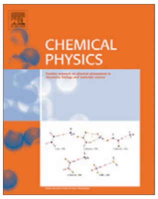
Chemical Physics 375 (2010) 508–513

Contents lists available at ScienceDirect

Chemical Physics

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



A microscopic mechanism for increasing thermoelectric efficiency

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ARTICLE INFO

Article history:
Available online 10 June 2010

Keywords:
Thermoelectricity
Nonlinear dynamics
Onsager coefficients

ABSTRACT

We study the coupled particle and energy transport in a prototype model of interacting one-dimensional system: the disordered hard-point gas, for which numerical data suggest that the thermoelectric figure of merit ZT diverges with the system size. This result is explained in terms of a microscopic mechanism, namely the local equilibrium is characterized by the emergence of a broad stationary "modified Maxwell–Boltzmann velocity distribution", of width much larger than the mean velocity of the particle flow.

1. Introduction

Thermoelectricity is an old field: the Seebeck effect, that is, the conversion of temperature differences into electricity, was discovered in 1821. However, a strong interest in thermoelectric phenomena arose only in the 1950's, when Ioffe discovered that doped semi-conductors exhibited much larger thermoelectric effect than did other materials. He also proposed that semi-conductors could be used to build solid-state home refrigerators. Such refrigerators would be long-lived, silent, maintenance-free, and environmentally benign. Ioffe's suggestion initiated an intense research activity in semi-conductors physics [1–3]. However, in spite of all efforts and consideration of all type of semi-conductors, thermoelectric refrigerators have still poor efficiencies compared to compressor-based refrigerators. Today, thermoelectric devices are mainly used in situations in which reliability and quiet operation are more important than the cost. Applications include equipments in medical applications, space probes, etc.

In the last decade, there has been an increasing pressure to find better thermoelectric materials with higher efficiency. The reason is the strong environmental concern about chlorofluorocarbons used in most compressor-based refrigerators. Also the possibility to generate electric power from waste heat using thermoelectric effect is becoming more and more interesting [1–4].

The thermodynamic efficiency can be conveniently written in terms of the so-called figure of merit $ZT = (\sigma S^2/\kappa)T$, where σ is the electric conductivity, S is the thermoelectric power (Seebeck coefficient), κ is the thermal conductivity, and T is the temperature. Ideal Carnot efficiency is recovered in the limit $ZT \to \infty$. In spite of the worldwide research efforts for identifying thermoelectric materials with high ZT values, so far the best thermoelectric materials are characterized by values of $ZT \sim 1$, at room temperature. Values $ZT > 3$ are considered to be essential for thermoelectric devices to compete in efficiency with mechanical power generation and refrigeration.

The challenge lies in engineering a material for which the values of σ, S, and κ can be controlled in order to optimize thermoelectric efficiency. The problem is that the different transport coefficients are interdependent, thus making optimization extremely difficult. On the other hand, thermodynamics does not impose any upper bound on ZT, so that efficient thermoelectric devices could in principle be engineered. The present understanding of the possible microscopic mechanisms leading to an increase of ZT is quite limited, with few exceptions. Notably, Refs. [5,6] showed that the optimal density of states in a thermoelectric material is a delta function. Such sharp energy-filtering allows to reach, in principle, the Carnot efficiency.

Here, we consider the problem of increasing thermoelectric efficiency from a new perspective, that is, we pursue a dynamical system approach. Understanding from first principles and from nonlinear dynamics simulations the microscopic mechanisms that can be implemented to control the heat flow [7] might prove useful not only for thermoelectric phenomena but also for the design and engineering of thermal diodes and transistors. In this paper, our plan is to compute transport coefficients and thermoelectric efficiency from first principles, namely from the underlying microscopic dynamical processes which are known to be predominantly nonlinear in nature. In a previous work [8], the thermoelectric

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doi:10.1016/j.chemphys.2010.06.009

problem has been investigated by numerical solution of the microscopic equations of motion. Inspired by the kinetic theory of ergodic gases and chaotic billiards, a simple microscopic mechanism for increasing thermoelectric efficiency was proposed. More precisely, the cross transport of particles and energy in open classical ergodic billiards was considered. It has been shown that, in the linear response regime, the thermoelectric efficiency can approach Carnot efficiency for sufficiently complex charge carrier molecules. Indeed, the figure of merit has been found to be a growing function of the number $d_{\rm int}$ of internal degrees of freedom, $ZT=(d+1+d_{\rm int})/2$, where d is the geometric dimension.

In spite of the abstract nature of the model, the above paper opens the possibility for a theoretical understanding of the basic microscopic requirements that a classical dynamical system must fulfill in order to lead to a high thermoelectric figure of merit. In particular, the question arises whether inter-particle interaction might increase the effective number of degrees of freedom, thus leading to a higher figure of merit than in the non-interacting idealized d dimensional gas, where $ZT=(d+1)/2$. Along these lines a detailed numerical study of the cross heat and particle transport has been performed for an open one-dimensional disordered hard-point gas [9]. It has been found that ZT diverges as a power-law in thermodynamic limit, $ZT\propto N^b$, where N is the average number of particles in the system and $b\approx 0.79$. Even though the above result could be, in principle, very interesting, no indication was given concerning the microscopic mechanism which is responsible for the increase of ZT. On the other hand, a theoretical understanding is needed in order to obtain useful hints for increasing thermodynamic efficiency in more realistic models.

In this paper, we propose a mechanism which explains the large thermoelectric quality factor ZT numerically observed in Ref. [9]. This mechanism requires local equilibrium, as naturally expected in systems with the mixing property, and the emergence, in the linear response regime, of an out-of-equilibrium "modified Maxwell–Boltzmann velocity distribution" of width much larger than the mean velocity of the particle flow. Such broad distribution limit is opposite to the limit of peaked distribution, corresponding to the delta-like energy-filtering put forward in Refs. [5,6]. We provide numerical evidence supporting the effectiveness of the broad-distribution mechanism in the hard-point gas model.

Our paper is organized as follows. Sections 2–4 review introductory material on coupled particle and energy transport, modeling stochastic baths, and thermoelectric efficiency of the one-dimensional ideal non-interacting gas. In Section 5, we present numerical results for thermodynamic transport coefficients for the disordered hard-point gas model. Finally, the obtained numerical results are explained in terms of a mechanism based on the emergence of a broad stationary out-of-equilibrium velocity distribution. Concluding remarks are drawn in Section 6.

2. The thermoelectric figure of merit *ZT*

Let us focus our attention on a conductor in which both electric and heat current flow in one-dimension (say, parallel to the x-direction). Assuming local equilibrium, a local entropy (per unit volume) s can be defined, and the rate of entropy production reads [10]

$$\dot{s}=J_u\partial_x\left(\frac{1}{T}\right)+J_\rho\partial_x\left(-\frac{\mu}{T}\right), \tag{1}$$

in which J_u and J_ρ are the energy and particle current densities (fluxes) and $\partial_x(1/T)$, $-\partial_x(\mu/T)$ the associated generalized forces (affinities), where T is the temperature and μ the electrochemical potential.

Assuming that the generalized forces are small, the relationship between fluxes and forces is linear and described by the phenomenological non-equilibrium thermodynamic kinetic Eqs. [10,11]

$$J_u=L_{uu}\partial_x\left(\frac{1}{T}\right)+L_{u\rho}\partial_x\left(-\frac{\mu}{T}\right), \tag{2}$$

$$J_\rho=L_{\rho u}\partial_x\left(\frac{1}{T}\right)+L_{\rho\rho}\partial_x\left(-\frac{\mu}{T}\right), \tag{3}$$

with $L_{\alpha,\beta}$ $(\alpha,\beta\in\{u,\rho\})$ Onsager coefficients. In the absence of magnetic fields, due to microscopic reversibility of the dynamics, the Onsager reciprocity relation $L_{u\rho}=L_{\rho u}$ holds.

In analogy with the relation $dQ=TdS$, the heat current density J_q can be defined by the relation

$$J_q=TJ_s, \tag{4}$$

with

$$J_s=\frac{1}{T}J_u-\frac{\mu}{T}J_\rho, \tag{5}$$

current density of entropy, and therefore

$$J_q=J_u-\mu J_\rho. \tag{6}$$

The entropy production rate equation can then be written in terms of the fluxes J_q and J_ρ and of the corresponding generalized forces $\partial_x(1/T)$ and $-(1/T)\partial_x\mu$:

$$\dot{s}=J_q\partial_x\left(\frac{1}{T}\right)+J_\rho\left(-\frac{\partial_x\mu}{T}\right), \tag{7}$$

while the linear relationship between fluxes and forces reads as follows:

$$J_q=\widetilde{L}_{qq}\partial_x\left(\frac{1}{T}\right)+\widetilde{L}_{q\rho}\left(-\frac{\partial_x\mu}{T}\right), \tag{8}$$

$$J_\rho=\widetilde{L}_{\rho q}\partial_x\left(\frac{1}{T}\right)+\widetilde{L}_{\rho\rho}\left(-\frac{\partial_x\mu}{T}\right), \tag{9}$$

with $\widetilde{L}_{\rho\rho}=L_{\rho\rho},\widetilde{L}_{q\rho}=\widetilde{L}_{\rho q}$ (Onsager relation), $\widetilde{L}_{q\rho}=L_{u\rho}-\mu L_{\rho\rho}$, $\widetilde{L}_{qq}=L_{uu}-2\mu L_{u\rho}+\mu^2L_{\rho\rho}$. Note that, if we call $\mathbf{L}$ and $\widetilde{\mathbf{L}}$ the 2×2 Onsager matrices with matrix elements $L_{\alpha\beta}$ $(\alpha,\beta\in\{u,\rho\})$ and $\widetilde{L}_{\gamma\delta}$ $(\gamma,\delta\in\{q,\rho\})$, it turns out that $\det\widetilde{\mathbf{L}}=\det\mathbf{L}$.

The Onsager coefficients can be expressed in terms of more familiar quantities, the electric conductivity σ, the thermal conductivity κ, and the Seebeck coefficient (thermopower) S. Let us first consider the case in which the thermal gradient vanishes, $\partial_xT=0$, and the system is homogeneous, so that the chemical potential μ_c is uniform. Since the electrochemical potential μ is composed of a chemical part μ_c and an electric part μ_e, $\mu=\mu_c+\mu_e$, it turns out that for a homogeneous isothermal system $\partial_x\mu=\partial_x\mu_e$. The electric current $J_e=eJ_\rho$, with e charge of the conducting particles, is then given by $J_e=\sigma\mathcal{E}=-(\sigma/e)\partial_x\mu_e$, with $\mathcal{E}$ external electric field applied to the system. The quantities μ_c and μ_e cannot be determined separately by the theory of irreversible thermodynamics [12]: only their combination $\mu=\mu_c+\mu_e$ appears in the kinetic Eqs. (2) and (3). Based on this equivalence, we can write $J_\rho=J_e/e=-(\sigma/e^2)\partial_x\mu$ even when $\mu_c\neq 0$, provided $\partial_xT=0$, whence Eq. (9) gives

$$\sigma=\frac{e^2}{T}\widetilde{L}_{\rho\rho}=\frac{e^2}{T}L_{\rho\rho}. \tag{10}$$

The heat conductivity κ is defined as the heat current density per unit temperature gradient for zero electric current: $J_q=-\kappa\partial_xT$, at $J_e=0$. Solving the two kinetic equations (8) and (9) simultaneously, we obtain

$$\kappa=\frac{1}{T^2}\frac{\det\widetilde{\mathbf{L}}}{\widetilde{L}_{\rho\rho}}=\frac{1}{T^2}\frac{\det\mathbf{L}}{L_{\rho\rho}}. \tag{11}$$

Finally, the Seebeck coefficient S is defined as the change in electrochemical potential per unit charge, $-\partial_x\mu/e$, per unit change