rather than at constant p_e (see [56, (5.30)]). This makes consistent the expressions used by Barnard, Mahan and Haase, and leads again to the conclusion that (31) implies vanishing α_ϕ, Π_ϕ and Q_e^*.

Before we discuss further implications of (31), it is in order to mention the argument raised by S. Kjelstrup [57]. The Seebeck coefficient and the transported entropy of the electrons $S_e^* = -e\alpha$ are transport properties and not equilibrium properties. In particular, Kjelstrup envisioned the Peltier coefficient $\Pi = -TS_e^*/e$ as a transference coefficient for heat, which is not an equilibrium property. Therefore, relations between α and the partial entropy of the electrons, as proposed by Rockwood, or between α and $(\partial\mu/\partial T)_n$, which is another equilibrium property of the electrons, are mixing concepts of different nature, and do not contribute to the understanding of the thermoelectricity concepts [57].

Noteworthy, the contradictory views of all these authors do not affect the validity of (24)–(27). Although we do not aim at solving the controversy, which can be traced back to Thomson's interpretation of the Thomson coefficient as the specific heat of the electron [58, 59], there are a few comments that could be made. First, traditional thermodynamicists work out transport equations in order to describe the observed phenomena but they do not make models or theories to estimate the values of the transport coefficients. On the contrary, attempts to relate the thermoelectric coefficients to electron properties have been customary in the quantum theory of thermoelectricity. Other theories, like Kubo's linear response theory [55], have also been used for the same purpose. Second, although Kjelstrup was certainly right when stressing that the Seebeck and Peltier coefficients are transport properties, the attempts to find their relation to equilibrium properties can be understood from the fact that the entropy production only involves the thermal and electrical conductivities. And third, any proposed relation should be tested against experiments to confirm its validity. To the best of our knowledge, neither Rockwood's nor Petersen and Shastry's relations agree with experimental observations [60, 61].

We turn now back to the estimations of the Seebeck coefficients from the temperature derivatives of μ. It is well known in statistical thermodynamics that the characteristic state function of a Fermi gas can be derived using the grand canonical ensemble (i.e. using T, V and $\lambda = \exp(\mu/k_B T)$ as the independent variables) as

$$p_e(T,\lambda) = \frac{2k_B T}{\Lambda^3} F_{5/2}(\lambda), \tag{32}$$

where $p_e(T,\lambda)$ is the pressure of the Fermi gas, $\Lambda(T) \propto T^{-1/2}$ is the thermal de Broglie wavelength of the

electrons,

$$F_j(\lambda) \equiv \frac{1}{\Gamma(j)} \int_0^\infty \frac{x^{j-1}}{\lambda^{-1}\mathrm{e}^x + 1}\mathrm{d}x \tag{33}$$

is the Fermi integral of index j, and $\Gamma(j)$ is the gamma function. From (32) and the Gibbs–Duhem equation, the electron concentration $n = (\partial p_\mathrm{e}/\partial\mu)_T = (\lambda/k_\mathrm{B}T)(\partial p_\mathrm{e}/\partial\lambda)_T$ can be evaluated as $n = (2/\Lambda^3)F_{3/2}(\lambda)$, using $\lambda \mathrm{d}F_j/\mathrm{d}\lambda = F_{j-1}$, and therefore

$$\left(\frac{\partial\mu}{\partial T}\right)_n = \frac{\mu}{T} + \frac{k_\mathrm{B}T}{\lambda}\left(\frac{\partial\lambda}{\partial T}\right)_n = \frac{\mu}{T} - \frac{3k_\mathrm{B}}{2}\frac{F_{3/2}(\lambda)}{F_{1/2}(\lambda)}. \tag{34}$$

In the case of metals and degenerate semiconductors, the approximation

$$F_j(\mathrm{e}^{\mu/k_\mathrm{B}T}) \approx \frac{(\mu/k_\mathrm{B}T)^j}{\Gamma(j+1)}\left[1 + j(j-1)\frac{\pi^2}{6}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2\right] \tag{35}$$

leads to $F_{3/2}/F_{1/2} \approx (2\mu/3k_\mathrm{B}T) + (\pi^2 k_\mathrm{B}T/9\mu)$ and $\mu \approx \varepsilon_\mathrm{F}[1 - (\pi^2/12)(T/T_\mathrm{F})^2]$, where $\varepsilon_\mathrm{F} = k_\mathrm{B}T_\mathrm{F}$ is the Fermi energy, and

$$\frac{1}{e}\left(\frac{\partial\mu}{\partial T}\right)_n \approx -\frac{\pi^2 k_\mathrm{B}}{6e}\frac{T}{T_\mathrm{F}} < 0. \tag{36}$$

In semiconductors with a small electron concentration, $F_j(\lambda) \approx \lambda \approx n\Lambda^3/2$ and

$$\frac{1}{e}\left(\frac{\partial\mu}{\partial T}\right)_n \approx -\frac{k_\mathrm{B}}{e}\left[\ln(2/n\Lambda^3) + \frac{3}{2}\right] < 0. \tag{37}$$

Since $k_\mathrm{B}/e = 86.7\,\mu\mathrm{V/K}$ and T is always a few orders of magnitude smaller than the Fermi temperature $T_\mathrm{F} = \varepsilon_\mathrm{F}/k_\mathrm{B}$ of a metal, it is accepted that (36) and (37) explain the typical orders of magnitude of the Seebeck coefficient of metals and semiconductors [50].

In conclusion, the electric field $\boldsymbol{E} = -\nabla\phi$ can be used as driving force and the corresponding transport equations are (24)–(27). The effective Seebeck coefficient $\alpha_\phi = \alpha + S_\mathrm{e}/e$ or $\alpha_\phi = -(Q_\mathrm{e}^*/eT) = -(S_\mathrm{e}^* - S_\mathrm{e})/e$ should not be considered equal to zero as suggested by (31) because this equation has not been confirmed by experiments. In case an estimate for the partial entropy S_e is needed, $S_\mathrm{e} = -(\partial\mu/\partial T)_p \approx -(\partial\mu/\partial T)_n$ can be used.

2.7 Quantum theory of thermoelectricity

In the quantum theory of thermoelectricity [22, 23, 62], the probability of finding one electron at time t in a volume element $\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{k}$ around the position $(\boldsymbol{r}, \boldsymbol{k})$ in phase space is $f(t, \boldsymbol{r}, \boldsymbol{k})\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{k}$, where $f(t, \boldsymbol{r}, \boldsymbol{k})$ is the distribution function and $\boldsymbol{k}$ is the electron wave vector. Under equilibrium conditions ($\nabla T = \boldsymbol{0}$, $j = 0$), the distribution function is the Fermi–Dirac function, $f_0(\boldsymbol{r}, \boldsymbol{k}) = 1/(1 + \exp[(\varepsilon - \mu)/k_\mathrm{B}T])$, where $\varepsilon(\boldsymbol{k})$ is the electron energy and $\mu(\boldsymbol{r})$ is the chemical potential of the electrons. The non-equilibrium distribution function f must be obtained as the solution of the Boltzmann transport equation, which under steady-state conditions and within the relaxation time approximation reduces to [23]

$$-\frac{\delta f}{\tau(\boldsymbol{k})} = \boldsymbol{v}\cdot\nabla_r f + \frac{\boldsymbol{F}}{\hbar}\cdot\nabla_{\boldsymbol{k}} f \approx \boldsymbol{v}\cdot\nabla_r f_0 + \frac{\boldsymbol{F}}{\hbar}\cdot\nabla_{\boldsymbol{k}} f_0. \tag{38}$$

Here $\delta f \equiv f - f_0$, $\tau(\boldsymbol{k})$ is the relaxation time, $\hbar$ is the reduced Planck constant, $\boldsymbol{F} = e\nabla\phi$ is the electric force, and $\boldsymbol{v} = \nabla_{\boldsymbol{k}}\varepsilon/\hbar$ is the (group) velocity of the electrons. The gradient of the Fermi–Dirac distribution $f_0(\boldsymbol{r}, \boldsymbol{k})$ in $\boldsymbol{k}$-space is $\nabla_{\boldsymbol{k}} f_0 = (\partial f_0/\partial\varepsilon)_{T,\mu}\hbar\boldsymbol{v}$, and its spatial gradient is

$$\nabla_r f_0 = T\left(\frac{\partial f_0}{\partial\varepsilon}\right)_{T,\mu}\nabla\left(\frac{\varepsilon - \mu}{T}\right). \tag{39}$$

Thus, the perturbation of the distribution function can be evaluated as

$$\delta f \approx \tau(\boldsymbol{k})\left(\frac{\partial f_0}{\partial\varepsilon}\right)_{T,\mu}\boldsymbol{v}\cdot\left[T\nabla\left(\frac{\mu}{T}\right) - e\nabla\phi + \varepsilon\nabla\ln T\right]. \tag{40}$$

This equation implies that $\boldsymbol{X}_\mathrm{e} = -\nabla\phi + (T/e)\nabla(\mu/T)$ is the electrical driving force in the quantum formalism. Then, equation (7) imposes that the corresponding "thermal" flux density is

$$\boldsymbol{J}_\mathrm{u} = \boldsymbol{J}_\mathrm{Q} + \mu\boldsymbol{J}_\mathrm{n} = \boldsymbol{J}_\mathrm{E} - \phi\boldsymbol{j}. \tag{41}$$

The total energy is the sum of internal energy and electrostatic potential energy, and $\boldsymbol{J}_\mathrm{u}$ can be identified as the flux density of internal energy. Under steady-state conditions, its divergence is $\nabla\cdot\boldsymbol{J}_\mathrm{u} = \boldsymbol{j}\cdot\boldsymbol{E}$, because the power $\boldsymbol{j}\cdot\boldsymbol{E}$ of the force due to the external electric field acting on the electrons is dissipated as internal energy.

In the quantum theory, the internal energy flux density and the electron flux density are evaluated as $\boldsymbol{J}_\mathrm{u} = (1/4\pi^3)\int \varepsilon\boldsymbol{v}\delta f\,\mathrm{d}\boldsymbol{k}$ and $\boldsymbol{J}_\mathrm{n} = (1/4\pi^3)\int \boldsymbol{v}\delta f\,\mathrm{d}\boldsymbol{k}$, where $1/4\pi^3$ is the density of states in $\boldsymbol{k}$-space; the electron contribution to the heat flux density is then $\boldsymbol{J}_\mathrm{Q} = \boldsymbol{J}_\mathrm{u} - \mu\boldsymbol{J}_\mathrm{n} = (1/4\pi^3)\int(\varepsilon-\mu)\boldsymbol{v}\delta f\,\mathrm{d}\boldsymbol{k}$. Substitution of (38) into these expressions for the flux densities leads to the transport equations [22, 23, 28]

$$\begin{pmatrix}\boldsymbol{J}_\mathrm{u}\\ \boldsymbol{j}\end{pmatrix} = \begin{pmatrix}T\kappa_\mathrm{u} & \Pi_\mathrm{u}\sigma\\ \Pi_\mathrm{u}\sigma & \sigma\end{pmatrix}\begin{pmatrix}-\nabla\ln T\\ (T/e)\nabla(\mu/T) - \nabla\phi\end{pmatrix}, \tag{42}$$

where $\kappa_\mathrm{u} = \kappa + T(\alpha_\mathrm{u})^2\sigma$ and the effective Peltier coefficient is

$$T\alpha_\mathrm{u} = \Pi_\mathrm{u} \equiv \Pi - \frac{\mu}{e} = -\frac{\mu + TS_\mathrm{e}^*}{e} = -\frac{H_\mathrm{e} + Q_\mathrm{e}^*}{e}, \tag{43}$$

because the chemical potential is $\mu = \tilde{\mu} + e\phi = H_\mathrm{e} - TS_\mathrm{e}$, where H_e and S_e are the partial enthalpy and partial entropy of the electrons, respectively.

The major advantage of this formalism resides in its contribution to the physical understanding of thermoelectric phenomena, providing a clear insight about the controversial expressions reducing the thermoelectric coefficients to equilibrium properties. The microscopic expressions of these coefficients involve a relaxation time τ associated with the scattering phenomena, which evidences that they are transport coefficients. Because τ is a function of the electron wavevector $\boldsymbol{k}$ or energy $\varepsilon(\boldsymbol{k})$, the three transport coefficients κ, σ and α_u can be related to three transport integrals that involve different powers of ε (see [23]). Thus, although all thermoelectric phenomena are associated to the perturbation of only one function f, the flux densities cannot be expressed in terms of a single driving force because different gradients have different coefficients. Moreover, the "electrical" driving force $\boldsymbol{X}_\mathrm{e} = -\nabla\phi + (T/e)\nabla(\mu/T)$ physically shows that electrons are material particles with electric charge whose spatial redistribution responds not only to electric fields but also to the gradient of its chemical potential. The associated thermal flux density $\boldsymbol{J}_\mathrm{u}$ is actually considered as a possible choice for the heat flux density [20, 31, 32], although this is so not customary in thermoelectricity.

2.8 Thermoelectricity in terms of the observable electric potential

Recently, a new formulation of the thermoelectricity transport equations based on experimentally observable quantities has been proposed [36–40]. The observable electric potential when the potential difference in (18) is measured with probes of material R is defined as [36–38]

$$\nabla\psi \equiv -\nabla\tilde{\mu}/e + \alpha_\mathrm{R}\nabla T, \tag{44}$$

where α_R is the Seebeck coefficient of the probes R. This equation can be considered as a definition of the local quantity $\nabla\psi$ in terms of the local gradients $\nabla\tilde{\mu}$ and ∇T in the conductor and the value that the Seebeck coefficient α_R of the probes R would have at the local temperature T. Equivalently, as explained in [36–38], it can be considered as a differential relation between the change $\mathrm{d}\psi$ in the electric potential measured between two probes R connected to the conductor when one of them undergoes a differential displacement $\mathrm{d}\vec{r}$ between points whose difference in temperature and electrochemical potential of the electrons are $\mathrm{d}T$ and $\mathrm{d}\tilde{\mu}$.

When the probes are of the same material as the conductor under study, the observable electric potential ψ is the same as the Ohmic potential, and this formalism reduces to the Ohmic formalism; but only the

Thomson effect can be observed then in isotropic conductors. Eliminating $\nabla\tilde{\mu}$ from (4) and (36), the dissipation function is transformed to

$$T\pi_s = -(\boldsymbol{J}_Q - \Pi_R \boldsymbol{j}) \cdot \nabla \ln T - \boldsymbol{j} \cdot \nabla\psi \tag{45}$$

and therefore the conjugate flux densities of $\{-\nabla \ln T, -\nabla\psi\}$ are $\{\boldsymbol{J}_Q - \Pi_R \boldsymbol{j}, \boldsymbol{j}\}$. The transport equations (9) become

$$\begin{pmatrix} \boldsymbol{J}_Q - \Pi_R \boldsymbol{j} \\ \boldsymbol{j} \end{pmatrix} = \begin{pmatrix} T\kappa_\psi & (\Pi - \Pi_R)\sigma \\ (\Pi - \Pi_R)\sigma & \sigma \end{pmatrix} \begin{pmatrix} -\nabla \ln T \\ -\nabla\psi \end{pmatrix}, \tag{46}$$

where $\kappa_\psi = \kappa + T(\alpha - \alpha_R)^2\sigma$. An alternative presentation is [36, 37]

$$\begin{pmatrix} \boldsymbol{J}_s - \alpha_R \boldsymbol{j} \\ \boldsymbol{j} \end{pmatrix} = \begin{pmatrix} \kappa_\psi/T & (\alpha - \alpha_R)\sigma \\ (\alpha - \alpha_R)\sigma & \sigma \end{pmatrix} \begin{pmatrix} -\nabla T \\ -\nabla\psi \end{pmatrix}. \tag{47}$$

In (46), Π is the Peltier coefficient of the electronic conductor under study and Π_R that of the probes. The choice of the flux densities $\{\boldsymbol{J}_s - \alpha_R \boldsymbol{j}, \boldsymbol{j}\}$ was not explained or justified by J. Garrido in [36, 37], as he does not mention the dissipation function. Interestingly, in the more recent publications [38–40], Garrido and A. Casanovas conclude that a combination of the formalisms presented above, in particular (12) and (20), are the most useful for the observation of thermoelectric phenomena.

The main advantage of this formalism is that it uses an observable electric potential which is defined experimentally, within the spirit of thermodynamics. A significant drawback is that the thermal equation in this formalism involves a flux density $\boldsymbol{J}_Q - \Pi_R \boldsymbol{j}$ of little experimental significance, which may explain the resort to the total energy flux equation (20).

3 Conclusions

A review of the different formalisms employed in the literature, with a clear description of their fundamentals, and a systematic classification has been presented. The expressions of the divergences of heat, internal energy, total energy and entropy flux densities have also been derived. Since the rules of irreversible thermodynamics must be obeyed, the flux densities and forces have to be identified from the entropy production rate. Its expression has been derived from the charge, energy and entropy balance equations. We have shown that the different formalisms of the equations of thermoelectricity correspond to different choices of the "electrical" driving force (typically, an electric potential gradient) and the "thermal" (i.e., energy) flux density. The formalisms corresponding to the following electrical driving forces have been explained and their corresponding "thermal" flux densities have been clearly identified: (i) $\nabla\tilde{\mu}/e$, (ii) $-\nabla\phi$ (Maxwell electric field), (iii) $-\nabla\phi_{ohm}$ (negative Ohmic potential gradient), and (iv) $-\nabla\psi$ (negative electric potential gradient observable with probes of material R); see Table 2 as well as [50, Table I] which is congruent, except for notation. Also, the formalisms using the internal energy and the total energy flux densities have been explained and their respective "electrical" driving forces, (v) $-\nabla\phi + T\nabla(\mu/T)/e$ and (vi) $T\nabla(\tilde{\mu}/T)/e$, have been identified and explained. Although it may also be found in the literature [9], the expression of the electric field as the positive gradient of a voltage V, $\boldsymbol{X}_e = \nabla V$, has not been commented because it is a just a different sign convention.

This review has focused on demonstrating the compatibility of apparently different transport equations and the expressions for the dissipation of energy. The present review is particularly useful in identifying the compatible pairs of fluxes and forces. Moreover, it has been shown that a distinct set of effective Seebeck and Peltier coefficients satisfying Thomson's second relation $\Pi_i = T\alpha_i$ exists in every formalism, as well as a corresponding thermal conductivity $\kappa_i = \kappa + T(\alpha_i)^2\sigma$. Since the measured Seebeck coefficient corresponds to the electrochemical formalism that uses $\boldsymbol{X}_e = \nabla\tilde{\mu}/e$, the existence of different sets of Seebeck and Peltier coefficients has no implications on the reported values. Finally, since the transport equations and coefficients in the other formalisms must be related to the measured Seebeck coefficient, a clear advantage of the electrochemical formalism is evidenced.

The effective thermoelectric coefficients in the other formalisms cannot be measured, but they should not be considered useless. In particular, the electrostatic formalism has been found useful when the Poisson

Formalism i	$\boldsymbol{J}_{\mathrm{T},i} = \boldsymbol{J}_Q + T(\boldsymbol{\alpha}_i - \boldsymbol{\alpha})\boldsymbol{j}$	$\boldsymbol{X}_{\mathrm{e},i} = \boldsymbol{\alpha}_i\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e + (\boldsymbol{\alpha}_i - \boldsymbol{\alpha})\nabla T$
electrochemical	$T\boldsymbol{J}_{\mathrm{s}} \equiv \boldsymbol{J}_{\mathrm{Q}}$	$-\nabla\tilde{\phi} = \alpha\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e$
Thomson	$\boldsymbol{J}_{\mathrm{E}} = \boldsymbol{J}_{\mathrm{Q}} - (\tilde{\mu}/e)\boldsymbol{j}$	$T\nabla(\tilde{\mu}/T)/e = \alpha_{\mathrm{E}}\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e - (\tilde{\mu}/Te)\nabla T$
Ohmic	$\boldsymbol{J}_{\mathrm{Q,cond}} = \boldsymbol{J}_{\mathrm{Q}} - T\alpha\boldsymbol{j}$	$-\nabla\phi_{\mathrm{ohm}} \equiv \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e + (S_{\mathrm{e}}^*/e)\nabla T$
electrostatic	$\boldsymbol{J}'_{\mathrm{Q}} = \boldsymbol{J}_{\mathrm{Q}} + (TS_{\mathrm{e}}/e)\boldsymbol{j}$	$-\nabla\phi = \alpha_\phi\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e + (S_{\mathrm{e}}/e)\nabla T$
quantum	$\boldsymbol{J}_{\mathrm{u}} = \boldsymbol{J}_{\mathrm{Q}} - (\mu/e)\boldsymbol{j}$	$-\nabla\phi + T\nabla(\mu/T)/e = \alpha_{\mathrm{u}}\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e - (\mu/Te)\nabla T$
observable	$\boldsymbol{J}_{\mathrm{Q}} - T\alpha_{\mathrm{R}}\boldsymbol{j}$	$-\nabla\psi = (\alpha - \alpha_{\mathrm{R}})\nabla T + \boldsymbol{j}/\sigma = \nabla\tilde{\mu}/e + (S_{\mathrm{e,R}}^*/e)\nabla T$

Table 2. Comparison of the energy flux densities and the "electrical" driving forces in the different formalisms evidencing their connection through the difference of the effective and the actual Seebeck coefficients. Note also that $\boldsymbol{J}_{\mathrm{T},i} = -\kappa\nabla T + \Pi_i\boldsymbol{j}$ with $\Pi_i = T\alpha_i$.

equation of electrostatics is required to describe the spatial variations of the electrostatic potential inside a non-isothermal inhomogeneous conductor [50]. Unfortunately, there are some old and recent controversies in the literature regarding the estimations of the Seebeck coefficient and of the effective Seebeck coefficient in the electrostatic formalism. Although the motivation of this work is not to solve them, the different opinions have been critically discussed and some aspects have been, hopefully, clarified.

A Appendix

The local equilibrium hypothesis of irreversible thermodynamics accepts the validity of the Euler equation $U = TS - pV + \mu\mathrm{N}$ and the Gibbs equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$ for a volume element of the conductor. Introducing the volume densities of internal energy and entropy, u and s, and the electron concentration n, and substituting equations like $\mathrm{d}U = u\mathrm{d}V + V\mathrm{d}u$ in the Gibbs equation, its equivalent form in terms of volume densities is obtained [19]:

$$\mathrm{d}u = T\mathrm{d}s + \mu\mathrm{d}n. \tag{48}$$

This equation is preferred to its equivalent form $\mathrm{d}u - e\phi\mathrm{d}n = T\mathrm{d}s + \tilde{\mu}\mathrm{d}n$ because $\mathrm{d}u - e\phi\mathrm{d}n$ could only be written as $\mathrm{d}(u - e\phi n)$ when the electric potential ϕ is external and not affected by the electron distribution; this is the main reason why it is convenient not to include the electrostatic contributions inside the internal energy u (see [19, 42]) but to consider them separately, e.g., as it is done in (55) below.

Because of (48), the relation between the flux densities of internal energy, heat and number of electrons is [19, 30]

$$\boldsymbol{J}_{\mathrm{u}} = \boldsymbol{J}_{\mathrm{Q}} + \mu\boldsymbol{J}_{\mathrm{n}} \tag{49}$$

and the time variations of the volume densities must satisfy the equation

$$\frac{\partial u}{\partial t} = T\frac{\partial s}{\partial t} + \mu\frac{\partial n}{\partial t}. \tag{50}$$

Equation (49) is equivalent to (2), $\boldsymbol{J}_{\mathrm{E}} = \boldsymbol{J}_{\mathrm{Q}} + \tilde{\mu}\boldsymbol{J}_{\mathrm{n}}$ with $\boldsymbol{J}_{\mathrm{E}} = \boldsymbol{J}_{\mathrm{u}} + \phi\boldsymbol{j}$ and $\boldsymbol{j} = -e\boldsymbol{J}_{\mathrm{n}}$.

The charge, internal energy, heat, entropy and total energy balance equations [19, 42] are, respectively,

$$\frac{\partial n}{\partial t} + \nabla\cdot\boldsymbol{J}_{\mathrm{n}} = 0, \tag{51}$$

$$\frac{\partial u}{\partial t} + \nabla\cdot\boldsymbol{J}_{\mathrm{u}} = \pi_{\mathrm{u}} = \boldsymbol{j}\cdot\boldsymbol{E}, \tag{52}$$

$$T\frac{\partial s}{\partial t} + \nabla\cdot\boldsymbol{J}_{\mathrm{Q}} = \pi_{\mathrm{Q}} = \boldsymbol{j}\cdot\tilde{\boldsymbol{E}} = -\boldsymbol{J}_{\mathrm{n}}\cdot\nabla\tilde{\mu}, \tag{53}$$

$$\frac{\partial s}{\partial t} + \nabla\cdot\boldsymbol{J}_{\mathrm{s}} = \pi_{\mathrm{s}} = \boldsymbol{J}_{\mathrm{Q}}\cdot\nabla\frac{1}{T} - \frac{1}{T}\boldsymbol{J}_{\mathrm{n}}\cdot\nabla\tilde{\mu}, \tag{54}$$

$$\frac{\partial u}{\partial t} - e\phi\frac{\partial n}{\partial t} + \nabla\cdot\boldsymbol{J}_{\mathrm{E}} = 0, \tag{55}$$

where π_u, π_Q, π_s are the volume densities of production rate of internal energy, heat and entropy; charge and total energy are conserved and their production rates vanish. Introducing (51), (52) and (54) into (50), the entropy production rate of (1) is obtained. The time derivatives in (51)–(55) vanish in stationary states, and the production rates of internal energy, heat and entropy are, respectively,

$$\pi_u = \nabla \cdot \boldsymbol{J}_u = \boldsymbol{j} \cdot \boldsymbol{E} = \frac{1}{\sigma} j^2 + \alpha_\phi \boldsymbol{j} \cdot \nabla T, \tag{56}$$

$$\pi_Q = \nabla \cdot \boldsymbol{J}_Q = \boldsymbol{j} \cdot \tilde{\boldsymbol{E}} = \frac{1}{\sigma} j^2 + \alpha \boldsymbol{j} \cdot \nabla T = -\nabla \cdot (\kappa \nabla T) + (\alpha + \tau) \boldsymbol{j} \cdot \nabla T, \tag{57}$$

$$\pi_s = \nabla \cdot \boldsymbol{J}_s = \boldsymbol{J}_Q \cdot \nabla \frac{1}{T} + \frac{1}{T} \nabla \cdot \boldsymbol{J}_Q = \frac{\kappa}{T^2} (\nabla T)^2 + \frac{1}{T\sigma} j^2. \tag{58}$$

Since the total energy is conserved (see equation (22)), its divergence vanishes:

$$0 = \nabla \cdot \boldsymbol{J}_E = -\nabla \cdot (\kappa \nabla T) + \boldsymbol{j} \cdot \nabla \Pi - \boldsymbol{j} \cdot \tilde{\boldsymbol{E}} = -\nabla \cdot (\kappa \nabla T) - \frac{1}{\sigma} j^2 + \tau \boldsymbol{j} \cdot \nabla T. \tag{59}$$

Noting that the contribution of the Thomson effect is sometimes misleading, some authors prefer to present the production rate of heat as [43, 45]

$$\nabla \cdot \boldsymbol{J}_Q = \boldsymbol{j} \cdot \tilde{\boldsymbol{E}} - \nabla \cdot (\kappa \nabla T) - \frac{1}{\sigma} j^2 + \tau \boldsymbol{j} \cdot \nabla T. \tag{60}$$

Nomenclature

e	> 0, elementary charge (C)
$\boldsymbol{E}$	$\equiv -\nabla\phi$, (Maxwell) electric field ($\mathrm{Vm^{-1}}$)
$\tilde{\boldsymbol{E}}$	$\equiv -\nabla\tilde{\phi}$, (Landau) "electric field" ($\mathrm{Vm^{-1}}$)
H_e	partial enthalpy of the electrons (J)
$\boldsymbol{j}$	electric current density ($\mathrm{Am^{-2}}$)
$\boldsymbol{J}_E$	total energy flux density ($\mathrm{Wm^{-2}}$)
$\boldsymbol{J}_n$	flux density of electrons ($\mathrm{m^{-2}s^{-1}}$)
$\boldsymbol{J}_Q$	$\equiv T\boldsymbol{J}_s$, heat flux density ($\mathrm{Wm^{-2}}$)
$\boldsymbol{J}'_Q$	$\equiv \boldsymbol{J}_u - H_e\boldsymbol{J}_n$, reduced heat flux density ($\mathrm{Wm^{-2}}$)
$\boldsymbol{J}_{Q,\mathrm{cond}}$	conduction heat flux density ($\mathrm{Wm^{-2}}$)
$\boldsymbol{J}_s$	entropy flux density ($\mathrm{WK^{-1}m^{-2}}$)
$\boldsymbol{J}_T$	generic "thermal" flux density ($\mathrm{Wm^{-2}}$)
$\boldsymbol{J}_u$	$= T\boldsymbol{J}_s + \mu\boldsymbol{J}_n$, internal energy flux density ($\mathrm{Wm^{-2}}$)
k_B	Boltzmann's constant ($\mathrm{JK^{-1}}$)
n	electron concentration ($\mathrm{m^{-3}}$)
p	pressure (Pa)
Q_e^*	$\equiv T(S_e^* - S_e)$, electron heat of transport (J)
$\boldsymbol{q}$	"generic" heat flux density ($\mathrm{Wm^{-2}}$)
S_e	partial entropy of the electrons ($\mathrm{JK^{-1}}$)
S_e^*	$\equiv -e\alpha$, transported entropy of the electrons ($\mathrm{JK^{-1}}$)
T	temperature (K)
V	volume ($\mathrm{m^3}$)
$\boldsymbol{X}_e$	"electric" driving force ($\mathrm{Vm^{-1}}$)
$\boldsymbol{Y}_e$	"electric" driving force in entropic formalism ($\mathrm{VK^{-1}m^{-1}}$)
α	Seebeck coefficient ($\mathrm{VK^{-1}}$)
α_i	effective Seebeck coefficient in formalism i ($\mathrm{VK^{-1}}$)
ϕ	electrostatic potential (V)
ϕ_{ohm}	Ohmic electric potential (V)

$\tilde{\phi}$ $\equiv -\tilde{\mu}/e$, electrochemical potential per electron charge (V)
ψ observable electric potential with probes R (V)
κ (open-circuit) thermal conductivity ($\mathrm{WK^{-1}m^{-1}}$)
κ_ϕ (isoelectric) thermal conductivity ($\mathrm{WK^{-1}m^{-1}}$)
$\tilde{\kappa}$ $= \kappa + T\alpha^2\sigma$, (iso-$\tilde{\mu}$) thermal conductivity ($\mathrm{WK^{-1}m^{-1}}$)
λ $\equiv \exp(\mu/k_\mathrm{B}T)$, absolute activity of the electrons (1)
$\tilde{\lambda}$ $\equiv \exp(\tilde{\mu}/k_\mathrm{B}T)$, absolute electrochemical activity of the electrons (1)
$\tilde{\mu}$ $= \mu - e\phi$, electrochemical potential of the electrons (J)
μ $= H_\mathrm{e} - TS_\mathrm{e}$, chemical potential of the electrons (J)
Π Peltier coefficient (V)
Π_i effective Peltier coefficient in formalism i (V)
π_s density of entropy production rate ($\mathrm{WK^{-1}m^{-3}}$)
σ (isothermal) electrical conductivity ($\Omega^{-1}\mathrm{m^{-1}}$)
τ Thomson coefficient ($\mathrm{VK^{-1}}$)

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