Influence of electron and phonon temperature on the efficiency of thermoelectric conversion

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ABSTRACT

In the framework of Extended Irreversible Thermodynamics it is developed a two-temperature model (for electrons and phonons, respectively) of thermoelectric effects. The expression of the maximum efficiency in terms of these two temperatures is derived as well. It is proved that, for the electron temperature higher than the phonon temperature, the two-temperature model yields an efficiency which is higher with respect to that of the single-temperature model. Two possible experiments to estimate the electron temperature are suggested.

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1. Introduction

Thermoelectricity is actually viewed as a very interesting source of electric power because of its ability to convert heat flow directly into electricity. In particular, thermoelectric devices as energy converters are easily scalable and do not have moving parts, or liquid fuels. These excellent features make them applicable in almost any situation where large quantities of heat tend to go to waste, from clothing to large industrial facilities.

Whilst the thermoelectric materials have been known and understood for quite some time, so far they have not been efficient enough to be used commercially. Currently, many research groups are investing their efforts in finding new materials with appropriate properties to better use thermoelectric effects, creating so efficient thermoelectric devices. A good thermoelectric material will have very poor thermal conductivity λ, but a very high electrical conductivity σ_e, so that the so-called figure-of-merit $Z = \epsilon^2 \sigma_e / \lambda$, with ϵ being the Seebeck coefficient, which is the main responsible of the thermoelectric efficiency, is as high as possible.

Indeed, the advent of nanotechnology is widening the range of applicability of thermoelectric materials. In fact, the nanostructures used in materials maintain good electrical conductivity, while reducing the thermal conductivity. The performances of thermoelectric devices can thus be enhanced with the use of nanotechnology-based materials that have improved thermoelectric properties and good solar energy absorption abilities. Thermoelectric materials based on Bi_2Te_3, for example, stand out as perfect examples highlighting the role of nanomaterials for thermoelectric devices. Carbon nanotubes and graphene sheets as thermoelectric materials also exhibit improved thermoelectric properties. In general, the usage of nanostructures smaller than the wavelength of light enhances the scattering of photons decreasing so the thermal conductivity. This decreasing in the thermal conductivity seems to be the most vital benefit of nanostructuring for thermoelectric materials.

Although it is very clear the importance of using nanotechnology in thermoelectricity, the design of good thermoelectric nanodevices is still far from its optimal solution. This principally because the physics at nanoscale presents some dark points, as for instance the role played by memory, nonlocal and nonlinear effects, as well as the appropriate definition of temperature in non-equilibrium situations [1–5].

In Ref. [6] we have investigated the influence of nonlocal effects on the figure-of-merit in cylindrical nanowires, and predicted how it depends on the features of the transversal section. In the present paper, instead, we focus our attention especially on the role of the temperature and on the possibility of accounting for different values for electron and phonon temperature. Our investigation starts

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Nomenclature

c_v	specific heat at constant volume
$c_v^{(e)}$	specific heat at constant volume of electrons
$c_v^{(p)}$	specific heat at constant volume of phonons
$\mathbf{E}$	electric-field vector
$\mathbf{i}$	electric-current density vector
$\mathbf{J}^{(s)}$	specific-entropy flux vector
$\mathbf{q}$	overall local heat-flux vector
$\mathbf{q}^{(e)}$	local heat-flux vector due to electrons
$\mathbf{q}^{(p)}$	local heat-flux vector due to phonons
s	specific entropy
T	average temperature
T_e	electrons temperature
T_p	phonons temperature
u	specific internal energy
u_e	specific internal energy of electrons
u_p	specific internal energy of phonons
Z	figure-of-merit

Greek symbols

ϵ	Seebeck coefficient
η	thermoelectric efficiency
λ	total thermal conductivity
λ_e	electrons thermal conductivity

λ_p	phonons thermal conductivity
μ_e	electron chemical potential
Π	Peltier coefficient
ρ	mass density
$\varrho^{(e)}$	specific electric charge
Σ	thermodynamic state space
σ_e	electrical conductivity
$\sigma^{(s)}$	rate of entropy-density production
τ_e	relaxation time of electrons
τ_i	relaxation time of electric charges
τ_p	relaxation time of phonons

Subscripts

e	electrons
eff	effective
i	electric-current density
max	maximum
p	phonons

Superscripts

(e)	electrons
(p)	phonons
(s)	entropy

by the observation that, as the electron mean-free path ℓ_e is usually shorter than the phonon mean-free path ℓ_p, when heat propagates in a system whose characteristic size L is such that $\ell_e < L < \ell_p$, it is expected a very high number of electron collisions, and only scant phonon collisions. This yields that the electron temperature T_e may reach its local-equilibrium value, whereas the phonon temperature T_p is still far from its own local-equilibrium value. Conversely, when the electron mean-free path (corresponding to the electron–phonon collisions) is large, one may have the so-called phenomenon of "hot electrons", namely, a population of electrons whose average kinetic energy (i.e., the kinetic temperature) is considerably higher than that of the phonons [7,8]. Another situation in which it is possible to have different temperatures for phonons and electrons is when a high-frequency electromagnetic radiation is used to supply energy to the system, since in such a case the electrons receive energy at a rate higher than that at which they give energy to the phonons. Therefore, it would be interesting to find possible ways to measure both temperatures [9,10].

Besides being appealing from the theoretical point of view, accounting for two different temperatures is also important in practical applications, since it leads to a more realistic computation of the thermodynamic efficiency of the thermoelectric devices.

Here we develop a mesoscopic model of enhanced thermoelectric equations which account for different phonon and electron temperatures. Following the way drawn in Refs. [6,11], we also assume that the overall heat flux $\mathbf{q}$ has two different contributions: the phonon heat flux $\mathbf{q}^{(p)}$ and the electron heat flux $\mathbf{q}^{(e)}$, in such a way that $\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$.

The layout of the paper is the following. In Section 2, we develop a theoretical model describing thermoelectric effects when the electrons and the phonons do not have the same temperature. As a consequence of the second Kelvin relation, we suggest a possible way to measure those temperatures. In Section 3, as a practical application of that model, we determine the efficiency of a thermoelectric generator. We point out that the difference between electron and phonon temperature can contribute to improve the thermoelectric efficiency. In Section 4 we draw the

main conclusions and we underline that our model may also cope with the phonon-drag phenomenon, suggesting so a further experiment to check both the electron and the phonon temperature.

2. The phenomenological laws

The analysis of coupled transport processes is one of the outstanding aspects of the classical theory of nonequilibrium thermodynamics [3,12]. In the present section we aim to derive the phenomenological laws describing the thermoelectric effects whenever the different heat carriers (i.e., the phonons and the electrons in our case) no longer have the same temperature.

Since we assume that the heat carriers behave as a mixture of gases flowing through the crystal lattice [13,14], it seems logical to suppose that the internal energy of phonons per unit mass u_p, the internal energy of electrons per unit mass u_e and the electrical charge per unit mass of electrons $\varrho^{(e)}$ belong to the state space. In particular, we assume that those state-space variables are ruled by the following evolution 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, $\mathbf{E}$ as the electric field, and $\mathbf{i}$ as the electric-current density [6]. We note that the summation of Eqs. (1a) and (1b) turns out the well-known energy-balance equation

$$\rho\partial_t u + \nabla \cdot \mathbf{q} = \mathbf{E} \cdot \mathbf{i}$$

obtained in Ref. [15] in the absence of a magnetic field, once the total internal energy per unit mass of the system u is supposed to be given by the constitutive relation

$$u = u_p + u_e \tag{2}$$

According with the basic principles of Extended Irreversible Thermodynamics (EIT) [3,5], we may assume that the fluxes of previous unknown variables (namely, $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$) are the other