Mechanics Research Communications 68 (2015) 77–82

Contents lists available at ScienceDirect

Mechanics Research Communications

journal homepage: www.elsevier.com/locate/mechrescom

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

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 27 February 2015
Accepted 8 March 2015
Available online 21 March 2015

Dedicated to Prof. Bruno A. Boley, on the occasion of his ninetieth birthday.

Keywords:
Thermoelectric effects
Thermoelectric efficiency
Two-temperature model

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 efficiency is optimal are determined as well.

1. Introduction

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 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]), and 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 for thermoelectric rigid conductors, 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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http://dx.doi.org/10.1016/j.mechrescom.2015.03.002
0093-6413/

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

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

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

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

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

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

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 the 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