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Influence of nonlinear effects on the efficiency of a thermoelectric generator

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Abstract. We propose a nonlinear model for thermoelectric coupling which is based on the thermomass theory of heat conduction. We show that in this model, the second Kelvin relation and the classical Onsager relations are no longer satisfied simultaneously, namely if one holds, then the other one breaks down, and viceversa. As a function of the different breaking, we evaluate the efficiency of a thermoelectric generator. The influence of the electric-charge gradient on the efficiency of thermoelectric coupling is investigated as well.

Keywords. Thermomass theory · Nonlinear effects · Onsager symmetry · Maximum efficiency · Thermoelectric generator.

1. Introduction

Classical irreversible thermodynamics [1–3] provides a natural theoretical framework for coupled transport processes. The thermoelectric effects (i.e., the possibility of coupling thermal transport and electric current) are nowadays among the most explored coupled phenomena, since they offer a promising possibility in energy management [4–6]. From the very beginning, in the analysis of thermoelectric effects, it has been used the so-called *second Kelvin relation* (SKR) $\Pi = \epsilon T$, Π being the Peltier coefficient, ϵ the Seebeck coefficient, and T the temperature. This relation, stated by Lord Kelvin since 1854, expresses a substantial and useful connection between the Peltier effect (namely, the heating, or cooling, of an electrified junction) and the Seebeck effect (i.e., the conversion of temperature differences into electricity).

The search of new strategies for improving the efficiency in the thermoelectric-energy conversion has led to some generalizations of the governing equations describing thermoelectric effects [7–9] from the theoretical point of view and to intensive studies on nanoscale devices from the practical point of view. Indeed, at nanoscale (or in fast perturbations), the classical Fourier law is no longer applicable to have detailed descriptions of the heat conduction [3,5,10–16]. Thus, several theoretical models, going beyond it and accounting for memory, nonlocal, and nonlinear effects [15,17–23] have been developed in the past decades.

Among them, an enhanced heat-transport equation has been recently obtained in the framework of thermomass (TM) theory [24–28] in which the heat flow is due to a gas-like collection of heat carriers, characterized by an effective mass density and flowing through the medium due to a thermomass-pressure gradient. This collection is made by massive quasi-particles of heat carriers, i.e., the thermons, which are representative of the vibrations of the molecules generated by heating the conductor and whose mass may be calculated from the Einstein's mass-energy duality. In gases and liquids, the thermons are supposed to be attached on the molecules or atoms of the medium. In solids, the thermomass gas will be the phonon gas for crystals, attached on the electron gas for pure metals, or just both of them for systems in which the heat carriers are phonons and electrons [24–28].

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In TM theory, the heat-transport equation reads [25]

$$\tau_{\mathrm{tm}} \frac{\partial \mathbf{q}}{\partial t} - \rho c_v \frac{\partial T}{\partial t} \mathbf{l} + \nabla \mathbf{q} \cdot \mathbf{l} + \lambda \left(1 - b\right) \nabla T + \mathbf{q} = \mathbf{0} \tag{1}$$

wherein ρ is the mass density of the medium, c_v is the specific (i.e., per unit of mass) heat capacity of the solid, λ is the thermal conductivity,

$$\tau_{\mathrm{tm}} = \frac{\lambda}{2\gamma \rho c_v^2 T}$$

is the relaxation time in the TM theory [26,29,30] with dimensionless parameter γ being the Grüneisen constant,

$$b = \frac{q^2}{2\gamma \rho^2 \left(c_v T\right)^3}$$

stands for a dimensionless number which is called thermal Mach number of the drift velocity relative to the thermal-wave speed in the heat-carrier collection, and

$$\mathbf{l} = \frac{\lambda \mathbf{q}}{2\gamma \rho c_v \left(c_v T\right)^2}$$

denotes a characteristic-length vector [29,30]. In fact, the physical dimensions of $|\mathbf{l}|$ are meters, as it can be directly inferred by the dimensional analysis Eq. (1). It conceptually differs from the mean-free path of thermons and characterizes the strength of the non-Fourier effects introduced by Eq. (1) [29,30]. Moreover, in practical applications and for conceivable values of $\mathbf{q}$, $|\mathbf{l}|$ attains values which are always much smaller than those of the mean-free path of the thermons.

Beside to describe relaxational effects, Eq. (1) incorporates information on the characteristic length of the system (i.e., nonlocal effects) and accounts for nonlinear phenomena. In the linear case (i.e., when the terms which contain the quantities $(\partial T / \partial t)\, \mathbf{l}$, $\nabla \mathbf{q} \cdot \mathbf{l}$ and q^2 are negligible), Eq. (1) takes the same form of the classical Cattaneo's equation [31], even though, from the experimental point of view, the relaxation time of TM theory is two orders of magnitude higher than that of the Cattaneo's theory and, in silicon films, it predicts a much slower response to the thermal perturbations [32]. The compatibility of Eq. (1) with the basic principles of continuum physics has been explored in Ref. [30].

Although Eq. (1) has been fruitfully used to study some interesting features of heat transfer in small systems [29,33–35], in modeling thermoelectric effects, its role has not yet been explored. In doing this, to account for the additional heat-flux production due to the Peltier effect, we have to modify Eq. (1) as

$$\tau_{\mathrm{tm}} \frac{\partial \mathbf{q}}{\partial t} - \rho c_v \frac{\partial T}{\partial t} \mathbf{l} + \nabla \mathbf{q} \cdot \mathbf{l} + \lambda \left(1 - b\right) \nabla T + \mathbf{q} = \Pi \mathbf{i} \tag{2}$$

since the Peltier effect is just the production of an heat flux by an electrified junction of different materials. In Eq. (2), $\mathbf{i}$ means the electric-current density, which we express (as it is standard in classical thermoelectricity) by the constitutive equation

$$\mathbf{i} = -\sigma_e \epsilon \nabla T + \sigma_e \mathbf{E} \tag{3}$$

wherein $\mathbf{E}$ is the electric field, and σ_e is the electric conductivity. Finally, the electric field $\mathbf{E}$ is regarded as a given external force [1,5].

In more details, in the present paper, we explore the consequences of the coupling of Eqs. (2) and (3) with the local balance of energy

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{q} + \mathbf{E} \cdot \mathbf{i} \tag{4}$$

where u is the specific internal energy, together with the local balance of the electric charge

$$\rho \frac{\partial z}{\partial t} = -\nabla \cdot \mathbf{i} \tag{5}$$

with z as the electric charge per unitary mass.

For the sake of simplicity, we assume that the electric charge is due to the motion of electrons only and that the production of electric charge in our system is zero. In Eq. (4), the term $\mathbf{E} \cdot \mathbf{i}$ accounts for the expenditure of power due to the propagation of electric current. However, we do not include in Eq. (4) any additional rate of work due to the thermomass pressure. This is tantamount to assume that such a power is negligible with respect to the power expended by the electric-charge motion. In this way, in the absence of electric field, Eq. (4) reduces to the classical energy balance in solid crystals which is expected in classical phonons hydrodynamics [36]. As a consequence of the hypotheses above, the evolution in time of our thermoelectric crystal will be represented by the solutions of the nonlinear system (2)–(5), which are continuous curves (with respect to the parameter t), in the state space $S = \{u,\ z,\ \mathbf{q}\}$ [3,5].

It is not difficult to prove that, whenever the nonlinear effects may be neglected, the model above allows to prove the validity of the SKR by means of the Onsager relations [37,38] (OR), stating the symmetry of the transport coefficients linking the thermodynamic fluxes with the conjugated thermodynamic forces.

Although in the linear approximation the OR are satisfied in all the known situations and comply with the experimental evidences [2,3,39,40], in the nonlinear regime, these relations may result no longer valid [41]. Thus, in practical applications at nanoscale, it is natural to investigate whether the OR still hold, or if they suffer a break [42]. In particular, in what follows we prove that, as a consequence of the nonlinearity of Eq. (2), the SKR may break down even if the OR hold.

The paper runs as follows.

In Sect. 2, we evaluate the system (2)–(5) in the linear regime and briefly review the classical proof given in irreversible thermodynamics of the validity of the SKR.

In Sect. 3, we neglect the effects due to the chemical potential of the electric charges and show that in the nonlinear regime one of the following conditions may occur: (i) the OR hold, but the SKR breaks down; (ii) the SKR holds, but the OR break down; (iii) both the OR, and SKR break down. In all the situations above, we evaluate the efficiency of a thermoelectric generator and show that in the cases i) and ii) it may be enhanced with respect to the case considered in Sect. 2.

In Sect. 4, we take into account the effects of the chemical potential of the electric charges, since these effects may be interesting in the so-called "functionally graded materials," in which material inhomogeneity plays a relevant role [43,44]. Since in this case, the constitutive equations for the heat flux and for the electric current are modified, we get a more general expression of the thermodynamic efficiency, which depends on the gradient of the temperature and the gradient of the electric charge. In this section, we also investigate the possibility of determining a maximum for such efficiency. To this end, we postulate that the maximum of the efficiency corresponds to a minimum of the rate of entropy production, or, equivalently, to a minimum of the rate of energy dissipated along the process. We prove that such a criterion offers a manageable and physically sound method for determining the conditions under which the efficiency is optimal.

Final remarks on the thermoelectric coupling in TM theory are given in Sect. 5.

In closing this section let us observe that from the practical point of view, a thermoelectric device (for example, a thermocouple, a radioisotope thermoelectric generator, a thermoelectric coolers, etc) is a combination of p-n junctions which are connected electrically and thermally in series and parallel, respectively. Since each p-n junction generates a small voltage difference, a lot of junctions are necessary to generate the desirable output voltage. Although, in principle, modeling the junction between the two different materials deserves consideration, our aim here is only to analyze the consequences of accounting for Eq. (1) in modeling thermoelectric effects. Therefore, remaining on a general level, we sketch the thermoelectric device as a cylindrical nanowire[1] under the action of an electric field $\mathbf{E}$ and crossed by an electrical current $\mathbf{i}$. Moreover, we assume that the properties and composition of our system change continuously, i.e., that the limits of the material functions on both sides of any junction coincide.

2. SKR in the linear regime

As we previously observed, it is well known that in the linear regime, the validity of SKR may be proved owing to the OR, by applying a simple thermodynamic procedure [1,5]. In the nonlinear regime, instead, the same procedure leads to the conclusion that in some cases, the OR may loose their validity. Thus, to illustrate our general method of investigation, let us first apply it to the linear case, by considering a rigid nanowire in which the heat flux is stagnated, i.e., $\partial \mathbf{q}/\partial t = \mathbf{0}$ in Eq. (2). Moreover, we suppose that the nonlinear terms in that equation are negligible, in such a way that it reduces to the usual constitutive for $\mathbf{q}$ in the thermoelectric coupling [1,5], i.e.,

$$\mathbf{q} = -\lambda \nabla T + \Pi \mathbf{i} \tag{6}$$

In this situation, denoting by s the specific entropy, we may write the following Gibbs relation [1,3,5]

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial u}\right)\frac{\partial u}{\partial t} + \left(\frac{\partial s}{\partial z}\right)\frac{\partial z}{\partial t} \Leftrightarrow T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \frac{\mu_z}{z}\frac{\partial z}{\partial t} \tag{7}$$

wherein we used the usual definition of the absolute temperature, i.e., $T^{-1} = \partial s/\partial u$ and that of specific chemical potential due to the electric charge, i.e., $\mu_z = -Tz\partial s/\partial z$. The coupling of Eq. (7) with Eqs. (4) and (5) yields

$$\begin{aligned} \rho\frac{\partial s}{\partial t} &= -\frac{\nabla \cdot \mathbf{q}}{T} + \frac{\mathbf{E}\cdot\mathbf{i}}{T} + \left(\frac{\mu_z}{zT}\right)\nabla\cdot\mathbf{i} \\ &= -\nabla\cdot\left(\frac{\mathbf{q}}{T} - \frac{\mu_z}{zT}\mathbf{i}\right) + \frac{1}{T}\left[-\frac{\mathbf{q}}{T}\cdot\nabla T + \frac{\mu_z}{Tz}\mathbf{i}\cdot\nabla T - \mathbf{i}\cdot\nabla\left(\frac{\mu_z}{z}\right) + \mathbf{E}\cdot\mathbf{i}\right] \end{aligned} \tag{8}$$

Recalling that the usual form of the local balance of entropy is

$$\rho\frac{\partial s}{\partial t} = -\nabla\cdot\mathbf{J}_s + \sigma_s \tag{9}$$

with $\mathbf{J}_s$ as the entropy flux, and $\sigma_s \geq 0$ as the local entropy production, then a simple comparison between Eqs. (8) and (9) leads to

$$\mathbf{J}_s = \frac{\mathbf{q}}{T} - \frac{\mu_z}{zT}\mathbf{i} \tag{10a}$$

$$\sigma_s = \frac{1}{T}\left[-\frac{\mathbf{q}}{T}\cdot\nabla T + \frac{\mu_z}{Tz}\mathbf{i}\cdot\nabla T - \mathbf{i}\cdot\nabla\left(\frac{\mu_z}{z}\right) + \mathbf{E}\cdot\mathbf{i}\right] \tag{10b}$$

Equation (10a) turns out the usual result of classical irreversible thermodynamics according to which the entropy flux is given by the sum of the thermodynamic affinities (i.e., the partial derivatives of the entropy with respect to the independent variables) times the corresponding fluxes [45].

The result in Eq. (10b), instead, allows to point out useful relations among the different phenomenological coefficients involved in our theoretical model. To see this, let us suppose for a while that the contribution due to the chemical potential of the electrons is negligible, namely $\mu_z/z = 0$. In this case, the entropy flux reads $\mathbf{J}_s = \mathbf{q}/T$, and Eq. (10b) reduces to

$$T\sigma_s = \mathbf{E}\cdot\mathbf{i} - \left(\frac{\nabla T}{T}\right)\cdot\mathbf{q} \tag{11}$$

---

[1] From the theoretical point of view, it is well known that the use of quantum wires with a constant transversal section, the diameter of which should be smaller than 10 nm, may enhance the performances in the thermoelectric-energy conversion.

According with the classical Onsager approach [1], we may regard the right-hand side of Eq. (11) as a bilinear product of the thermodynamic forces

$$\mathbf{X}^{(j)} = \left\{ \mathbf{E}, -\frac{\nabla T}{T} \right\}, \quad j = 1, 2$$

and their conjugated thermodynamic fluxes

$$\mathbf{J}^{(i)} = \{ \mathbf{i}, \mathbf{q} \}, \quad i = 1, 2$$

respectively. Thus, a sufficient condition to ensure that the right-hand side of Eq. (11) is always non-negative is to assume that each $\mathbf{J}^{(i)}$ is given by a linear combination of all the vectors $\mathbf{X}^{(i)}$, namely,

$$\mathbf{J}^{(i)} = \sum_j L_{ij} \mathbf{X}^{(j)}$$

wherein L_{ij} are the phenomenological transport coefficients. From the practical point of view, this is a tantamount to suppose that the following linear relations hold

$$\mathbf{q} = -L_{11} \frac{\nabla T}{T} + L_{12} \mathbf{E} \tag{12a}$$

$$\mathbf{i} = -L_{21} \frac{\nabla T}{T} + L_{22} \mathbf{E} \tag{12b}$$

which allow to identify the phenomenological coefficients L_{ij} by simple comparisons. In fact, observing that the coupling of Eqs. (3) and (6) gets

$$\mathbf{q} = -\left(\lambda + \Pi \sigma_e \epsilon \right) \nabla T + \Pi \sigma_e \mathbf{E} \tag{13}$$

then the comparison of Eqs. (13) and (3) with Eqs. (12a) and (12b), respectively, yields

$$L_{11} = \left(\lambda + \Pi \sigma_e \epsilon \right) T \tag{14a}$$

$$L_{12} = \Pi \sigma_e \tag{14b}$$

$$L_{21} = \sigma_e \epsilon T \tag{14c}$$

$$L_{22} = \sigma_e \tag{14d}$$

Finally, by the OR $L_{12} = L_{21}$, the SKR $\Pi = \epsilon T$ ensues.

3. Thermoelectric coupling in the nonlinear regime

The generation of electrical energy from thermal energy by thermoelectric devices is one of the most important goals of the current energy management. Many research groups are focusing their attention on the search of different strategies to enhance the efficiency in the thermoelectric-energy conversion, defined as

$$\eta = \frac{P_{\mathrm{el}}}{\dot{Q}_{\mathrm{tot}}} \tag{15}$$

with P_{el} being the electric-power output, and $\dot{Q}_{\mathrm{tot}}$ being the total heat supplied per unit time.

The analysis of the efficiency of a thermoelectric generator, in which the heat flux drives the electrical one, has been performed in deep in the linear regime, and it is almost simple to be treated from the theoretical point of view when simplifying assumptions hold. For example, let us consider a single thermoelectric nanowire generator of length L, the two sides of which are steadily kept at the different temperatures T_{h} (the hotter temperature) and T_{c} (the colder one) in such a way that both a quantity of heat per unit time uniformly flows through the system, and an uniform electric current is produced by the Seebeck effect. Moreover, we assume that our system may be considered as almost homogeneous and that the different material functions may be taken as constants.

In such a case, if we take into account Eqs. (3) and (6), making use of the approximation $\nabla T \simeq \Delta T/L$, we get

$$P_{\mathrm{el}} = i\int_0^L E d\zeta = i\epsilon\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right) - \frac{i^2 L}{\sigma_e} \tag{16a}$$

$$\dot{Q}_{\mathrm{tot}} = \frac{\lambda\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)}{L} + \Pi i \tag{16b}$$

with ζ denoting the position of the points of the system. Note that in principle, the Seebeck coefficient may assume either a positive value (for example, in the case of a p-type semiconductor wherein the current is brought by holes), or a negative one (for example, in the case of a n-type semiconductor wherein the current is carried by electrons). Our main conclusions here will be derived under the assumption that $\epsilon > 0$. However, the case $\epsilon < 0$ also deserves consideration and will be the subject of future studies. In this case, from Eq. (15), we have that the thermoelectric efficiency in the linear regime reads

$$\eta = \frac{i\epsilon\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right) - \dfrac{i^2 L}{\sigma_e}}{\lambda\dfrac{\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)}{L} + i\Pi} = \eta_c\left[\frac{\epsilon x - x^2\lambda\sigma_e^{-1}}{T_{\mathrm{h}}^{-1} + \epsilon x}\right] \tag{17}$$

once the SKR has been used. In Eq. (17) $\eta_c = \left(1 - T_{\mathrm{c}}/T_{\mathrm{h}}\right)$ means the usual Carnot efficiency, and

$$x = \frac{iL}{\lambda\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)} \tag{18}$$

denotes the ratio between the intensity of the electric current and that of the heat flux. The search of the x value which maximizes Eq. (17) allows to point out, for example, useful information about the way of enhancing the performances of a thermoelectric device in the linear regime.

Here, we aim to extend a similar analysis to the nonlinear regime. In this case, we have to observe at first that the heat flux is no longer given by Eq. (6), but it transforms in

$$\mathbf{q} = -\nabla\mathbf{q}\cdot\mathbf{l} - \lambda\left(1 - b\right)\nabla T + \Pi\mathbf{i} \tag{19}$$

To treat with Eq. (19) in the very general case is cumbersome since, due to the nonlinear term $\nabla\mathbf{q}\cdot\mathbf{l}$ therein, one should know a priori how $\mathbf{q}$ (as well as $\mathbf{E}$ and T) depends on ζ. However, interesting information can be obtained if we make simplifying assumptions which do not hurt with the generality. Therefore, let us suppose that both $\mathbf{q}$ and $\mathbf{E}$ take a constant value in any transversal section along the longitudinal axis ζ, as well as that $\mathbf{q}$ and $\mathbf{i}$ are parallel. Then, by the balance of energy (4), we obtain

$$\nabla\cdot\mathbf{q} = \frac{\partial q\left(\zeta\right)}{\partial\zeta} = \mathbf{E}\cdot\mathbf{i}$$

which allows the following further approximation

$$\nabla\mathbf{q}\cdot\mathbf{l} = \frac{\partial q\left(\zeta\right)}{\partial\zeta}\mathbf{l} = \mathbf{E}\cdot\mathbf{i}\frac{\mathbf{q}\lambda\rho}{2\gamma c_v\left(\rho c_v T\right)^2} \cong \frac{\lambda\rho\overline{E}\overline{q}}{2\gamma c_v\left(\rho c_v\overline{T}\right)^2}\mathbf{i} \cong \overline{E}\overline{l}\mathbf{i} \tag{20}$$

where $\overline{E}$, $\overline{q}$, $\overline{T}$ and $\overline{l}$ denote the mean values of $|\mathbf{E}|$, $|\mathbf{q}|$, T and $|\mathbf{l}|$ on the interval $[0, L]$. We also explicitly note that $\overline{l}$ in Eq. (20) (which we introduced here just for the sake of a formal simplicity), has to be meant as a positive constant, which is related to well known and measurable quantities.

The coupling of Eqs. (19) and (20) gets

$$\mathbf{q} = -\left[\lambda\left(1 - b\right) + \sigma_e\epsilon\left(\Pi - \overline{E}\overline{l}\right)\right]\nabla T + \sigma_e\left(\Pi - \overline{E}\overline{l}\right)\mathbf{E} \tag{21}$$

so that, comparing Eqs. (21) and (3), with Eqs. (12a) and (12b), respectively, we obtain

$$L_{11} = \lambda\left(1-b\right)T + \sigma_e \epsilon\left(\Pi - \overline{El}\right)T \tag{22a}$$

$$L_{12} = \sigma_e\left(\Pi - \overline{El}\right) \tag{22b}$$

$$L_{21} = \sigma_e \epsilon T \tag{22c}$$

$$L_{22} = \sigma_e \tag{22d}$$

By the analysis of Eqs. (22b) and (22c), it is easy to infer that the following different conditions may occur, which point out that the investigation of the validity of the OR in the present nonlinear situation deserves consideration, since, beside its intrinsic theoretical interest, it allows to evaluate in a more precise way the efficiency of thermoelectric generator.

3.1. The OR hold and the SKR breaks down

If one assumes that the OR hold, then from Eqs. (22b) and (22c) the condition $L_{12} = L_{21}$ yields

$$\Pi = \epsilon T + \overline{El} \tag{23}$$

namely the SKR is no longer valid. In this case, due to the contribution of the nonlinear terms in the constitutive equation of the heat flux, the total heat supplied per unit of time becomes

$$\dot{Q}_{\mathrm{tot}} = \frac{\lambda\left(1-b\right)\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)}{L} + \left(\Pi - \overline{El}\right)i \tag{24}$$

while the electrical power obtained is still given by Eq. (16a). Then, from Eq. (15) the following thermoelectric efficiency ensues:

$$\eta = \frac{i\epsilon\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right) - \dfrac{i^2 L}{\sigma_e}}{\lambda\left(1-b\right)\dfrac{\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)}{L} + i\epsilon T} = \eta_c\left[\frac{\epsilon x - x^2\lambda\sigma_e^{-1}}{\left(1-b\right)T_{\mathrm{h}}^{-1} + \epsilon x}\right] \tag{25}$$

once Eq. (23) has been taken into account.

By the expression above, we infer that the nonlinear term $\nabla\mathbf{q}\cdot\mathbf{l}$ does not influence η which, instead, is affected by the further nonlinear term $\lambda b \nabla T$. This results in an increasing of η, depending, through b, on the intensity of the heat flux. Therefore, if the OR hold but the SKR breaks down, there is an improvement of the thermoelectric-device performances due to a reduction in the effective thermal conductivity $\lambda\left(1-b\right)$. However, one should notice that such an increase is bounded by the constraint that the latter quantity has to remain always positive. The positivity of this parameter in TM theory is related to a well-known phenomenon, confirmed by several experiments and referred to as the occurrence of "flux limiters" [46].

3.2. The SKR holds and the OR break down

If one assumes that the SKR holds, then from Eqs. (22b) and (22c), the condition $\Pi = \epsilon T$ yields $L_{12} \neq L_{21}$, that is, the OR are no longer valid.

In this case, it is easy to observe that the thermoelectric efficiency becomes

$$\eta = \frac{i\epsilon\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right) - \dfrac{i^2 L}{\sigma_e}}{\lambda\left(1-b\right)\dfrac{\left(T_{\mathrm{h}} - T_{\mathrm{c}}\right)}{L} + i\left(\epsilon T - \overline{El}\right)} = \eta_c\left[\frac{\epsilon x - x^2\lambda\sigma_e^{-1}}{\left(1-b\right)T_{\mathrm{h}}^{-1} + \left(\epsilon - \overline{El}T_{\mathrm{h}}^{-1}\right)x}\right] \tag{26}$$

From Eq. (26), it follows that in contrast with previous case, if there is a breaking in the OR and the validity of the SKR, an enhancement in η is obtained not only by the reduction in the effective thermal conductivity $\lambda(1-b)$, but also by means of the second nonlinear term $\nabla\mathbf{q}\cdot\mathbf{l}$. In this case, new interesting strategies seem to arise, since in nanoscale engineering, the main part of researchers is trying to obtain higher efficiencies only by reducing the thermal conductivity.

3.3. Both the OR hold and the SKR break down

From the theoretical point of view, the analysis of Eqs. (22b) and (22c) may also suggest that neither the OR, nor the SKR may longer hold. In such a situation, the thermoelectric efficiency becomes

$$\eta = \frac{i\epsilon\left(T_{\mathrm{h}}-T_{\mathrm{c}}\right)-\dfrac{i^2L}{\sigma_e}}{\lambda(1-b)\dfrac{\left(T_{\mathrm{h}}-T_{\mathrm{c}}\right)}{L}+i\left(\epsilon T-\overline{El}\right)} = \eta_c\left[\frac{\epsilon x - x^2\lambda\sigma_e^{-1}}{(1-b)\,T_{\mathrm{h}}^{-1}+\left(\Pi-\overline{El}\right)T_{\mathrm{h}}^{-1}x}\right] \tag{27}$$

which clearly points out that it is directly affected by both nonlinear terms again. However, in such a case, since no any relation between Π and ϵT can be inferred in principle, we cannot say whether there is an improvement of η, or not. In fact, although in this situation, we still have a reduction in the effective thermal conductivity (which would lead to an enhancement in η), for any value of x, the term $\left(\Pi-\overline{El}\right)$ may attain either larger or smaller values with respect to both the corresponding terms ϵT_{h} and $\left(\epsilon T_{\mathrm{h}}-\overline{El}\right)$ in Eqs. (25) and (26), respectively. Thus, the denominator of Eq. (27) may also attain larger values with respect to both the denominator of Eq. (25) and that of Eq. (26), so that the nonlinear term $\nabla\mathbf{q}\cdot\mathbf{l}$ leads to a worsening of the performances of a thermoelectric device.

4. The effects of the electric charge

In previous sections, we always neglected the contribution arising from the term μ_z/z in Eqs. (10). This simplifying assumption seems logical in homogeneous systems. In the case of a junction of two different materials, instead, the term μ_z/z, as well as all the material functions (which we treated as constant values), should be represented, instead, by stair-shaped functions. Indeed, in recent year, functionally graded materials (FGMs) [47], i.e., a new class of advanced materials with varying properties over a changing dimension, are attracting the attention of scientists due to their unique properties. In particular, their versatility allows the use of these materials in thermoelectric applications, too. In FGMs, the particular properties change continuously, or quasi-continuously, along one direction, and this implies that the different material functions may be assumed continuous, or quasi-continuous. In thermoelectric devices, the conversion efficiency can be substantially improved by adjusting the carriers' concentration along the material's length. This can be achieved by employing a functionally graded thermoelectric material (FGTM), with the carriers' concentration optimized for operation over the specific temperature gradient [43,44].

In this case, it may be also interesting to investigate the consequences of including in the entropy flux the term $(\mu_z/Tz)\,\mathbf{i}$ before neglected, having present that the local entropy production is now given by the full version of Eq. (10b). Here, we pursue this analysis under the further hypotheses $\mu_z=\mu_z(u,z)$ and $T=T(u)$, so that we are allowed to write

$$\frac{\mu_z}{z}=\tilde{f}(u,z)=f(T,z)\Rightarrow\nabla\tilde{f}(u,z)=\nabla f(T,z)=\frac{\partial f}{\partial T}\nabla T+\frac{\partial f}{\partial z}\nabla z \tag{28}$$

wherein, owing to the positive definiteness of the specific heat $c_v = du/dT$, we have expressed u as a function of T. In this way, the rate of energy dissipation per unitary volume $T\sigma_s$ becomes

$$T\sigma_s = \left(\mathbf{E} + \frac{f}{T}\nabla T\right)\cdot\mathbf{i} - \left(\frac{\partial f}{\partial T}\mathbf{i} + \frac{\mathbf{q}}{T}\right)\cdot\nabla T - \frac{\partial f}{\partial z}\mathbf{i}\cdot\nabla z \tag{29}$$

Again, according with the classical Onsager approach [1], we regard the right-hand side of Eq. (29) as a bilinear product of the generalized thermodynamical forces

$$\mathbf{X}^{(j)} = \left\{\left(\mathbf{E} + \frac{f}{T}\nabla T\right), \nabla T, \nabla z\right\}, \quad j = 1, 2, 3$$

and of their conjugated thermodynamical fluxes

$$\mathbf{J}^{(i)} = \left\{\mathbf{i}, \left(-\frac{\partial f}{\partial T}\mathbf{i} - \frac{\mathbf{q}}{T}\right), -\frac{\partial f}{\partial z}\mathbf{i}\right\}, \quad i = 1, 2, 3$$

respectively, and write each of the latter as a linear combination of the formers, namely,

$$\mathbf{i} = L_{11}\left(\mathbf{E} + \frac{f}{T}\nabla T\right) + L_{12}\nabla T + L_{13}\nabla z \tag{30a}$$

$$-\frac{\partial f}{\partial T}\mathbf{i} - \frac{\mathbf{q}}{T} = L_{21}\left(\mathbf{E} + \frac{f}{T}\nabla T\right) + L_{22}\nabla T + L_{23}\nabla z \tag{30b}$$

$$-\frac{\partial f}{\partial z}\mathbf{i} = L_{31}\left(\mathbf{E} + \frac{f}{T}\nabla T\right) + L_{32}\nabla T + L_{33}\nabla z \tag{30c}$$

In particular, the substitution of Eq. (30a) in Eq. (30b) gets

$$\begin{aligned}\mathbf{q} = &-\left(\frac{1}{2}\frac{\partial f^2}{\partial T}L_{11} + T\frac{\partial f}{\partial T}L_{12} + L_{21}f + L_{22}T\right)\nabla T - \left(T\frac{\partial f}{\partial T}L_{11} + L_{21}T\right)\mathbf{E}\\ &-\left(T\frac{\partial f}{\partial T}L_{13} + L_{23}T\right)\nabla z\end{aligned} \tag{31}$$

To derive useful information on the phenomenological coefficients, Eqs. (30a) and (31) may be compared with the following generalization of the constitutive Eqs. (3) and (21)

$$\mathbf{i} = -\sigma_e\epsilon\nabla T + \sigma_e\mathbf{E} + \alpha\nabla z \tag{32a}$$

$$\mathbf{q} = -\left[\lambda(1-b) + \sigma_e\epsilon\left(\Pi - \overline{El}\right)\right]\nabla T + \sigma_e\left(\Pi - \overline{El}\right)\mathbf{E} + \Pi\alpha\nabla z \tag{32b}$$

wherein α is a positive constant, in such a way that the usual convention that the electric current is in the opposite direction of the motion of the electrons is respected. That comparison leads to the following identifications

$$L_{11} = \sigma_e \tag{33a}$$

$$L_{12} = -\sigma_e\left(\epsilon + \frac{f}{T}\right) \tag{33b}$$

$$L_{13} = \alpha \tag{33c}$$

$$L_{21} = -\sigma_e\left[\frac{\partial f}{\partial T} + \frac{\left(\Pi - \overline{El}\right)}{T}\right] \tag{33d}$$

$$L_{22} = \frac{\lambda(1-b)}{T} + \frac{\sigma_e\left(\Pi - \overline{El}\right)}{T}\left(\epsilon + \frac{f}{T}\right) + (\sigma_e\epsilon)\frac{\partial f}{\partial T} + \left(\frac{\sigma_e}{2T}\right)\frac{\partial f^2}{\partial T} \tag{33e}$$

$$L_{23} = -\alpha\left(\frac{\partial f}{\partial T} + \frac{\Pi}{T}\right) \tag{33f}$$

Equations (33b) and (33d) lead to the same conclusions of Sect. 3. In particular, from those relations, if we assume that the OR hold, i.e., $L_{12} = L_{21}$, we have

$$\Pi = \epsilon T + f - T\frac{\partial f}{\partial T} + \overline{El} \tag{34}$$

showing the breakdown of the SKR. Note that Eq. (34) turns out the SKR whenever both the role of the nonlinear term $\overline{El}$ and that of the gradient of the electric charge (expressed through the function f) are neglected in the constitutive equation for the heat flux (32b).

4.1. The thermoelectric efficiency

In what follows, we study the role played by the gradient of the electric charges on the thermoelectric efficiency. In doing this, we assume that the OR do no longer hold, i.e., we disregard Eq. (34). By some lengthy calculations similar to those made in Sect. 3, we can put the thermodynamic efficiency (15) in the following form

$$\eta\left(x,y\right) = \eta_c \left\{ \frac{\epsilon x - x^2\lambda\sigma_e^{-1} - \alpha\sigma_e^{-1}y^2}{T_{\mathrm{h}}^{-1}\left[1 - b + \left(\Pi - \overline{El}\right)x - \alpha y^2\right]} \right\} \tag{35}$$

wherein x is still given by Eq. (18), and

$$y = \sqrt{\frac{1}{\lambda}\left|\frac{z_c - z_h}{T_h - T_c}\right|}$$

Although the couple (x, y) which optimizes the efficiency may be searched by investigating the maximum of the function $\eta\left(x,y\right)$, here we apply a different procedure, which is based on the mathematical analysis of the local rate of entropy production along the thermoelectric process.

The analysis of the rate of entropy production is a useful mean in the modeling of nonequilibrium phenomena. For instance, it is postulated that in nonequilibrium processes, the appropriate constitutive equations are the ones that maximize the rate of entropy production, allowing the system to proceed faster toward the equilibrium [48,49]. Here we assume that as it can be physically expected, the best efficiency corresponds to a minimum of the rate of energy dissipated along the process. This is logical, since the thermoelectric efficiency is related to the irreversibility induced by the heat and electrical transport.

To proceed further, we use Eqs. (32) in order to eliminate $\mathbf{E}$ and $\mathbf{q}$ in Eq. (29), getting so

$$T\sigma_s = \frac{i^2}{\sigma_e} + f_1\nabla T\cdot\mathbf{i} - f_2\mathbf{i}\cdot\nabla z + \frac{\lambda}{T}\left(1 - b\right)\left(\nabla T\right)^2 - \frac{\alpha\overline{El}}{T}\nabla z\cdot\nabla T \tag{36}$$

with

$$f_1\left(z,T\right) = \epsilon + \frac{f}{T} - \frac{\partial f}{\partial T} - \frac{\Pi - \overline{El}}{T} \tag{37a}$$

$$f_2\left(z,T\right) = \frac{\alpha}{\sigma_e} + \frac{\partial f}{\partial z} \tag{37b}$$

At this point, we observe that, since σ_s is the local rate of entropy production along the process of energy conversion, the right-hand side of Eq. (36) may be interpreted as the local rate of energy dissipated along the same process. In this way, in order to obtain the values of (x, y) guaranteeing the optimal efficiency, we are allowed to calculate the minima, if they exist, of the right-hand side of Eq. (36).

In terms of the variables x and y defined above, this is equivalent to calculate the points of minimum of the following function

$$g\left(x,y\right) \equiv T\sigma_s \left[\frac{L}{\lambda\left(T_h - T_c\right)}\right]^2 = \frac{x^2}{\sigma_e} - \frac{x}{\lambda} f_1 - f_2 x y^2 - A y^2 + \frac{1-b}{\lambda T} \tag{38}$$

wherein

$$A = \frac{\alpha \overline{El} L^2}{T\lambda}$$

is a constant value. The stationary points for $g\left(x,y\right)$ are the solutions of the following algebraic system

$$\begin{cases} \dfrac{\partial g}{\partial x} = \dfrac{2x}{\sigma_e} - \dfrac{f_1}{\lambda} - f_2 y^2 = 0 \\ \dfrac{\partial g}{\partial y} = -2 f_2 x y - 2 A y = 0 \end{cases} \tag{39}$$

Since, by definition, x is a strictly positive quantity, by direct calculations we have that

$$\left[x = \frac{\sigma_e f_1}{2\lambda}; y = 0\right] \tag{40}$$

is the only physical admissible stationary point of the function $g\left(x,y\right)$. That solution allows us to obtain also the following thermodynamic restriction on the function f_1

$$f_1 \geq 0 \Longrightarrow \epsilon + \frac{f}{T} - \frac{\partial f}{\partial T} - \frac{\Pi - \overline{El}}{T} \geq 0 \tag{41}$$

Now, we have to investigate the sign of the second derivatives of g, which are given by

$$\frac{\partial^2 g}{\partial x^2} = \frac{2}{\sigma_e} \tag{42a}$$

$$\frac{\partial^2 g}{\partial y^2} = -2 f_2 x - 2A \tag{42b}$$

$$\frac{\partial^2 g}{\partial x \partial y} = \frac{\partial^2 g}{\partial y \partial x} = -2 f_2 y \tag{42c}$$

It is evident that $\partial^2 g/\partial x^2$ is always positive, while $\partial^2 g/\partial x \partial y$ vanishes in correspondence of the solution (40). Then, in order to make positive the determinant of the Hessian matrix of $g\left(x,y\right)$, it is necessary and sufficient that $\partial^2 g/\partial y^2$ is positive. This yields

$$\frac{\sigma_e f_1 f_2}{4} + \frac{\alpha \overline{El} L^2}{T} \leq 0 \tag{43}$$

The conditions (41) and (43) can be interpreted as constraints on f, namely on the chemical potential due to the electric charge. In fact, if the inequalities (41) and (43) are satisfied, then the efficiency of the thermoelectric-energy conversion gets a maximum in correspondence of the point determined in Eq. (40), in that the rate of energy dissipated by the process of conversion gets a minimum.

5. Discussion

In this paper, we have proposed a new theoretical model for thermoelectric coupling, which is based on the TM theory of heat conduction. We have shown that if the nonlinear terms entering the evolution equation for the heat flux are taken into account, one of the following situations may occur: (i) the OR hold, but the SKR breaks down; (ii) the SKR holds, but the OR break down; (iii) both the OR and SKR break down. In all the situations above, we have evaluated the efficiency of a thermoelectric generator. We have observed that the analytical form of the efficiency changes for the three different cases. This could be a useful mean to investigate what of the situations above is true in the practical applications. In fact, the efficiency could be evaluated by measuring directly the quantities P_{el} and $\dot{Q}_{\text{tot}}$, and then comparing the value so obtained with the theoretical ones given by the relations (25), (26) and (27), one may infer what really happens in practical applications. That way, the results of Sect. 3 have not only a practical importance, but they can be also related to a fundamental thermodynamic problem, namely the validity of the OR in the nonlinear regime. It is worth noticing that the OR have been already investigated in TM theory, in the absence of current circulation [40]. However, here we have applied a different approach, by relating their validity to the efficiency of thermoelectric coupling.

We have also investigated the effects due to the chemical potential of the electric charges. Under the hypothesis of stationary fluxes, we postulated new constitutive equations for the heat flux and for the electric current and proved that the new terms entering these equations strongly influence the thermodynamic efficiency. We have obtained suitable conditions to guarantee that such an efficiency is optimal. To achieve that task, we have assumed that, in correspondence of the optimal efficiency, the local rate of energy dissipation gets a minimum. Such an assumption, far from being a physical principle well established and confirmed by the experimental evidence (as for instance, second law of thermodynamics), represents only a manageable and physically sound criterion to calculate the conditions of optimal efficiency. Furthermore, it seems to comply with other approaches to nonequilibrium processes [48,49], exploiting the points of maximum of the rate of entropy production to get information on the form of the constitutive equations. Finally, its validity may be easily tested by accordance with the experiments, for instance by comparison of the efficiency given by Eq. (35), evaluated in the point (40), with the measured one.

From the mathematical point of view, the criterion proposed here is not difficult to apply, and so it could provide important information in those nonlinear cases in which also nonlocal effects are considered, as for instance when the evolution of the is governed by a nonlinear generalization of the classical Guyer–Krumhansl equation [17,18].

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