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P. Rogolino, A. Sellitto, V.A. Cimmelli*

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- We estimate the efficiency of a one-dimensional thermoelectric generator, pointing out its dependence on the presence of two temperatures.
- The optimal value of the thermoelectric efficiency is calculated.

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Influence of the electron and phonon temperature and of the electric-charge density on the optimal efficiency of thermoelectric nanowires

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ABSTRACT

In this paper we study the thermodynamic efficiency of thermoelectric generators in which the heat transport is driven by phonons and electrons. It is assumed that the phonon temperature and the electron temperature are different, and that the electric-charge density is nonuniform. The mean temperature is defined by observing that the internal energy of the system is the same either in the presence of two temperatures, or of one temperature. In steady states, we determine the influence of the gradients of the mean temperature and of the electric-charge density on the theoretical values of the thermoelectric efficiency. The physical conditions under which such an efficiency is optimal are determined as well.

1. Introduction

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Thermoelectric effects involve a fundamental interplay between electric and thermal properties of a system. The two primary thermoelectric effects are the Seebeck effect and the Peltier effect, which can be used to derive all other thermoelectric effects when combined with the laws of thermodynamics. The Seebeck effect describes how a temperature difference creates a charge flow, while the Peltier effect describes how an electrical current can create a heat flow.

Since the initial discovery of those effects, in the early 1800s, a solid theoretical foundation has been developed on thermoelectric materials [1]. The efficiency of thermoelectric energy converters is determined by the non-dimensional product ZT between the temperature T, and the material parameter $Z = \epsilon^2\sigma_e/\lambda$, with ϵ being the Seebeck coefficient, σ_e the electrical conductivity, and λ the thermal conductivity of the material, called figure-of-merit. Since the higher ZT, the higher the efficiency of a thermoelectric device, in the last decades several studies have been developed in order to improve Z. To date, the best reported ZT values are in the 2–3 range, and one of the current tasks in design of nanostructured materials is to achieve $ZT \simeq 3$, or larger. Although this is a good result, the range of applicability of thermoelectric materials is still susceptible to be extended.

The advent of nanotechnologies, on the one side, provides new ways to enhance the performances of thermoelectric materials (for example making nanocomposites, adding nanoparticles to a bulk material, or employing one-dimensional nanostructures [2,3]), on the other side, it requires to revisit the theoretical framework, since the physics at nanoscale shows several different behaviors with respect to that at macroscale [4–8]. Thus, the aim of the present paper is twofold, namely, to introduce a new theoretical model for thermoelectric effects, and to study its consequences on the efficiency of the thermoelectric energy conversion.

The paper runs as follows. In Section 2 we present a two-temperature model of thermoelectric rigid conductor, in which the different heat carriers (i.e., the electrons and phonons in the present paper) are allowed to have their own temperature. In Section 3, under the previous hypothesis, we estimate the efficiency of a one-dimensional thermoelectric generator, pointing out its dependence on the presence of two temperatures. The optimal value of this parameter is calculated as well. In Section 4 we summarize the main results and point out the physical conditions under which the performance of a thermoelectric device is enhanced.

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2. The two-temperature model

In the present section we develop a physical model for thermoelectric effects starting from the observation that, since the heat carriers (phonons and electrons in our case) behave as a mixture of gases flowing through the crystal lattice [9,10], each of them may be endowed with its own temperature [11]. According to the theory of fluid mixtures with different temperatures [12,13], we assume that each constituent obeys the same balance laws as a single fluid, in such a way that the time rates of the internal energy of phonons per unit mass u_p and of the internal energy of electrons per unit mass u_e, as well as the time rate of the electrical charge per unit mass of electrons ϱ_e are governed by the following partial differential equations

$$\rho\partial_t u_p = -\nabla\cdot\mathbf{q}^{(p)} \tag{1a}$$

$$\rho\partial_t u_e = -\nabla\cdot\mathbf{q}^{(e)} + \mathbf{E}\cdot\mathbf{i} \tag{1b}$$

$$\rho\partial_t \varrho_e = -\nabla\cdot\mathbf{i} \tag{1c}$$

with ρ as the mass density of the conductor, $\mathbf{E}$ as the electric field, and $\mathbf{i}$ as the electric-current density. Moreover, in Eq. (1a) $\mathbf{q}^{(p)}$ denotes the phonon contribution to the heat flux, and in Eq. (1b) $\mathbf{q}^{(e)}$ stands for the electron contribution to the heat flux [10]. They are such that the overall heat flux reads $\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$.

According to the basic principles of Extended Irreversible Thermodynamics [6,8,14], the thermodynamic theory in which the dissipative fluxes are considered as independent variables, we assume that the fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$ are state variables, too.

Along with the results obtained in Ref. [11], we assume that the evolution equations of those fluxes, respectively, are

$$\tau_p\partial_t\mathbf{q}^{(p)} + \mathbf{q}^{(p)} = -\lambda_p\nabla T_p - \lambda_{pe}\nabla T_e \tag{2a}$$

$$\tau_e\partial_t\mathbf{q}^{(e)} + \mathbf{q}^{(e)} = -\lambda_{ep}\nabla T_p - (\lambda_e + \sigma_e\epsilon\Pi)\nabla T_e + \sigma_e\Pi \times\left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho_e}\right)\right] + \left(\frac{\mu_e}{\varrho_e}\right)\mathbf{i} \tag{2b}$$

$$\tau_i\partial_t\mathbf{i} + \mathbf{i} = -\sigma_e\epsilon\nabla T_e + \sigma_e\left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho_e}\right)\right] \tag{2c}$$

wherein Π is the Peltier coefficient, τ_p, τ_e and τ_i are the relaxation times of phonons, electrons and electric current, respectively [10,15], λ_p and λ_e are the contributions to the thermal conductivity of the material due, respectively, to phonons and electrons [10,16], and the material functions λ_{pe} and λ_{ep} express the contributions to the thermal conductivity of the phonon-electron interactions [11]. Moreover, in Eq. (2), T_p is the phonon temperature, and T_e is the electron temperature, which are related to the average temperature T of the system as follows [11]

$$T = \frac{c_v^{(p)}T_p + c_v^{(e)}T_e}{c_v} \tag{3}$$

with $c_v^{(p)}$ and $c_v^{(e)}$ being the phonon and the electron specific heats at constant volume [17], respectively, and $c_v = c_v^{(p)} + c_v^{(e)}$ being the specific heat at constant volume of the whole system [18]. Finally,

$$\mu_e = -\varrho_e T_e\frac{\partial s}{\partial\varrho_e} \tag{4}$$

is the chemical potential due to the electrons.

Then, if we introduce the following quantities

$$\begin{cases} \alpha = \dfrac{c_v^{(e)}}{c_v}; \quad 1-\alpha = \dfrac{c_v^{(p)}}{c_v} \\ \beta_1 = \dfrac{T_e}{T}; \quad \beta_2 = \dfrac{T_p}{T} \end{cases} \tag{5}$$

then, from Eq. (3) we have

$$\alpha\beta_1 + (1-\alpha)\beta_2 = 1 \Leftrightarrow \beta_2 = \frac{1}{1-\alpha} - \left(\frac{\alpha}{1-\alpha}\right)\beta_1 \tag{6}$$

which clearly points out that if one is able to measure the single heat-carrier temperature (for example T_e, as suggested in Ref. [11]), then it is also possible to estimate the other temperature, provided that the average temperature T is known by experimental measurements.

Whenever the relaxation times of the dissipative fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$ are negligible, from Eqs. (2) the following constitutive equations for thermoelectric effects arise:

$$\mathbf{q} = -\Lambda_p\nabla T_p - \Lambda_e\nabla T_e + \left(\frac{\mu_e}{\varrho_e} + \Pi\right)\mathbf{i} \tag{7a}$$

$$\mathbf{i} = -\sigma_e\epsilon\nabla T_e + \sigma_e\left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho_e}\right)\right] \tag{7b}$$

with $\Lambda_p = \lambda_p + \lambda_{ep}$, and $\Lambda_e = \lambda_e + \lambda_{pe}$. The consequences of these equations on the efficiency of thermoelectric energy conversion, under the hypothesis of negligible μ_e/ϱ_e, have been studied in Ref. [11].

Here we go deeper in that analysis, and account not only for the effects due to the different temperatures, but also for those due to the term μ_e/ϱ_e. Nowadays, these effects play a relevant role in the so-called "functionally graded materials" (FGMs) [19], in which material inhomogeneity is exploited to enhance the efficiency of thermoelectric coupling [20–23]. Indeed, in recent years FGMs, i.e., a new class of advanced materials with varying properties over a changing dimension, are attracting the attention of many research groups. In FGMs the properties change continuously, or quasi continuously, along one direction, and this implies that the different material functions may be assumed to be continuous, or quasi-continuous. Their versatility allows the use of these materials in thermoelectric applications, too. In particular, the efficiency of thermoelectric devices can be 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 operating over a specific temperature gradient [20–23].

To achieve this task, we first notice that, as proved in Ref. [11], when the relaxation times of the fluxes are negligible, then the specific entropy s only depends on the unknown variables u_p, u_e and ϱ_e. In this way, from the definition of chemical potential (see Eq. (4)), it follows

$$\frac{\mu_e}{\varrho_e} = f(u_p; u_e; \varrho_e) \tag{8}$$

Due to the relation (8), the chain rule allows to rewrite Eq. (7b) as

$$\mathbf{i} = -\sigma_e\widetilde{\epsilon}\nabla T_e - \left(\sigma_e\epsilon\frac{\partial f}{\partial T_p}\right)\nabla T_p + \sigma_e\left(\mathbf{E} - \frac{\partial f}{\partial\varrho_e}\nabla\varrho_e\right) \tag{9}$$

wherein $\widetilde{\epsilon} = \epsilon + \partial f/\partial T_e$. We notice that in deriving Eq. (9) we used the constitutive relations $u_p = c_v^{(p)}T_p$ and $u_e = c_v^{(e)}T_e$.

The theoretical model for thermoelectric effects expressed by Eqs. (7a) and (9) is able to account both for different heat-carrier temperatures, and for a charge-carrier gradient.

3. Efficiency of thermoelectric nanowires

Motivated by the developments of research on new materials [24], let us calculate the efficiency of a thermoelectric generator arising from Eqs. (7a) and (9) for a one-dimensional nanodevice in steady conditions. From the geometrical point of view, we represent the system as a segment of length L, and denote the position

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of its points by the coordinate $\xi \in [0, L]$. We assume that the hot side (i.e., the right side, at $\xi = L$) is held at the temperature T^h, and the cold side (i.e., the left side, at $\xi = 0$) is held at the temperature T^c. Moreover, we suppose that an electric current and a quantity of heat enter uniformly into the hot side of the element. Then, according to Eq. (7b), the electric field **E** is parallel to the electric current **i**, namely, it is directed from the hotter side (i.e., the right side, at $\xi = L$) to the colder one (i.e., the left side, at $\xi = 0$).

Recognizing that in a one-dimensional setting, when a conductive material is subjected to a thermal gradient, the charge carriers migrate throughout the system from the hotter side to the colder one, and, in the open-circuit condition, they accumulate in the cold region, generating so an electric potential difference, we conclude that the electric-current density **i** and the temperature gradients ∇T_e and ∇T_p have to be opposite vectors, for arbitrary values of the material coefficients $\sigma_e\widetilde{\epsilon}$ and $(\sigma_e\epsilon)\partial f/\partial T_p$. As a consequence, by Eq. (9) we infer that $\partial f/\partial T_e > 0$ and $\partial f/\partial T_p > 0$. We 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 of a positive Seebeck coefficient. Moreover, since the electric current is always parallel and concordant to the gradient of the electric charge, still by Eq. (9) we conclude that $\partial f/\partial \mathcal{Q}_e < 0$.

In our case, the efficiency η of the thermoelectric generator is defined as the ratio of the electric power output (per unit area) $P_{\rm el}$ and the heat supplied (per unit area) per unit time $\dot{Q}$, namely,

$$\eta = \frac{P_{\rm el}}{\dot{Q}} \tag{10}$$

In calculating the right-hand side of Eq. (10), we explicitly observe that the loss of electrical power due to the Joule effect should be represented by negative terms, while the gain of useful electrical power generated by a temperature difference should yield positive terms. For the sake of simplicity, in the next we approximate the material parameters $\widetilde{\epsilon}$, σ_e, $\partial f/\partial T_p$ and $\partial f/\partial \mathcal{Q}_e$ by their mean values $\overline{\epsilon}$, $\overline{\sigma_e}$, $\overline{f_p}$ and $\overline{f_{\mathcal{Q}}}$ in $[0, L]$. This mathematical assumption, which allows our calculations to be reduced to a more simple level, is tantamount to suppose that those constitutive quantities suffer very small variations in $[0, L]$. Moreover, owing to the reduced length, we can approximate the gradients in Eq. (9) by their measured values $\Delta T_p/L$, $\Delta T_e/L$ and $\Delta \mathcal{Q}_e/L$, with $\Delta T_e = T_e^h - T_e^c$, $\Delta T_p = T_p^h - T_p^c$, and $\Delta \mathcal{Q}_e = {\mathcal{Q}_e}^h - {\mathcal{Q}_e}^c$.

In these conditions, the electric-power output is equal to the work made by the Coulomb force per unit time iE for moving the electric charges from $\xi = L$ to $\xi = 0$, namely,

$$P_{\rm el} = \int_L^0 iE d\xi = i\int_0^L -E d\xi = -\frac{i^2 L}{\overline{\sigma_e}} + \overline{\epsilon} i\Delta T_e + i\overline{f_p}\Delta T_p - i\left|\overline{f_{\mathcal{Q}}}\right|\Delta \mathcal{Q}_e \tag{11}$$

once the use of Eq. (9) is made. We note that Eq. (11) is in accordance with the convention above on the sign of terms which contribute to $P_{\rm el}$, since the negative signs in the first and fourth term of the right-hand side of Eq. (11) correspond to a loss of useful energy due to the well-known Joule effect, while the positive signs in the second and third term correspond to a gain of useful energy generated by the temperature differences ΔT_e and ΔT_p. This result constitutes a further proof that our previous conclusions on the sign of the terms $\partial f/\partial T_e$, $\partial f/\partial T_p$ and $\partial f/\partial \mathcal{Q}_e$ are correct.

On the other hand, since in our representation the cross section at the left-hand side of the nanowire is a point, the heat passing through it per unit time, which just represents the heat supplied to the system per unit time, is given by the absolute value of **q** evaluated in this point. In this way, the total heat supplied per unit time can be written as

$$\dot{Q} = \Lambda_p \frac{\Delta T_p}{L} + \Lambda_e \frac{\Delta T_e}{L} + (\Pi + \overline{f})i \tag{12}$$

wherein $\overline{f}$ is the mean value of the function f longwise L.

The coupling of Eqs. (11) and (12) with Eq. (10) yields

$$\eta = \frac{-\frac{i^2 L}{\overline{\sigma_e}} + \overline{\epsilon} i\Delta T_e + i(i\overline{f_p})\Delta T_p - i\left(\left|\overline{f_{\mathcal{Q}}}\right|\right)\Delta \mathcal{Q}_e}{\Lambda_p \frac{\Delta T_p}{L} + \Lambda_e \frac{\Delta T_e}{L} + (\Pi + \overline{f})i} \tag{13}$$

Then, if we define the new variables

$$\begin{cases} x = \dfrac{iL}{\Delta T} \\ y = \sqrt{\dfrac{\Delta \mathcal{Q}_e}{iL}} \end{cases} \tag{14}$$

by straightforward calculations, from Eq. (13) we get

$$\eta = \left(1 - \frac{T^c}{T^h}\right)\left[\frac{-\left(\frac{\lambda_{\rm eff}}{\overline{\sigma_e}\beta_1}\right)x^2 + \frac{\Gamma}{\beta_1}x - \left(\frac{\lambda_{\rm eff}^2}{\beta_1}\left|\overline{f_{\mathcal{Q}}}\right|\right)x^2 y^2}{\frac{\gamma+1}{T^h} + \overline{\epsilon}\left(1 + \frac{\delta}{\beta_1}\right)x}\right] \tag{15}$$

wherein $\lambda_{\rm eff} = \Lambda_p + \Lambda_e$, $\Gamma = \overline{\epsilon}\beta_1 + \beta_2\overline{f_p}$, $\gamma = \Lambda_p\lambda_{\rm eff}^{-1}(\beta_2\beta_1^{-1} - 1)$, and $\delta = \overline{f}/(\overline{\epsilon}T^h)$. Eq. (15) shows that the total efficiency can be written as $\eta = \eta_c\eta_r$, where

$$\eta_c = \left(1 - \frac{T^c}{T^h}\right) \tag{16}$$

is the usual Carnot efficiency (which represents an ideal limit, since it is obtained for a quasi-static transformation, which requires infinite time), and

$$\eta_r = \frac{-\left(\frac{\lambda_{\rm eff}}{\overline{\sigma_e}\beta_1}\right)x^2 + \frac{\Gamma}{\beta_1}x - \left(\frac{\lambda_{\rm eff}^2}{\beta_1}\left|\overline{f_{\mathcal{Q}}}\right|\right)x^2 y^2}{\frac{\gamma+1}{T^h} + \overline{\epsilon}\left(1 + \frac{\delta}{\beta_1}\right)x} \tag{17}$$

is a reduced efficiency, the value of which is always smaller than unit. Although in Refs. [25,26] it is shown that, in principle, even the Carnot efficiency is attainable, the actual devices have performances which are notoriously much more modest, that is, $\eta_r \ll 1$.

In order to find new strategies to enhance the thermoelectric efficiency, here we look for the couple of variables $x_{\rm opt}$ and $y_{\rm opt}$ which maximizes the reduced efficiency.

Moreover, if we introduce an effective figure-of-merit defined as

$$Z_{\rm eff} = \frac{(\overline{\epsilon})^2\overline{\sigma_e}}{\lambda_{\rm eff}}$$

then the standard analysis of the stationary points of a two-variable function turns out that in correspondence of the values

$$x_{\rm opt} = \frac{\gamma+1}{\overline{\epsilon}T(1+\delta\beta_1^{-1})}\left[-1 + \sqrt{1 + \left(\frac{\Gamma}{\overline{\epsilon}}\right)\left(\frac{Z_{\rm eff}T}{\gamma+1}\right)\left(1 + \frac{\delta}{\beta_1}\right)}\right] \tag{18a}$$

$$y_{\rm opt} = 0 \tag{18b}$$

of the variables, the reduced efficiency gets its maximum value, and the optimal efficiency (13) becomes

$$\eta_{\rm opt} = \frac{\eta_c(\gamma+1)}{\beta_1(1+\delta\beta_1^{-1})^2}\left[\frac{2}{Z_{\rm eff}T} + \frac{\Gamma(1+\delta\beta_1^{-1})}{\overline{\epsilon}(\gamma+1)} - \frac{2}{Z_{\rm eff}T}\sqrt{1 + \frac{\Gamma(1+\delta\beta_1^{-1})}{\overline{\epsilon}(\gamma+1)}Z_{\rm eff}T}\right] \tag{19}$$

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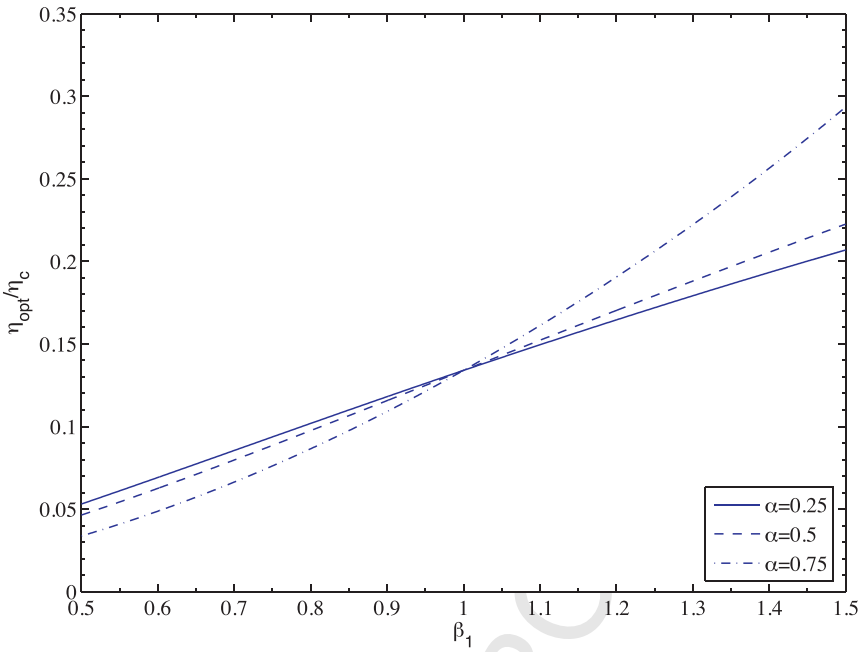

Fig. 1. Behavior of η_{opt}/η_c versus β_1 for three different values of the non-dimensional parameter $\alpha = c_v^{(e)}/c_v$ and for a fixed value of δ: theoretical results arising from Eq. (19) in the case of $f = f(\varrho_e)$.

Eq. (19), which generalizes the results obtained in Ref. [11] under the hypothesis that the terms proportional to μ_e/ϱ_e are negligible in Eqs. (7), points out that the optimum efficiency strongly depends not only on the two temperatures T_p and T_e, but also on the gradient of the charge carriers.

In particular, from Eq. (19) it is easy to see that

$$Z_{\text{eff}}T \to \infty \Rightarrow \eta \to \eta_c \left(\frac{\Gamma}{\widetilde{\epsilon}\beta_1}\right)\left(1+\frac{\delta}{\beta_1}\right)^{-1}$$

so that the material functions $\widetilde{\epsilon}$, $\partial f/\partial T_p$ and $\partial f/\partial \varrho_e$ must fulfill the following physical restriction

$$\left(\frac{\Gamma}{\widetilde{\epsilon}\beta_1}\right)\left(1+\frac{\delta}{\beta_1}\right)^{-1} \leq 1$$

This consideration, joined with the further observation that, whenever the terms in f can be neglected in Eq. (7), then $\eta \to \eta_c$ as $Z_{\text{eff}}T \to \infty$, allows to conclude that the presence of a non-vanishing gradient of the electric charges worsen the thermoelectric efficiency. This is logical, since the inhomogeneity in the charge density induces a current circulation inside the conductor and, as a consequence, an enhancement of the dissipation by Joule effect.

For the sake of illustration, in the next we evaluate f in correspondence of fixed values of T_e and T_p, so that $f = f(\varrho_e)$, and plot the ratio η_{opt}/η_c in such a situation. Although in a special case, this simplifying assumption allows us to show clearly in the next figures both the role played by the two temperatures, and the role played by the gradient of electric charges.

In Fig. 1 we plot the behavior of the ratio η_{opt}/η_c as a function of β_1, for three different values of the nondimensional parameter α, i.e., $\alpha = 0.25$, $\alpha = 0.5$ and $\alpha = 0.75$, and when $\delta = 1$. For the sake of illustration, in our computation we assumed that $\Lambda_p = \Lambda_e$, as the materials commonly used in thermoelectric applications show a phonon thermal conductivity which is approximately equal to the electron thermal conductivity, and supposed $Z_{\text{eff}}T = 1$.

As it can be seen, in this case the maximum efficiency increases for increasing values of β_1. This means that the bigger T_e with respect to T_p, the better the performance of the thermoelectric device. Indeed, Fig. 1 also allows to analyze the role played by $c_v^{(e)}$ and $c_v^{(p)}$, the latter being usually higher than the former. In fact, it points out that the (positive) slope of the curve $\eta_{opt} = \eta_{opt}(\beta_1)$ gradually decreases whenever α assumes very small values, whereas it takes an almost constant value when α reaches high enough values, in such a way that whenever $T_e > T_p$, the higher α, the higher η_{opt}. We also note that in Fig. 1 the value $\eta_{opt}/\eta_c = 0.13$, attained when $\beta_1 = 1$, corresponds to the case of a single-temperature model, namely, $T_e = T_p \equiv T$.

In Fig. 2, instead, we plot the behavior of the ratio η_{opt}/η_c as a function of δ, for three different values of the non-dimensional parameter α, i.e., $\alpha = 0.25$, $\alpha = 0.5$ and $\alpha = 0.75$, and when $\beta_1 = 0.5$. In obtaining the results of Fig. 2 we still assumed that $\Lambda_p = \Lambda_e$, and $Z_{\text{eff}}T = 1$. Along with previous observations about the role of the gradient of the electric charge, from Fig. 2 we infer that the smaller δ, the higher the performance of the thermoelectric device. Fig. 2 still allows to analyze the role of the different specific heats. In particular, we have that the smaller α, the higher η_{opt}. We note that these behaviors are in agreement with those of Fig. 1, since we are assuming that $\beta_1 < 1$. We would have the opposite behaviors if $\beta_1 > 1$.

4. Main conclusions

In this paper, on the example of a thermoelectric nanowire in steady-state conditions, we have analyzed the consequences of accounting both for different temperatures of the different heat carriers, and for the gradient of the electric-charge density. Our results arise from the theoretical two-temperature model in Eq. (7), the thermodynamic compatibility of which has been proved in Ref. [11], wherein the possibility of measuring the phonon and the electron temperatures was discussed as well.

For practical applications, the results presented above suggest that, in order to enhance the efficiency of thermoelectric energy conversion, it would be useful to have:

- the charge distribution as much homogeneous as possible, in such a way that $\bar{f} \to 0$ in Eq. (13);

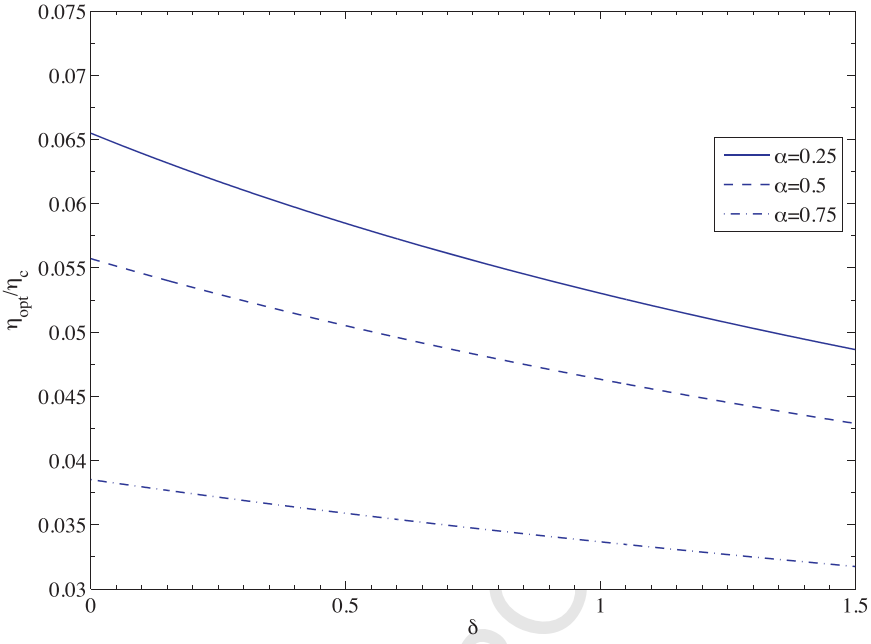

Fig. 2. Behavior of η_{opt}/η_c versus δ for three different values of the non-dimensional parameter $\alpha = c_v^{(e)}/c_v$ and for a fixed value of β_1: theoretical results arising from Eq. (19) in the case of $f = f(\varrho_e)$.

- the physical parameter $\frac{\beta_1}{\beta_2} = \frac{T_e}{T_p}$ as higher as possible;
- the electron specific heat $c_v^{(e)}$ as higher (respectively, smaller) as possible, and the phonon specific heat $c_v^{(p)}$ as smaller (respectively, higher) as possible, whenever $\frac{\beta_1}{\beta_2} > 1$ (respectively, $\frac{\beta_1}{\beta_2} < 1$).

Indeed, we already observed that the first of the conditions above minimizes the quantity of energy dissipated by the Joule effect. In FGTMs, if the nanodevice is composed by segments with different thermoelectric properties, it should be designed in such a way that the concentration of electric charge inside the different segments is either the same, or as much similar as possible.

The second condition ensures that in the device the electric phenomena are prevalent with respect to the thermal ones, in such a way that the energy dissipated by the diffusion of heat is limited. Finally, the third of the previous conditions can be interpreted as follows. If $T_e < T_p$, it limits the quantity of energy transported by the electrons which can be stored as internal energy, and maximizes the part of this energy which can be used to create an accumulation of charges and, as a consequence, a difference of electric potential. If, instead, $T_e > T_p$, it limits the part of the energy transported by the phonons which can be stored as internal energy, and maximizes the part of this energy which can be transformed in electrical energy.

The last two items above already emerged in Ref. [11], where the contribution of the electric chemical potential was considered negligible. The first item, instead, is new, and shed new light on the role of the charge density on the determination of the thermoelectric efficiency.

Indeed, in classical thermoelectricity all the efforts to improve the efficiency were focused on the enhancement of the figure-of-merit Z. Although this remains a very important parameter, here and in Ref. [11] we have shown that if a more realistic model is applied, by supposing that each of the heat carriers is endowed with its own temperature and by including the effects due to a nonuniform charge distribution, then there are new parameters beside Z, namely α, β_1 and $\bar{f}$, which can help to enhance the performance of the thermoelectric devices. This fact allows to analyze the problem of the efficiency from a different perspective, which will be exploited by us in forthcoming researches.

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