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Review

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Thermoelectric Material Tensor Derived from the Onsager–de Groot–Callen Model

Abstract: The Onsager–de Groot–Callen model describes thermoelectricity in the framework of the *thermodynamics of irreversible processes*, which uses rather abstract kinetic matrix and generalized forces to describe the flux of the substance-like quantities electric charge and thermal energy ("heat"). A brief review of the derivation of the basic equations according to this model is given. Primarily, this model relies on the total differential of energy as in Gibb's thermodynamics, but it then removes entropy to capture the energy production rate as a measure of irreversibility. Depending on the fluxes of interest, "proper" generalized forces are identified. The use of Onsager's reciprocal relations helps to determine the coefficients of a kinetic matrix to link the generalized forces with the generalized potentials. The present article places entropy back into the as-obtained basic equations. The equations are then transformed such that the flux densities of electric charge and entropy appear with equal ranks. The respective conjugated intensive variables electrochemical potential and temperature then appear as the thermodynamic potentials. Moreover, the thermoelectric material is described by a material-specific tensor, which is composed only of the isothermal electric conductivity, the Seebeck coefficient and the entropy conductivity. The result is identical to that recently obtained by Fuchs using a direct entropic approach, which does not require Onsager's reciprocal relations as a prerequisite. The benefit of this approach is the appearance of a material-specific *thermoelectric tensor* rather than a so-called *kinetic matrix*, which not only provides a new quality to the discussion but also facilitates descriptions of the thermoelectric phenomenon and the underlying energy conversion process. The latter can easily be understood as the transfer of energy from thermal to electric phenomenon or vice versa when fluxes of entropy and electric charge, as well as the local thermodynamic potentials temperature and electrochemical potential, are known.

Keywords: thermodynamic potentials, figure of merit, energy transfer

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1 Introduction

Thermodynamics describes physical processes using coupling intensive (potential-like) and their conjugated extensive (substance-like) quantities in a Gibbs fundamental form; see Falk and Ruppel (1976), Falk, Herrmann, and Schmid (1983). If one of the substance-like quantities involved in these processes flows, it is accompanied by energy as an additional substance-like quantity. In the following, we will address the amount of energy that flows together with a specific substance-like quantity by an analogy referencing the energy carrier (i.e. charge/electric or entropy/thermal). Regardless of this semantic assignment, we do consider energy as a quantity in its own right that does not change its nature when being transferred from one carrier to the other. The so-called energy transformation or energy conversion process is then easily understood as an exchange of carriers for the energy; see Callendar (1911), Falk, Herrmann, and Schmid (1983). Regarding the thermoelectric phenomenon, the relevant intensive variables are electrochemical potential $\tilde{\mu}$ and temperature T, and the conjugated substance-like quantities are electric charge q and entropy S. Although the concept of entropy is older than that of energy (see Falk 1985), the traditional approach for describing the thermoelectric phenomenon avoids explicitly addressing entropy and rather addresses thermal energy E, th. In this approach, an imbalance is introduced into the basic equations, which prevents the thermoelectric phenomenon from being easily understood. The aim of this article is to express the basic equations for the thermoelectric phenomenon in terms of Gibb's thermodynamics with charge and entropy as the relevant substance-like quantities. This approach has the advantage of enabling an intuitive understanding of thermoelectricity in accordance with the waterfall analogy, which was first formulated by Carnot (1824) in his famous report.

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2 The Onsager–de Groot–Callen Model

The Onsager–de Groot–Callen model of thermoelectric effects is described by Callen (1948), who applies the reciprocal relations of Onsager (1931a, 1931b) to the aforementioned phenomena and uses the description of the so-called *thermodynamics of irreversible processes*, which was extended by de Groot (1951). For a review, see also Goupil et al. (2011). At the basis of this theory lies the assumption of local equilibrium, which enables the use of a Gibbs fundamental form to find a relation between the internal energy, entropy and number of particles; see Callen (1948). Then, entropy is removed from the basic equations by treating the entropy production rate, which is calculated from the divergence of the energy current density field. Finally, through a symmetry argument, Onsager's theorem helps to include the reverse effect (thermoelectric to electrothermic). However, it is not necessary to consider the divergence of energy current density at this early stage. It can be treated later on, and entropy can be kept in equal rank to the number of particles. Let us begin with the outcome of the theory of the *thermodynamics of irreversible processes*. In this context, with the electrochemical potential $\tilde{\mu}$ and the absolute temperature T, Callen (1948) uses the following gradients as "proper" forces

$$\frac{1}{T}\nabla\tilde{\mu} \qquad [1]$$

and

$$\nabla\left(\frac{1}{T}\right) = \frac{0 - 1 \cdot \nabla T}{T^2} = -\frac{1}{T^2}\nabla T \qquad [2]$$

when the fluxes of interest (Callen 1948, eq. [18]) are the *particle (charge carrier) current density* $\mathbf{j}_n$

$$-\mathbf{j}_n = L_{11} \cdot \frac{1}{T} \cdot \nabla\tilde{\mu} + L_{12} \cdot \nabla\left(\frac{1}{T}\right) \qquad [3]$$

and the *heat (thermal energy) current density* $\mathbf{j}_{E,\mathrm{th}}$

$$\mathbf{j}_{E,\mathrm{th}} = L_{21} \cdot \frac{1}{T}\nabla\tilde{\mu} + L_{22} \cdot \nabla\left(\frac{1}{T}\right) \qquad [4]$$

The kinetic coefficients L_{11}, $L_{12} = L_{21}$ and L_{22} depend on the absolute temperature T, the electric charge q of the particle under consideration (i.e. of the charge carrier), the *entropy flow per particle* S^*, the isothermal specific electric conductivity σ_T and the specific heat conductivity $\lambda_{\mathbf{j}_n=0}$ in the case of a vanishing particle flux (i.e. $\mathbf{j}_n = 0$); the kinetic coefficients are as follows:

$$L_{11} = \frac{T}{q^2} \cdot \sigma_T \qquad [5]$$

$$L_{12} = -\frac{T^2}{q^2} \cdot \sigma_T \cdot S^* = L_{21} \qquad [6]$$

$$L_{22} = \frac{T^3}{q^2} \cdot \sigma_T \cdot S^{*2} + T^2 \cdot \lambda_{\mathbf{j}_n=0} \qquad [7]$$

Note that eq. [6] includes Onsager's reciprocal relation:

$$L_{12} = L_{21} \qquad [8]$$

Equations [3]–[7] can be condensed into a single equation:

$$\begin{pmatrix} -\mathbf{j}_n \\ \mathbf{j}_{E,\mathrm{th}} \end{pmatrix} = \begin{pmatrix} \frac{T}{q^2} \cdot \sigma_T & -\frac{T^2}{q^2} \cdot \sigma_T \cdot S^* \\ -\frac{T^2}{q^2} \cdot \sigma_T \cdot S^* & \frac{T^3}{q^2} \cdot \sigma_T \cdot S^{*2} + T^2 \cdot \lambda_{\mathbf{j}_n=0} \end{pmatrix} \cdot \begin{pmatrix} \frac{1}{T}\nabla\tilde{\mu} \\ -\frac{1}{T^2}\nabla T \end{pmatrix} \qquad [9]$$

Equation [9] is structured such that the flux densities under consideration, which are on the left, depend on a so-called *kinetic matrix* and *generalized forces*. The kinetic matrix in eq. [9] contains the absolute temperature T to the power of 1, 2 or 3, whereas the generalized forces contain it to inverse powers of 1 or 2. Clearly, the prefactors to the thermodynamic potential gradients in the generalized forces counterbalance the appearance of temperature T in the kinetic matrix. In principle, the temperature T can be shifted between the kinetic matrix and the generalized forces by increasing or decreasing the power at some positions. For example, among the infinite possibilities, one can find

$$\begin{pmatrix} -\mathbf{j}_n \\ \mathbf{j}_{E,\mathrm{th}} \end{pmatrix} = \begin{pmatrix} -\mathbf{j}_n \\ T \cdot \mathbf{j}_S \end{pmatrix} = \begin{pmatrix} \frac{T^2}{q^2} \cdot \sigma_T & -\frac{T^2}{q^2} \cdot \sigma_T \cdot S^* \\ -\frac{T^3}{q^2} \cdot \sigma_T \cdot S^* & \frac{T^3}{q^2} \cdot \sigma_T \cdot S^{*2} + T^2 \cdot \lambda_{\mathbf{j}_n=0} \end{pmatrix} \cdot \begin{pmatrix} \frac{1}{T^2}\nabla\tilde{\mu} \\ -\frac{1}{T^2}\nabla T \end{pmatrix} \qquad [10]$$

A solution such as eq. [10], however, is ruled out by the demanding symmetry of the kinetic matrix, which means that it fulfills Onsager's reciprocal relation as given in eq. [8]. In contrast, for the situation of the so-called *thermodynamics of irreversible processes*, the axiomatic setting of Onsager's reciprocal relation helps to select a specific form of the basic equation (as given by eq. [9]) among infinite possibilities and to find the "proper" settings of the generalized forces and of the kinetic matrix.

In the following section, it is shown that the explicit appearance of temperature T in the generalized forces and kinetic matrix, however, results from considering the heat flux density $\mathbf{j}_{E,\mathrm{th}}$ rather than the entropy flux density $\mathbf{j}_S$. In eq. [10], the entropy flux density $\mathbf{j}_S$ was written to show that the multiple appearances of temperature T on the right of the equality sign is caused, in principle, by introducing it on the left side.

3 From Generalized Forces to Thermodynamic Potential Gradients

Inserting eqs [5] and [6] into eq. [3] yields the *particle (charge carrier) current density* $\mathbf{j}_n$

$$\begin{aligned} -\mathbf{j}_n &= \frac{T}{q^2}\cdot\sigma_T\cdot\frac{1}{T}\cdot\nabla\tilde{\mu} + \left(-\frac{T^2}{q^2}\cdot\sigma_T\cdot S^*\right)\cdot\nabla\left(\frac{1}{T}\right) \\ &= \frac{\sigma_T}{q^2}\nabla\tilde{\mu} + \left(-\frac{T^2}{q^2}\cdot\sigma_T\cdot S^*\right)\cdot\left(-\frac{1}{T^2}\nabla T\right) \\ &= \frac{\sigma_T}{q^2}\nabla\tilde{\mu} + \frac{\sigma_T\cdot S^*}{q^2}\cdot\nabla T \end{aligned} \qquad [11]$$

Inserting eqs [6] and [7] into eq. [4] yields the *heat (thermal energy) current density* $\mathbf{j}_{E,\mathrm{th}}$

$$\begin{aligned} \mathbf{j}_{E,\mathrm{th}} &= -\frac{T^2}{q^2}\cdot\sigma_T\cdot S^*\cdot\frac{1}{T}\nabla\tilde{\mu} + \left(\frac{T^3}{q^2}\cdot\sigma_T\cdot S^{*2}\right)\cdot\nabla\left(\frac{1}{T}\right) \\ &\quad + T^2\cdot\lambda_{\mathbf{j}_n=0}\cdot\nabla\left(\frac{1}{T}\right) \\ &= -\frac{T}{q^2}\cdot\sigma_T\cdot S^*\nabla\tilde{\mu} + \frac{T^3}{q^2}\cdot\sigma_T\cdot S^{*2}\left(-\frac{1}{T^2}\nabla T\right) \\ &\quad + T^2\cdot\lambda_{\mathbf{j}_n=0}\cdot\left(-\frac{1}{T^2}\nabla T\right) \\ &= -T\cdot\frac{\sigma_T\cdot S^*}{q^2}\cdot\nabla\tilde{\mu} - \frac{T}{q^2}\cdot\sigma_T\cdot S^{*2}\cdot\nabla T - \lambda_{\mathbf{j}_n=0}\cdot\nabla T \end{aligned} \qquad [12]$$

If thermal conductivity is expressed by the specific entropy conductivity Λ rather than by the specific heat conductivity λ (see Job 1972; Fuchs 2010; Job and Rüffler 2011)

$$\lambda := T\cdot\Lambda \qquad [13]$$

replacing the heat current density

$$\mathbf{j}_{E,\mathrm{th}} := T\cdot\mathbf{j}_S \qquad [14]$$

by the underlying entropy flux density $\mathbf{j}_S$ leads to the following:

$$\begin{aligned} \mathbf{j}_S &= \frac{\mathbf{j}_{E,\mathrm{th}}}{T} = -\frac{\sigma_T\cdot S^*}{q^2}\cdot\nabla\tilde{\mu} - \frac{\sigma_T\cdot S^{*2}}{q^2}\cdot\nabla T - \frac{\lambda_{\mathbf{j}_n=0}}{T}\cdot\nabla T \\ &= \frac{\sigma_T\cdot S^*}{q^2}\cdot(-\nabla\tilde{\mu}) + \frac{\sigma_T\cdot S^{*2}}{q^2}\cdot(-\nabla T) + \Lambda_{\mathbf{j}_n=0}\cdot(-\nabla T) \\ &= \frac{\sigma_T\cdot S^*}{q^2}\cdot(-\nabla\tilde{\mu}) + \left(\frac{\sigma_T\cdot S^{*2}}{q^2} + \Lambda_{\mathbf{j}_n=0}\right)\cdot(-\nabla T) \end{aligned} \qquad [15]$$

The latter replacement clearly demonstrates that the thermal flux density as expressed by eq. [15] depends on the material parameters and on the negative potential gradients $-\nabla\tilde{\mu}$ and $-\nabla T$ (i.e. down-hill diffusion of entropy), as they are known from classical thermodynamics. The same is the case for the particle flux density $\mathbf{j}_n$. Taking into account that the *entropy flow per particle* S^* can be expressed as the *entropy flow per unit charge* α, which is the Seebeck coefficient of a thermoelectric material,

$$\alpha = \frac{S^*}{q} \qquad [16]$$

and combining eqs [11] and [15] makes it possible to write this important result in a more concise form:

$$\begin{pmatrix} \mathbf{j}_n \\ \mathbf{j}_S \end{pmatrix} = \begin{pmatrix} \dfrac{\sigma_T}{q^2} & \dfrac{\sigma_T\cdot\alpha}{q} \\ \dfrac{\sigma_T\cdot\alpha}{q} & \sigma_T\cdot\alpha^2 + \Lambda_{\mathbf{j}_n=0} \end{pmatrix} \cdot \begin{pmatrix} -\nabla\tilde{\mu} \\ -\nabla T \end{pmatrix} \qquad [17]$$

Both the particle flux density $\mathbf{j}_n$ and the entropy flux density thus depend on the negative gradient of the classical thermodynamic potentials (chemical potential for particles and temperature as the potential for entropy).

If one is interested in the charge flux density $\mathbf{j}_q$ rather than the particle flux density $\mathbf{j}_n$, it immediately follows from eq. [11] that

$$\begin{aligned} \mathbf{j}_q = q\cdot\mathbf{j}_n &= -\frac{\sigma_T}{q}\cdot\nabla\tilde{\mu} - \frac{\sigma_T\cdot S^*}{q}\cdot\nabla T \\ &= \frac{\sigma_T}{q}\cdot(-\nabla\tilde{\mu}) + \frac{\sigma_T\cdot S^*}{q}\cdot(-\nabla T) \end{aligned} \qquad [18]$$

which can be combined with eq. [15], considering eq. [16], to obtain:

$$\begin{pmatrix} \mathbf{j}_q \\ \mathbf{j}_S \end{pmatrix} = \begin{pmatrix} \sigma_T & \sigma_T\cdot\alpha \\ \sigma_T\cdot\alpha & \sigma_T\cdot\alpha^2 + \Lambda_{\mathbf{j}_q=0} \end{pmatrix} \cdot \begin{pmatrix} -\nabla\left(\frac{\tilde{\mu}}{q}\right) \\ -\nabla T \end{pmatrix} \qquad [19]$$

Because of eq. [18], we can change the subscript of the specific entropy conductivity (i.e. $\Lambda_{\mathbf{j}_q=0} = \Lambda_{\mathbf{j}_n=0}$). Equation [19] is identical to the relation obtained by Fuchs (2010,

2014) using a direct entropic approach without the need to set the axiomatic validity of Onsager's reciprocal relations. In contrast to the case with eqs [9] and [10] or further variants, a unique solution naturally appears with a symmetric *thermoelectric tensor*. Treating entropy as equal rank to electric charge thus pays off with Onsager's reciprocal relations as expressed by eq. [8] rather than requiring it as a prerequisite.

Equations [17] and [19] have a new quality. Rather than generalized forces, as in the case of eq. [9], negative gradients of classical thermodynamic potential gradients now appear, which allow for an easy interpretation of the down-hill diffusion of the respective conjugated extensive quantities. Most importantly, rather than a *kinetic matrix*, a material-specific *thermoelectric tensor* appears. This tensor does not explicitly show temperature T. However, all three material parameters, $\sigma = \sigma(T, \tilde{\mu}, p, \ldots)$, $\alpha = \alpha(T, \tilde{\mu}, p, \ldots)$ and $\Lambda = \Lambda(T, \tilde{\mu}, p, \ldots)$, implicitly depend on temperature T, as they do on the electrochemical potential $\tilde{\mu}$ or on the pressure p. In general, all three material parameters constitute tensors themselves but are often treated as scalars (i.e. the trace of a tensor). Equations [17] and [19] have the following structure: fluxes – thermoelectric material – potential gradients. It is thus clear that where the thermoelectric material is located creates the thermoelectric effect(s). From the thermoelectric tensor, one can directly determine the figure of merit for the thermoelectric material, as we will do later; see also Feldhoff and Geppert (2014).

4 Some Special Cases

Valuable insight into the thermoelectric phenomenon can be obtained if eq. [19] is considered for some special cases. Note that all the following considerations refer to the dynamic steady state.

4.1 Isothermal Conditions

According to eq. [19], in the case of isothermal conditions (i.e. $\nabla T = 0$), the electric charge flux density $\mathbf{j}_q$ obeys Ohm's law; see Job and Rüffler (2011):

$$\mathbf{j}_q = -\sigma_T \cdot \nabla\left(\frac{\tilde{\mu}}{q}\right) \qquad [20]$$

Equation [20] clearly shows why σ_T was assigned the subscript T, as it is indeed the specific electric conductivity under isothermal conditions.

Furthermore, the entropy current density $\mathbf{j}_S$ is:

$$\begin{aligned} \mathbf{j}_S &= -\sigma_T \cdot \alpha \cdot \nabla\left(\frac{\tilde{\mu}}{q}\right) \\ &= \alpha \cdot \mathbf{j}_q \end{aligned} \qquad [21]$$

Even in the absence of a temperature gradient, electric current carries entropy with it, and the magnitude and direction of its flow depend on the Seebeck coefficient α. Note that α may be positive or negative, and thus, the induced entropy flux may be in the same or in the opposite direction as the electric current; see Feldhoff and Geppert (2014). Equation [21] provides a clear meaning to the Seebeck coefficient α because *entropy flow per unit charge* was addressed in the context of eq. [16].

4.2 Electric Open-Circuit Conditions (Zero Electric Current)

In the case of an electric open circuit, the net electric flux will vanish (i.e. $\mathbf{j}_q = 0$), and eq. [19] yields:

$$0 = -\sigma_T \cdot \nabla\left(\frac{\tilde{\mu}}{q}\right) - \sigma_T \cdot \alpha \cdot \nabla T \qquad [22]$$

Here, one can observe a linear relationship between the two thermodynamic potential gradients, which clearly balance out. In the case of good electric conductors, the electrochemical potential gradient $\nabla(\tilde{\mu}/q)$ is dominated by the electric potential gradient $\nabla\varphi$ rather than by the chemical potential $\nabla(\tilde{\mu}/q)$. Moreover, if the thermal and electrochemical potential gradients are balanced over a conductor of length L, the gradients can be substituted by their drop along this length. Finally, from eq. [22], we can derive:

$$\begin{aligned} \alpha &= -\frac{\nabla\left(\frac{\tilde{\mu}}{q}\right)}{\nabla T} = -\frac{\nabla\left(\frac{\mu}{q} + \varphi\right)}{\nabla T} \\ &\approx -\frac{\nabla\varphi}{\nabla T} \\ &\approx -\frac{\frac{\Delta\varphi}{L}}{\frac{\Delta T}{L}} \\ &= -\frac{\Delta\varphi}{\Delta T} \end{aligned} \qquad [23]$$

Equation [23] provides guidelines for experimentally estimating the Seebeck coefficient α. It can be measured by the quotient of the voltage drop $\Delta\varphi$ and the temperature drop ΔT along a conductor when the electric flux is suppressed by an instrument with high electric resistivity.

Furthermore, eq. [19] yields Fourier's law under electric open-circuit conditions; see Job and Rüffler (2011). Here, we use eq. [23] to simplify the expression.

$$\begin{aligned}\mathbf{j}_S &= \sigma_T \cdot \alpha \cdot \left(-\nabla\left(\frac{\tilde{\mu}}{q}\right)\right) + \left(\sigma_T \cdot \alpha^2 + \Lambda_{\mathbf{j}_q=0}\right) \cdot (-\nabla T)\\ &= \sigma_T \cdot \alpha^2 \cdot \nabla T - \sigma_T \cdot \alpha^2 \cdot \nabla T - \Lambda_{\mathbf{j}_q=0} \cdot \nabla T \\ &= -\Lambda_{\mathbf{j}_q=0} \cdot \nabla T\end{aligned} \qquad [24]$$

Equation [24] clearly shows why $\Lambda_{\mathbf{j}_q=0}$ was assigned subscript $\mathbf{j}_q = 0$, as it is indeed the specific entropy conductivity under vanishing electric flux.

4.3 Electric Short-Circuit Conditions (Isoelectrochemical Conditions)

Under isoelectrochemical conditions (i.e. $\nabla\tilde{\mu} = 0$), eq. [19] yields the entropy flux density as follows:

$$\begin{aligned}\mathbf{j}_S &= -\left(\sigma_T \cdot \alpha^2 + \Lambda_{\mathbf{j}_q=0}\right) \cdot \nabla T\\ &:= -\Lambda_{\tilde{\mu}} \cdot \nabla T\end{aligned} \qquad [25]$$

Clearly, eq. [25] provides Fourier's law under isoelectrochemical conditions; see Job and Rüffler (2011). Here, we use the specific entropy conductivity at constant electrochemical potential $\Lambda_{\tilde{\mu}}$, which is element 2,2 of the thermoelectric tensor defined by eq. [19]:

$$\Lambda_{\tilde{\mu}} := \sigma_T \cdot \alpha^2 + \Lambda_{\mathbf{j}_q=0} \qquad [26]$$

The specific entropy conductivity at constant electrochemical potential $\Lambda_{\tilde{\mu}}$ is composed of two terms. The second term is the specific entropy conductivity under electric open-circuit conditions $\Lambda_{\mathbf{j}_q=0}$, which does not couple to electric current; see Feldhoff and Geppert (2014). The first term of $\Lambda_{\tilde{\mu}}$ is the part of the specific entropy conductivity that couples to the electric charge current Λ_{cc}, and it is involved in the transfer of energy from entropy current to electric current or vice versa; see Feldhoff and Geppert (2014). It gets subscript cc to indicate its *charge-coupled* character. It is also known as the power factor.

$$\Lambda_{\mathrm{cc}} := \sigma_T \cdot \alpha^2 \qquad [27]$$

With the aid of eq. [27] we can derive a Fourier-type equation for the charge-coupled entropy flux density $\mathbf{j}_{S,\mathrm{cc}}$:

$$\mathbf{j}_{S,\mathrm{cc}} = -\Lambda_{\mathrm{cc}} \cdot \nabla T \qquad [28]$$

Now let us examine the electric current density $\mathbf{j}_q$ in case of isoelectrochemical conditions, which follows from eq. [19] as follows:

$$\begin{aligned}\mathbf{j}_q &= -\sigma_T \cdot \alpha \cdot \nabla T\\ &= -\frac{\Lambda_{\mathrm{cc}}}{\alpha} \cdot \nabla T\\ &= \frac{1}{\alpha} \cdot \mathbf{j}_{S,\mathrm{cc}}\end{aligned} \qquad [29]$$

The charge-coupled entropy current clearly carries electric charge with it. The magnitude is given by $\frac{1}{\alpha}$, which then has the meaning of *electric charge flow per unit entropy* while only the charge-coupled part of flowing entropy is taken into account. In this context, it is worth examining the relation of Peltier and Seebeck coefficients as discussed by Fuchs (2010, 2014).

It is also interesting to write eq. [19] with the charge-coupled and non-coupling entropy conductivities being separated:

$$\begin{aligned}\begin{pmatrix}\mathbf{j}_q\\ \mathbf{j}_S\end{pmatrix} &= \begin{pmatrix}\sigma_T & \Lambda_{cc} \cdot \frac{1}{\alpha}\\ \sigma_T \cdot \alpha & \Lambda_{cc}\end{pmatrix} \cdot \begin{pmatrix}-\nabla(\frac{\tilde{\mu}}{q})\\ -\nabla T\end{pmatrix}\\ &+ \begin{pmatrix}0 & 0\\ 0 & \Lambda_{j_q=0}\end{pmatrix} \cdot \begin{pmatrix}-\nabla(\frac{\tilde{\mu}}{q})\\ -\nabla T\end{pmatrix}\end{aligned} \qquad [30]$$

The second term is purely irreversible, while the first term includes the energy transfer between entropy and charge current or vice versa. Written this way, the first term shows a tensor with specific electric conductivity in the first column and specific entropy conductivity in the second column. The non-diagonal elements show these conductivities multiplied by coupling factors. The *entropy flow per unit charge* α (Peltier effect) and the *electric charge flow per unit entropy* $\frac{1}{\alpha}$ (Seebeck effect) appear indeed as reciprocal quantities.

5 Figure of Merit of Thermoelectric Material

The figure of merit of a thermoelectric material can easily be determined from the thermoelectric tensor of eq. [19] by applying arguments similar to those proposed by Feldhoff and Geppert (2014). Here, we refer directly to the different terms of isoelectrochemical entropy conductivity $\Lambda_{\tilde{\mu}}$ in eq. [26]. A dimensionless *figure of merit* is given simply by the ratio of the two terms involved:

$$f = \frac{\Lambda_{\mathrm{cc}}}{\Lambda_{\mathbf{j}_q=0}} = \frac{\sigma_T \cdot \alpha^2}{\Lambda_{\mathbf{j}_q=0}} := zT \qquad [31]$$

For a good thermoelectric material, we can expect the charge-coupled specific entropy conductivity Λ_{cc} to be large compared to the non-coupling specific entropy conductivity $\Lambda_{\mathbf{j}_q=0}$. This directly leads to the demand for high value of figure of merit *f*. By setting $f = zT$, we indicate that the figure of merit as defined by eq. [31] is identical to the figure of merit zT commonly used in the field of thermoelectricity; see Ioffe (1957), Goupil et al. (2011). This can easily be observed with the aid of eq. [13]:

$$zT = \frac{\sigma_T \cdot \alpha^2}{\lambda_{\mathbf{j}_n=0}} \cdot T \qquad [32]$$

Recall that eq. [32] was derived by Ioffe (1957) through a thermodynamic analysis of a device composed of two dissimilar thermoelectric materials with identical properties but opposite signs of the Seebeck coefficient α. Here, we obtain it for a single material as function of local temperature *T*, i.e. $zT = zT(T) = f(T)$, because all three material-specific parameters σ, α, Λ depend on temperature, as was discussed in the context of eq. [19]. Note that Ioffe (1957) introduced the first figure of merit $z = \frac{\sigma_T \cdot \alpha^2}{\lambda_{\mathbf{j}_n=0}}$, but as in expressions of the efficiency of thermoelectric generators and refrigerators, the figure of merit z always appears in a product with the mean temperature of the device; naturally, the dimensionless figure of merit zT was introduced; see also Ioffe (1960). For appropriate expressions of efficiency see Fuchs (2014). The advantage of eq. [31] over eq. [32] is that it shows the figure of merit to be a purely material-specific quantity, which only implicitly depends on temperature.

6 Energy Transfer in a Device

The total energy flux density $\mathbf{j}_E$ at position $\mathbf{x}$ can be expressed as the sum of the electric energy flux density $\mathbf{j}_{E,\mathrm{el}}$ and the thermal energy flux density $\mathbf{j}_{E,\mathrm{th}}$; see Feldhoff and Geppert (2014). With the local thermodynamic potentials and the flux densities of electric charge and entropy, which we obtain from eq. [19], we get:

$$\begin{aligned} \mathbf{j}_E(\mathbf{x}) &= \mathbf{j}_{E,\mathrm{el}}(\mathbf{x}) + \mathbf{j}_{E,\mathrm{th}}(\mathbf{x}) \\ &:= \frac{\tilde{\mu}(\mathbf{x})}{q} \cdot \mathbf{j}_q + T(\mathbf{x}) \cdot \mathbf{j}_S \\ &= \left(\frac{\tilde{\mu}(\mathbf{x})}{q}, \quad T(\mathbf{x}) \right) \cdot \begin{pmatrix} \mathbf{j}_q \\ \mathbf{j}_S \end{pmatrix} \end{aligned} \qquad [33]$$

Depending on the local value of the electrochemical potential $\tilde{\mu}(\mathbf{x})$ and the entropy potential $T(\mathbf{x})$ as well as on the local flux densities of electric charge $\mathbf{j}_q$ and entropy $\mathbf{j}_S$, energy is transferred from one flux to the other. In other words, energy is converted from thermal to electric energy or vice versa.

Figure 1 gives illustrative example of the working principle of a thermoelectric energy harvester, which transfers energy from entropy current to electric current. The external electric circuit provides for electric charge being fed from harvester's electric output, via an external load, to the electric input again. An electric ring current appears, which carries (electric) energy with it, which at the external load, can be transferred to some useful process. See Feldhoff and Geppert (2014) for a similar representation with some more details included. Thus, the working principle of the energy harvester is that entropy fluxes through the thermoelectric legs induce a circular electric current. Subsequently, energy is transferred from thermal process to electric process and then to external load.

Figure 2 gives the working principle with indication of profiles of temperature and electrochemical potential. Note that electric energy flux density increases throughout the device. External circuit to feed electric charge from harvester's electric output to electric input as well as external load to transfer (electric) energy to some useful process have been omitted in this figure.

Irreversibilities are included in eq. [33] by principle and can be quantified by the divergence of the respective vector field in analogy to the concept of the so-called *thermodynamics of irreversible processes*; see Callen (1948), Walstrom (1988). The divergence of the total energy flux density provides the density of dissipative energy flux, and the divergence of the entropy flux density provides the entropy production rate. Irreversibility has been addressed to some extent by Fuchs (2014) in his direct entropic approach to the thermoelectric phenomenon. In principle, irreversibilities in thermoelectric harvesting occur when the energy released by the sliding of entropy along temperature gradient cannot be transferred to raise electric charge along the electrochemical potential gradient. Instantly, entropy is locally generated to carry the excess energy, which together with the generated entropy is dissipated from the system; see Job and Rüffler (2011). Clearly, entropy is a universal quantity similar to energy. Familiarity with it can be found

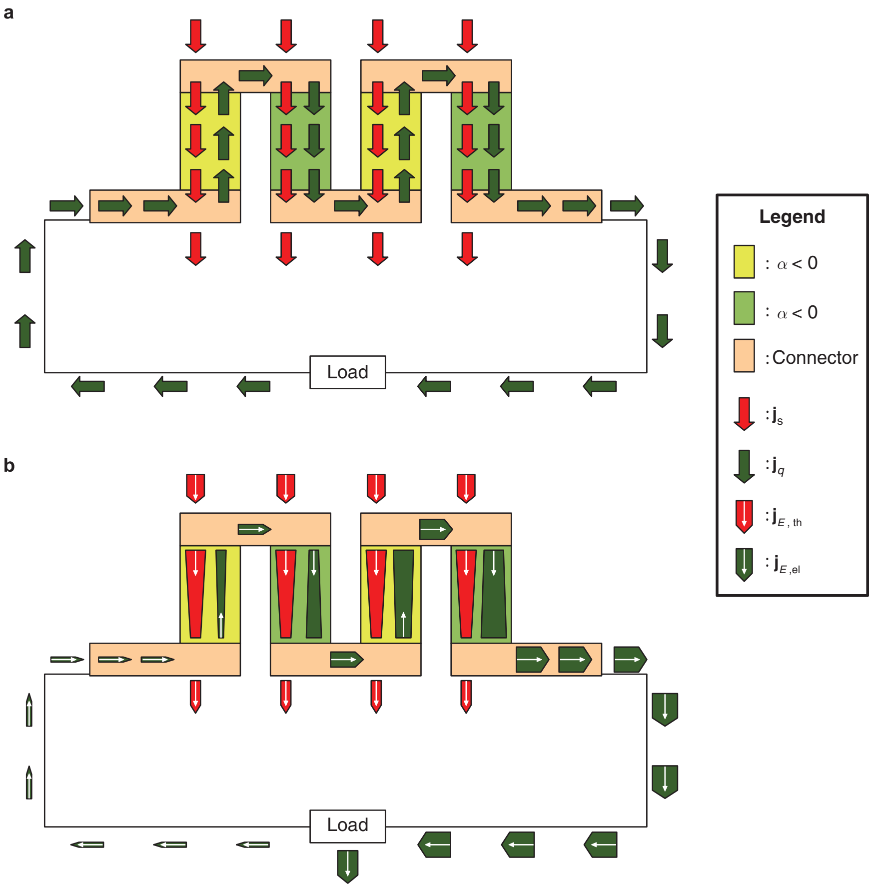

Figure 1: Thermoelectric energy harvester composed of a connector and legs of two dissimilar thermoelectric materials ($\alpha<0$ and $\alpha>0$), in which the flux densities of (a) entropy and charge and (b) thermal and electric energy are indicated. Note that the widths of the block arrows indicate the magnitude of the respective flux density. Entropy flows from the top (hot side) to bottom (cold side) and pumps electric charge from the left to right through the device. The pumping is enabled by the thermal energy flux density being larger on the top of each leg than on the bottom because of the local temperature difference. Note that the mutual direction of entropy and electric flux depends on the sign of the Seebeck coefficient α of the thermoelectric material. Consequently, in each leg, energy is transferred from entropy current to electric current. As a result, the electric energy flux density $\mathbf{j}_{E,\mathrm{el}}$ increases from left to right. Entropy production and dissipative currents of entropy and of (thermal) energy have been omitted.

already at school level; see Fuchs (1987), Herrmann (1998, 2000).

7 Conclusions

By putting entropy back into the Onsager–de Groot–Callen model, a material-specific thermoelectric tensor could be derived, which links flux densities of substance-like quantities electric charge and entropy to negative gradients of their classical thermodynamic potentials. The basic equation to describe thermoelectric phenomenon takes a rather simple form: flux densities–thermoelectric material–thermodynamic potential gradients. The thus obtained basic equation is identical with what Fuchs (2010, 2014) recently obtained by direct entropic approach without need to set Onsager's reciprocal relations as prerequisite. Figure of merit of thermoelectric material can be read immediately from the thermoelectric tensor. Thermoelectric energy harvesting becomes intuitively understandable as down-hill diffusion of entropy along temperature gradient and transfer of energy to charge current by pumping charge carrier up-hill along gradient of electrochemical potential. Conceptually, thermoelectricity is not different from any other process which provides energy transfer from one energy carrier to the other; see Falk and Herrmann (1981) for instructive examples of various processes.

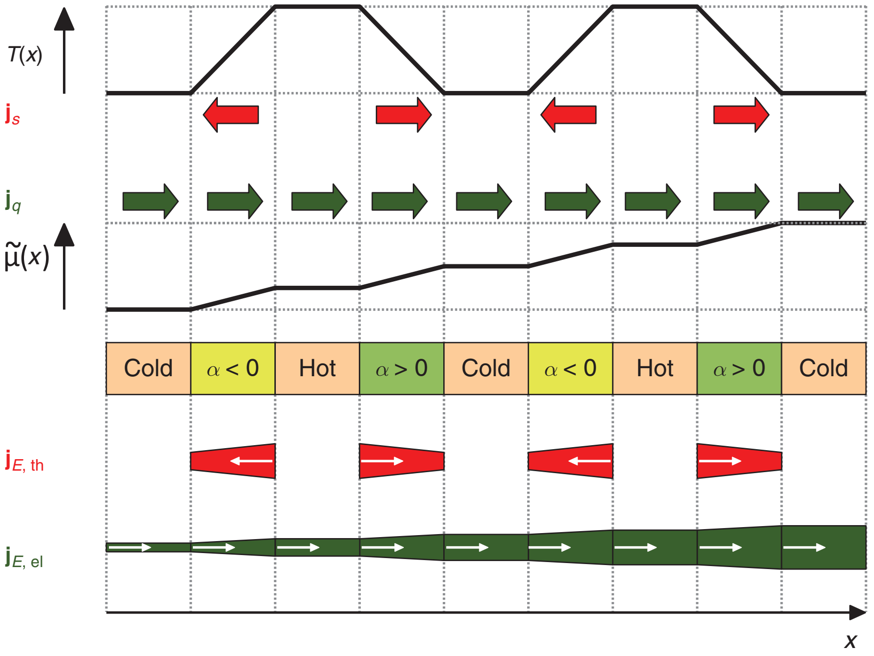

Figure 2: Linear chain model of a thermoelectric energy harvester with a connector material and two dissimilar thermoelectric materials, which exhibits alternating opposite signs of the Seebeck coefficient α when arranged along the horizontal coordinate x. The legend for Figure 1 applies here as well. While the connector material is under isothermal conditions (i.e. $\nabla T = 0$), the temperature profile $T(x)$ provides temperature gradients ∇T across the thermoelectric materials, which then sense the entropy flux density j_S as always pointing down-hill. According to eq. [19], the entropy flux induces an electric flux density j_q in each thermoelectric material and thus in the whole chain, which is electrically in a serial connection. The electric charge carrier is pumped up hill, i.e. to higher electrochemical potential $\tilde{\mu}$. The potential curves $T(x)$ and $\tilde{\mu}(x)$ give rise to the exchange of energy between fluxes of entropy and electric charge according to eq. [33]. The flux density of thermal energy $j_{E,\mathrm{th}}$ always points in the same direction as the entropy flux, while the flux density of electric energy $j_{E,\mathrm{el}}$ always points to the right of the chain. As a result, the electric output power (to the right) is distinctly larger than the electric input power (to the left). Note that the widths of the block arrows indicate the magnitude of the flux density. Entropy production and dissipative currents of entropy and of (thermal) energy have been omitted.

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