A simple continuum model leading to the reciprocity relation for thermoelectric effects

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ABSTRACT: In thermoelectricity, the Seebeck coefficient and the Peltier factor (which describes the coupling between currents of charge and of entropy) are equal. This is explained as a result of the Onsager reciprocity relations which are derived by means of statistical arguments. Here we show that this equality is suggested by reasoning based upon continuum physics. The expressions for the entropy production rate and the power of the various processes that occur in a thermoelectric device contain both material coefficients. Since we have independent information on the form of the dissipative and reversible terms in the expressions, we can derive the relation between the Seebeck coefficient and the Peltier factor by identifying these terms. This derivation is expected to simplify introductions to thermoelectricity.

I Introduction

Applications of thermoelectricity have met with increased interest in recent years.[1] Thermoelectric power generation in space or cooling of electronic devices are just two of the many examples.

The theory of thermoelectricity is not considered to be an introductory topic in general.[2] There are at least two reasons. First, the theory is part of irreversible thermodynamics which is commonly treated as an advanced subject. Second, we need the Onsager reciprocity relations which are proved on the basis of complex microscopic arguments.[3]

The first of these challenges is met by the dynamical theory of heat that introduces entropy and irreversible processes right from the beginning.[4] For learners, reasoning, derivations, and practical computations making use of the balance of entropy and of entropy generation become standard. For the second, we propose a simplified derivation of the relation between the Seebeck coefficient and the Peltier factor. It is based upon the same continuum physics model which is used to present the theory of thermoelectricity.

The Seebeck coefficient ε and the Peltier factor α are introduced as follows. The former establishes the relation between the temperature gradient and the gradient of the electrochemical potential μ_{ec} if no electric current is allowed to flow through the thermoelectric device:[5]

$$\nabla \mu_{ec} = -\varepsilon \nabla T \tag{1}$$

This is the formal expression of our knowledge gained from the use of thermocouples. A temperature difference of 1 K leads to an electro-chemical potential difference of ε volts.

The Peltier coefficient α is the factor that determines the coupling between currents of charge and of entropy.[6] It is observed that, even for isothermal conditions, entropy is transported through a thermoelectric cooling device (Peltier device) if an electric current j_q is made to flow through it. This observation is summarized as follows:

$$\mathbf{j}_S = \alpha \mathbf{j}_q \tag{2}$$

S and q refer to entropy and charge, respectively, $\mathbf{j}$ denotes a current density vector. Expressed graphically, an electric current sweeps α units of an entropy current along with it when there is no temperature difference. Note that the entropy flow in Eq. 2 is expected to be non-dissipative in contrast to conduction of entropy that is caused by a temperature gradient.

Since the phenomena of thermoelectric power generation and of Peltier cooling are assumed to be caused by the same underlying effect, we should expect a relation to exist between the Seebeck coefficient and the Peltier factor. In fact, as we know, they are equal. This can be shown to be a consequence of the dependence of the entropy production and the power upon fluxes, gradients, and material factors such as α and ε.

In the following three sections, we shall formulate the basic assumptions underlying the model of the thermoelectric effect (Section II), derive the form of the entropy production rate (Section III), and identify dissipative and reversible terms in the expression for the total power of the thermoelectric process (Section IV). The structure of the terms found in the entropy production rate and the total power lead us to the equality of the Seebeck coefficient and the Peltier factor. Finally, in Section V, we offer a graphical interpretation of the thermoelectric phenomenon based upon a simple differentiation between dissipative and non-dissipative parts of the coupled processes. A summary concludes the paper.

II Assumptions

We base our reasoning on the standard form of the laws used to model thermoelectricity. These are (1) the laws of balance of entropy and of charge (or of number of particles of the charge carrier); (2) the law of balance of energy supplemented by the expression for the total energy current in terms of the flows of entropy and charge; and (3) the constitutive laws for the flows of charge and entropy suggested by experiments.

We shall write the equations for the purely one-dimensional case with flows only in the axial direction of a rod made of a conducting material. Furthermore, we shall treat the steady-state case.

A. Laws of balance

The thermoelectric effect is the result of the coupled flow of entropy and charge in a conducting material. Therefore, we shall make use of the steady-state forms of the laws of balance of entropy[7] and of charge:

$$\frac{dj_S}{dx} = \pi_S \tag{3}$$

$$\frac{dj_q}{dx} = 0 \tag{4}$$

π_S is the density of the entropy production rate, and x denotes the independent spatial variable.

B. Energy

Energy is conserved, so the divergence of the total energy flux density must be equal to zero:

$$\frac{dj_E}{dx} = 0 \tag{5}$$

The total energy current j_E can be split into two terms, each arising from the transport of one of the basic quantities (i.e., entropy and charge):

$$j_E = T j_S + \mu_{ec} j_q \tag{6}$$

Here, T is the Kelvin temperature and μ_{ec} the electrochemical potential introduced above.[8]

C. Constitutive laws

There is one constitutive law for each of the fluxes of charge and of entropy. If we allow for an electric current through a thermoelectric generator, Eq. 1 is generalized to:

$$j_q = -\sigma \frac{d\mu_{ec}}{dx} - \sigma\varepsilon \frac{dT}{dx} \tag{7}$$

σ is the electric conductivity of the material. There is a combined thermo-electro-chemical potential (i.e., $\mu_{tec} = \mu_{ec} + \varepsilon T$) that gives rise to the electric current.

The second constitutive relation is a generalization of Eq. 2. Allowing for a temperature gradient we have:

$$j_S = \alpha j_q - k_S \frac{dT}{dx} \tag{8}$$

Here, k_S is the entropy conductivity of the material. Eq. 8 suggests that the entropy current consists of a non-dissipative and a dissipative term. If Eq. 7 is inserted into Eq. 8, the two laws may be summarized as follows:

$$\begin{aligned} j_q &= -\sigma \frac{d\mu_{ec}}{dx} - \sigma\varepsilon \frac{dT}{dx} \\ j_S &= -\sigma\alpha \frac{d\mu_{ec}}{dx} - \left(\sigma\alpha\varepsilon + k_S\right) \frac{dT}{dx} \end{aligned} \tag{9}$$

Onsager's relations assert that the matrix of coefficients multiplying the gradients is symmetric. In our case this means that we should expect the following relation to hold:

$$\alpha = \varepsilon \tag{10}$$

This we would like to demonstrate in the following sections.

III Entropy production

As stated in the Introduction, we shall gain additional information on the material coefficients of the theory, i.e., the Seebeck coefficient and the Peltier factor, by considering the form of the terms in the equation for the entropy production rate and for the power of the thermoelectric process (for the latter, see Section IV).

We begin with the law of balance of energy in Eq. 5 and insert Eq. 6. Taking into account the laws of balance of entropy and charge, the density of the entropy production rate is obtained:

$$T\pi_S = -j_S \frac{dT}{dx} - j_q \frac{d\mu_{ec}}{dx} \tag{11}$$

The two terms on the right hand side represent the thermal and the electric power of the processes, respectively. Since these contain non-dissipative parts, only the sum of the two terms can be equal to the entropy production rate. By itself, a single term does not represent a part of the entropy production rate. If we insert the constitutive laws of Eq. 7 and Eq. 8, we see that

$$T\pi_S = -\alpha j_q \frac{dT}{dx} + k_S \left(\frac{dT}{dx}\right)^2 + \frac{1}{\sigma} j_q^2 + \varepsilon j_q \frac{dT}{dx} \tag{12}$$

The first and the last of the terms are non-dissipative parts of the thermal and the electric power, respectively. Since they do not add to the production of entropy, their sum must cancel in Eq. 12. This leads immediately to $\alpha = \varepsilon$ (Eq. 10) and to

$$\pi_S = \frac{1}{T} k_S \left(\frac{dT}{dx}\right)^2 + \frac{1}{T}\frac{1}{\sigma} j_q^2 \tag{13}$$

This is what we should have expected from our knowledge of dissipation due to the conduction of entropy and of charge.[9]

IV Power of thermoelectric processes

Take the case of thermoelectric power generation. A current of entropy is established as a consequence of a temperature difference. This leads to an electric and two dissipative processes. The density of the power of the driving thermal process p_{th} is equal to

$$p_{th} = -j_S \frac{dT}{dx} \tag{14}$$

which can be expressed with the help of Eq. 7 and Eq. 8:

$$p_{th} = \frac{\alpha}{\sigma\varepsilon} j_q^2 + \frac{\alpha}{\varepsilon} j_q \frac{d\mu_{ec}}{dx} + k_S \left(\frac{dT}{dx} \right)^2 \qquad \textbf{(15)}$$

In this expression, we can interpret all three terms on the right hand side. The third is the dissipation rate as a consequence of thermal conduction. The first must represent the dissipation rate due to charge conduction, whereas the second determines the non-dissipative power of the electric process driven by a part of the input power.[10] The sum of the three terms must obviously equal the total power of the thermoelectric process. Again, these identifications lead us to conclude that the Seebeck coefficient and the Peltier factor should be equal.

V Thermo-electric potential and electro-thermal transport

The results of the previous two sections rest on the differentiation between irreversible and non-dissipative parts of the thermoelectric effect. They may be summarized in the following graphical interpretation of this phenomenon.

1. The transports of charge and of entropy are coupled according to Eq. 2. This leads to a non-dissipative part of the total entropy current (the dissipative part is due to conduction):

$$j_S = j_{S,cond} + j_{S,TE} = j_{S,cond} + \alpha j_q \qquad \textbf{(16)}$$

2. It is this coupling, i.e., the non-dissipative entropy transport, which leads to the thermo-electric potential (or rather, to its gradient):

$$\frac{d\mu_{TE}}{dx} = -\varepsilon \frac{dT}{dx} \qquad \textbf{(17)}$$

The assertion that 2 follows from 1 is equivalent to saying that the energy released as a consequence of the non-dissipative entropy transport is equal to the energy made available to the thermoelectric process:

$$j_{S,TE} \frac{dT}{dx} + j_q \frac{d\mu_{TE}}{dx} = 0 \qquad \textbf{(18)}$$

Once more this results in the equality of the Seebeck coefficient and the Peltier factor.

The steps and the reasoning presented here may be taken as a simple explanation of thermoelectricity.

VI Summary

If we accept some strong physical reasoning with regard to the nature of the dissipative processes inherent in thermoelectricity, we can apply the same equations used to model the phenomena to demonstrate the equality of the Seebeck coefficient and the Peltier factor.

The argument starts with the assumption that the only irreversibilities are the result of conduction of entropy and charge. As a consequence, we reason that the coupling of entropy currents to currents of electric charge causes a non-conductive flow of entropy (Eq. 2 and Eq. 16) which is non-dissipative; it leads to the reversible effect of a thermoelectric device. Since we know the expressions for the irreversibilities due to the conduction of charge and entropy, we have prior knowledge of the form of the entropy production rate: it should be as presented in Eq. 13. This immediately leads to the desired result.

Should we accept such reasoning? There are compelling reasons for doing this. The alternative would be to appeal to the Onsager relations. Simply appealing to someone's result without the accompanying proof is probably worth less to the learner than reasoning based on assumptions that can be motivated and whose consequences can be inspected. Moreover, the derivation of Onsager's reciprocity relations suffers from limitations.[11] Therefore, they are usually taken for granted at the macroscopic level. A general proof in macroscopic physics is still missing.[12]

References

[1] Discussions of important aspects of thermoelectricity can be found in P. L. Walstrom, "Spatial dependence of thermoelectric voltages and reversible heats," Am. J. Phys. **56**,890-894 (1988); J. M. Gordon, "Generalized power versus efficiency characteristics of heat engines: The thermoelectric generator as an instructive illustration," Am. J. Phys. **59**, 551-555 (1991). See also references therein.

[2] See for example M. W. Zemansky and R. H. Dittman: *Heat and Thermodynamics* (McGraw-Hill, Auckland, 1981), 6th ed. H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley & Sons, New York, 1985), 2nd ed.

[3] Callen (Reference 2), p. 314-316; Jou et al. (Reference 2), p. 124-127, and p. 309-311. The authors of the second book also provide detailed criticism of the classical derivations (p. 23).

[4] H. U. Fuchs, *The Dynamics of Heat* (Springer-Verlag, New York, 1996).

[5] μ_{ec} is the electro-chemical potential (of the charge carriers in the material) per charge of one mole of charge carriers,

i.e., it is the standard electro-chemical potential divided by the Faraday constant (see Reference 4, p. 470). If concentration differences and the temperature dependence of the chemical part of the potential can be neglected, μ_{ec} equals the electric potential (measured in volts). This is the case for a voltmeter used to measure the voltage across a thermoelectric device. For details see Walstrom (Reference 1).

[6] The factor $T\alpha$ is commonly called the *Peltier coefficient*. See for example, Zemansky and Dittman (Reference 2), p. 338.

[7] Reference 4, p. 360.

[8] For background on the first term, see Reference 4, p. 314, and p. 592-599 for a generalized proof; see also Zemansky and Dittman in Reference 2, p. 434. In the introductory form of the dynamical theory of heat, this relation between currents of entropy and associated energy currents is taken for granted, based upon analogies between different phenomena (see Reference 2, Chapter 1). For this and for the general relation, see also G. Falk, F. Herrmann, and G. B. Schmid, “Energy forms or energy carriers?,” Am. J. Phys. **51**,1074-1077 (1983); H. Burkhardt, “Systems physics: A uniform approach to the branches of classical physics,” Am. J. Phys. **55**,344-350 (1987); and H. U. Fuchs, “Entropy in the teaching of introductory thermodynamics,” Am. J. Phys. **55**,215-219 (1987).

[9] While the steps that lead from Eq. 12 to (Eq. 13) may be convincing on physical grounds, they are not necessary for purely mathematical reasons. For the entropy production rate in Eq. 12 to be strictly non-negative, we only require $k_S \geq 0$, $\sigma \geq 0$, and $4k_S/\sigma \geq (\varepsilon - \alpha)^2$.

[10] Integration of the second term for the thermoelectric generator shows that this term is indeed equal to the rate at which energy is made available to the user of the device, if we set $\varepsilon = \alpha$. See also Walstrom (Reference 1).

[11] The thermodynamic fluxes are supposed to be time derivatives of state variables (Jou et al. in Reference 2, p. 124-127). However, the heat flux vector and the viscous pressure tensor cannot be expressed in such a form in classical irreversible thermodynamics. The restriction can only be lifted in extended irreversible thermodynamics (see Jou et al. in Reference 2, p. 309-311).

[12] For a proof in a special case, see I. Müller, *Thermodynamics* (Pitman, Boston, 1985), p. 203-208.