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Thermoelectric phenomena via an interacting particle system

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Received 22 July 2004

Published 19 January 2005

Online at stacks.iop.org/JPhysA/38/1005

Abstract

We present a mesoscopic model for thermoelectric phenomena in terms of an interacting particle system, a lattice electron gas dynamics that is a suitable extension of the standard simple exclusion process. We concentrate on electronic heat and charge transport in different but connected metallic substances. The electrons hop between energy cells located alongside the spatial extension of the metal wire. When changing energy level, the system exchanges energy with the environment. At equilibrium the distribution satisfies the Fermi–Dirac occupation law. Installing different temperatures at two connections induces an electromotive force (Seebeck effect) and upon forcing an electric current, an additional heat flow is produced at the junctions (Peltier heat). We derive the linear response behaviour relating the Seebeck and Peltier coefficients as an application of Onsager reciprocity. We also indicate the higher order corrections. The entropy production is characterized as the anti-symmetric part under time reversal of the space–time Lagrangian.

PACS numbers: 05.30.Fk, 71.10.Ca, 73.63.–b

1. Introduction

The goal and motivation of the paper comes from exploring nonequilibrium behaviour via the theory of spatially extended stochastic dynamics; a standard reference is [1]. We present an interacting particle system for the standard thermoelectric phenomena such as the Seebeck and the Peltier effects. Second, we show how the steady-state fluctuation theorem rigorously reproduces the phenomenological linear response theory. Finally, the model also provides a testing ground for deriving higher order response functions and for exploring the nonequilibrium theory beyond linearity.

Thermoelectric systems provide a phenomenology for the foundations of nonequilibrium thermodynamics. Standard examples of thermoelectric phenomena are the Peltier effect

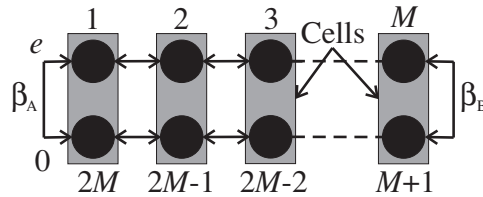


Figure 1. Scheme of the set-up of the toy model.

(1834)—electric current through different metallic conductors will in general cause production or absorption of heat at the junctions, and the Seebeck effect (1826)—an e.m.f. (electromotoric or thermoelectric force) will appear in the circuit if the junctions are maintained at a different temperature (thermocouple). They are discussed in the standard textbooks such as [2] and except for a short reminder in section 6.2 we assume the reader familiar with the basic facts.

As written in the first line of Onsager's 1931 article on reciprocal relations, 'When two or more irreversible transport processes (heat conduction, electrical conduction and diffusion) take place simultaneously in a thermodynamic system the processes may interfere with each other'. Reciprocity relations are the most well-known realizations of that and Thomson was probably the first (in 1854) to propose them. Onsager took up the derivation of the reciprocity relations now named after him [3]. In the second half of the previous century the linear response theory added the response relations such as these of Green and Kubo from which the Onsager relations are explicitly visible.

More recent history has seen a revival in addressing questions on the construction of nonequilibrium statistical mechanics. One proposed generalization of (linear) fluctuation–dissipation relations has been the so-called fluctuation theorem, both in its transient and in its steady-state version. For steady states, it gives a symmetry in the distribution of the variable entropy production. We derive it here in section 5.2. Section 6 explains how it leads to the phenomenological relations between Seebeck and Peltier coefficients. Not emphasized in the literature so far is that this fluctuation symmetry is useless for higher order response functions; it is unable to produce a useful relation for the second-order derivatives of the current around equilibrium. We observe in section 7 how to remedy the situation for our particular model.

The physical origin of the model is discussed in section 3.1. From the point of view of the standard theory of interacting particle systems, it is an adaptation of exclusion processes, see [4] and [5] for mathematical background. In that way it is easy to simulate and it thus offers an environment for studying analytically less accessible aspects of thermoelectric phenomena (such as the influence of disorder). From the point of view of solid state physics, it can be seen as the result of time-dependent perturbation theory to transport problems in metals. We only keep the electron hopping with transition probabilities that satisfy a local detailed balance condition.

The details of the model are explained in section 3 while, as a warm-up, section 2 contains its most simplified form.

2. Toy model for heat conduction

Consider a lattice rectangle of height 2 and width M , see figure 1. Each of the $2M$ sites can be occupied by at most one particle. Think of the rectangle as a 'metal wire' of size M in which each couple of sites $(x, 2M + 1 - x)$ forms one cell with two energy levels that can

each be occupied by one electron. The energy difference between the two levels is taken equal to a constant $e > 0$.

We consider a Markov process on the state space $K = \{0, 1\}^{2M}$ in which particles can hop on nearest-neighbour sites. The hopping is symmetric (subject only to the simple exclusion rule of one particle per site) except for the bonds $(2M, 1)$ and $(M, M + 1)$. More specifically, an elementary transition consists of randomly picking a site x and changing the configuration η into the new configuration $T_x\eta$ which remains equal to η on all sites y except for $y = x$, $T_x\eta(x) = \eta(x + 1)$ and for $y = x + 1$, $T_x\eta(x + 1) = \eta(x)$. The transition rate for $\eta \rightarrow T_x\eta$ is equal to

$$\begin{aligned} & \exp[\beta_A e(\eta(x + 1) - \eta(x))/2], & \text{if } x = 2M \\ & \exp[\beta_B e(\eta(x) - \eta(x + 1))/2], & \text{if } x = M \\ & 1, & \text{otherwise.} \end{aligned} \quad (2.1)$$

The number of particles is conserved in the evolution and the β_A and β_B are the only (other) parameters in the model. In words, the particles jump to nearest neighbour cells but remain on the same energy level (no effective scattering in the bulk). In the left and right end cells, particles undergo thermal transitions; they can change energy level at inverse temperatures β_A and β_B , respectively. The system is thus at its both ends in contact with a heat reservoir and one expects a heat current flowing whenever they have unequal temperatures.

The model satisfies the condition of detailed balance when left and right $\beta_A = \beta_B = \beta$: for each function F of the total particle number, the probability

$$\rho_\beta(\eta) = \frac{1}{Z} F\left(\sum_{x=1}^{2M} \eta(x)\right) \exp\left[-\beta e \sum_{x=1}^M \eta(x)\right], \quad \eta \in K$$

is stationary and reversible for the dynamics. These equilibrium weights are completely determined by the number of particles $\sum_{x=1}^M \eta(x)$ in the upper energy level. In order to make our calculations possible we make the use of the equivalence of ensembles to express the single site marginal in terms of chemical potentials. In equilibrium, the grand-canonical set-up is made by attaching particle reservoirs with chemical potential $\mu_A = \mu_B = \mu$ to the left and right side of the system. For this set-up, we now make the choice $F(n) = \exp[\beta\mu n]$; ρ_β is a homogeneous product measure with single site marginal

$$n_\beta(x) \equiv \text{Prob}_{\rho_\beta}[\eta(x) = 1] = \frac{1}{\exp[\beta(e(x) - \mu)] + 1} \quad (2.2)$$

where $e(x) = 0$ or e depending on whether the x is ‘down’ $M + 1 \leq x \leq 2M$ or ‘up’ $1 \leq x \leq M$ in the energy cell.

If the reservoir temperatures are unequal, when $\beta_A \neq \beta_B$, there is no explicit expression for the stationary measures but we do know the density profile $n(x) \equiv \text{Prob}_\rho[\eta(x) = 1]$ in a stationary measure ρ . In the bulk and because of the symmetric exclusion rule, there is a linear density profile in both the upper and the lower energy layers:

$$\begin{aligned} n(x) &= n_u^A + \frac{x-1}{M-1} [n_u^B - n_u^A], & 1 \leq x \leq M \\ n(x) &= n_d^A + \frac{2M-x}{M-1} [n_d^B - n_d^A], & M+1 \leq x \leq 2M \end{aligned}$$

but the density in each cell (containing the couple $(x, 2M + 1 - x)$, $1 \leq x \leq M$) is constant for a canonical system due to particle conservation: $n(x) + n(2M + 1 - x) = n_u^B + n_d^B = n_u^A + n_d^A$. In the steady state, there is no particle current between cells but there may be a heat current.

On the upper energy layer particles transport an energy equal to e ; giving rise to a steady energy current, taken negative in the x -direction since we will heat up side B , equal to

$$\langle J_Q \rangle = e \frac{n_u^B - n_u^A}{M - 1}. \quad (2.3)$$

Remember that n_u^A and n_u^B are steady densities (left and right on the upper energy layer depending on M , β_A and β_B). On the other hand, as $M \uparrow +\infty$ (very long wire) these densities tend to their respective equilibrium values as, for example, from (2.2)

$$n_u^A \rightarrow \frac{1}{\exp(\beta_A[e - \mu_A]) + 1}, \quad n_u^B \rightarrow \frac{1}{\exp(\beta_B[e - \mu_B]) + 1}. \quad (2.4)$$

That is an application of convergence results for a sequence of Markov processes, see, e.g., chapter 4.9 in [6]. It should be emphasized that μ_A and μ_B are a function of β_A and β_B , respectively, and of course as well of the particle density. An expression for μ_A and μ_B may be derived by solving the following identity:

$$\rho = \frac{1}{2}(n_u^B + n_d^B) = \frac{\frac{1}{2}}{\exp(\beta_B[e - \mu_B]) + 1} + \frac{\frac{1}{2}}{\exp(\beta_B[-\mu_B]) + 1}.$$

Naturally the identity for side A is similar.

As a result of (2.4), the heat current (2.3) satisfies the stationary Fourier law with

$$0 < \kappa \equiv \lim_M M \langle J_Q \rangle < +\infty. \quad (2.5)$$

Writing out the right-hand side of (2.3) with the substitution (2.4) for $\beta_A = 1/T$ and $\beta_B = 1/(T + \epsilon)$, we get a heat conductivity equal to

$$\lambda \equiv \lim_{\epsilon \rightarrow 0} \frac{\kappa T}{\epsilon} = \mu^2 H(0) + (\mu - e)^2 H(e) + \frac{(\mu H(0) + (\mu - e)H(e))^2}{H(0) + H(e)}$$

with $H(e) = 1/4 \cosh^2(\beta(\mu - e))$. The last term is the contribution due to the canonical ensemble whereas the first two terms would also occur in a derivation for a grand-canonical set-up.

We conclude that this toy model already shows electronic heat conductivity in a clear and simple way.

The next section extends the model by allowing multiple *upper* and *lower* energy levels and by interpreting the *upper* and *lower* levels as characterizing two different but connected metal wires, see figure 2. Again at the two junctions there may be different temperatures and we will also consider the case where electric power is applied.

3. The general model

3.1. Physical input

Metals are excellent conductors of both heat and electricity. Already the empirical law of Wiedemann and Franz (1835) relating thermal and electrical conductivities, points to the electrons as heat carriers. While say for the specific heat of a metal at room temperature there is no observable electronic contribution, for nonequilibrium purposes mostly electrons are responsible for heat and charge transport. As the electron mass is small, even at room temperatures and for typical metallic electron densities, the Maxwell–Boltzmann and Fermi–Dirac distributions are very different. Therefore, the Pauli exclusion principle must play a role and the quantization into energy levels, even if only near the Fermi energy, must be part of any physical model of transport in metals.

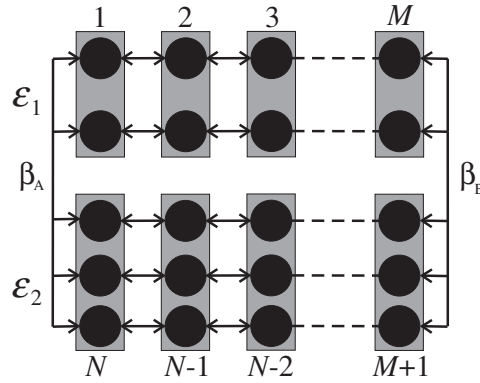


Figure 2. Generalized set-up.

On the other hand, a fully quantum mechanical and microscopic treatment of transport problems is typically out of reach. We have here a system with extremely many degrees of freedom and one usually finds refuge in perturbation theory. The electrons are moving almost independently but subject to (weak) interactions with phonons, impurities and imperfections. When the average time between collisions multiplied with the Fermi energy is larger than Planck's constant (as is the case in metals), Fermi's golden rule can be applied to the transition probabilities between electronic states and in ways similar to that for the Boltzmann equation, one obtains a master equation.

The resulting model that we take up in the present paper is mesoscopic (only electrons moving on a lattice) and while it is thus physically motivated from time-dependent perturbation theory for quantum mechanical processes, it fits perfectly well in the classical theory of interacting particle systems.

One imagines two wires connected at their ends. The wires (long thin bars) consist of a large array of cells, discrete lattice points, at which are located a finite number of energy levels. Free electrons are hopping between nearest-neighbour cells, subject to an exclusion rule and with transition rates that are specified via a local detailed balance condition.

We start by introducing the general set-up. The simplest version was already in the previous section and other simplifications follow later, see section 3.6.

3.2. State space

Consider a ring of N points or cells. The situation one should keep in mind is that of connecting two different wires, the first of length M , the second of length $N - M$. To each cell in the first wire, $1 \leq k \leq M$, is assigned a set \mathcal{E}_1 of $n_1 \geq 1$ energy levels, and to each cell in the second wire, $M + 1 \leq k \leq N$, is assigned a set \mathcal{E}_2 of $n_2 \geq 1$ energy levels. The set of energy levels at cell k is in general denoted by \mathcal{E}_k but it should be understood that it equals \mathcal{E}_1 if $k \in \{1, \dots, M\}$ and that $\mathcal{E}_k = \mathcal{E}_2$ for $k \in \{M + 1, \dots, N\}$. A general element of \mathcal{E}_k is written as e, e', \dots . These are the electronic states (we ignore spin). There can be at most one particle per energy level and we write $x = (k, e)$, $\eta(x) = \eta(k, e) \in \{0, 1\}$ for $e \in \mathcal{E}_k$. The total configuration space is thus $K = \times_{k=1}^M \{0, 1\}^{n_1} \times_{k=M+1}^N \{0, 1\}^{n_2}$ and its elements are denoted by η, ξ, \dots

3.3. Transitions

In each of the two wires particles can hop within the same energy level to nearest-neighbour cells. That is subject to the exclusion rule and possibly biased in one direction via some

external field. We write $E_k \geq 0$ for the electric field over the bond $(k, k+1)$. One can think of a gradient in chemical potential which is locally installed but the details of the ‘battery’ will be of no concern here. One imagines that the two wires are in a heat bath at inverse temperature β (Boltzman’s constant k_B is set equal to 1) except possibly for the junction $(M, M+1)$ which is kept at a different temperature.

Fixing $k = 1, 2, \dots, M-1, M+1, \dots, N-1$ for the ‘bulk’ bonds $(k, k+1)$, the exchange operator associated with energy level $e \in \mathcal{E}_k$ is

$$\begin{aligned} (V_k^e \eta)(k, e) &= \eta(k+1, e), \\ (V_k^e \eta)(k+1, e) &= \eta(k, e), \\ (V_k^e \eta)(x) &= \eta(x), \quad \text{otherwise} \end{aligned}$$

and such an exchange of occupations $\eta \rightarrow V_k^e \eta$ takes place at rate $\exp[\beta E_k (\eta(k, e) - \eta(k+1, e))/2]$. At the junctions, $k = M$ or $k = N$, particles can also hop but now to an arbitrary energy level of the other wire. These transitions are described via the exchange operator $T_k^{e, e'}$ for $e \in \mathcal{E}_k, e' \in \mathcal{E}_{k+1}$:

$$\begin{aligned} (T_k^{e, e'} \eta)(k, e) &= \eta(k+1, e'), \\ (T_k^{e, e'} \eta)(k+1, e') &= \eta(k, e), \\ (T_k^{e, e'} \eta)(x) &= \eta(x), \quad \text{otherwise} \end{aligned}$$

and

$$\eta \rightarrow T_k^{e, e'} \eta, \quad \text{at rate} \quad \exp[\beta^k (E_k + e - e') (\eta(k, e) - \eta(k+1, e'))/2]$$

describes a local detailed balance condition. We set $\beta^N = \beta$ and at the other junction $\beta^M = \beta + \Delta$. $\Delta \neq 0$ means that one junction is maintained at a different temperature.

Obviously, the V_k are just a special case of the T_k . An immediate generalization would be to allow transitions with $T_k^{e, e'}$ everywhere, also in the bulk, or to allow on-site thermal exchanges. That would break bulk energy conservation but it would allow to describe thermal exchanges with the environment at all cells, e.g., from scattering. In the same sense, it is no problem to add more junctions (connecting more than two wires). As we have it now, the bath’s role in the bulk is purely as a work reservoir. One could also imagine adding particle reservoirs. By that we mean selecting one or more cells k on which at energy level $e \in \mathcal{E}_k$, we have the transitions

$$\begin{aligned} (A_k^e \eta)(k, e) &= 1 - \eta(k, e), \\ (A_k^e \eta)(x) &= \eta(x), \quad \text{otherwise.} \end{aligned}$$

These break particle conservation: particles flow in or out with rates

$$\eta \rightarrow A_k^e \eta, \quad \text{at rate} \quad a_k \exp[\beta(e - \mu_k)(\eta(k, e) - \frac{1}{2})] \quad (3.1)$$

where μ_k is the chemical potential. We will not deal with these generalizations more explicitly. It is possible to include them but soon the notation starts to get heavy. Let it be clear however that in no way do we need to introduce a temperature or chemical potential associated with the *internal* local conditions of the cells in the wire. Such *close to equilibrium* conditions are mostly present in phenomenological treatments of thermoelectric effect.

3.4. Dynamics

We consider a continuous time Markov process on \mathcal{K} consisting of the two types of elementary transitions $T_k^{e, e'}$ and V_k^e introduced above. For fixed sets of energy levels \mathcal{E}_k and spatial

extensions M and N , the remaining parameters are E_k (electric field at bond $(k, k + 1)$), β and Δ (inverse temperatures).

For $E_k > 0$ work is being done on the system and the particles jump preferentially forward, i.e., in the direction $k \rightarrow k + 1$. Energy is not (necessarily) preserved in the transition $T_k^{e,e'}$ but the total number of particles is conserved (at least when the $a_k = 0$ in (3.1), which we will assume hereafter).

The backward generator L of the Markov process is a sum

$$L = \sum_{k \neq M, N} L_k + L_M + L_N \tag{3.2}$$

with

$$L_k f(\eta) = \sum_{e \in \mathcal{E}_k} \exp[\beta E_k (\eta(k, e) - \eta(k + 1, e)) / 2] [f(V_k^e \eta) - f(\eta)]$$

$$L_N f(\eta) = \sum_{e \in \mathcal{E}_N, e' \in \mathcal{E}_1} \exp[\beta (E_N + e - e') (\eta(N, e) - \eta(1, e')) / 2] [f(T_N^{e,e'} \eta) - f(\eta)]$$

and

$$L_M f(\eta) = \sum_{e \in \mathcal{E}_M, e' \in \mathcal{E}_{M+1}} \exp[(\beta + \Delta) (E_M + e - e') (\eta(M, e) - \eta(M + 1, e')) / 2] \times [f(T_M^{e,e'} \eta) - f(\eta)].$$

Denoting the general rate as $r(\eta, \eta')$ (of course depending on all possible parameters), we have

$$L f(\eta) = \sum_{\eta'} r(\eta, \eta') [f(\eta') - f(\eta)] \tag{3.3}$$

summarizing (3.2); the master equation for the probabilities at time t is as usual

$$\frac{d}{dt} \text{Prob}_t(\eta) = \sum_{\eta'} [r(\eta', \eta) \text{Prob}_t(\eta') - r(\eta, \eta') \text{Prob}_t(\eta)].$$

For every initial configuration η_0 the above defines the process $\eta_t, t \geq 0$.

We are interested in a stationary regime for fixed (but imagined very large) spatial extensions M and N . Let ρ denote a stationary measure for the above Markov process. It could depend, for example, on the particle density.

We write P_ρ^τ for the stationary process over the time interval $[0, \tau]$; $\omega = (\eta_t)_{t=0}^\tau$ is a path as sampled from P_ρ^τ . We will assume that there is a finite positive constant C with

$$\frac{1}{C} \leq \frac{\rho(\eta')}{\rho(\eta)} \leq C \tag{3.4}$$

for each pair η, η' that can be connected via the transitions outlined above.

In general, we know very little about this stationary process; under equilibrium conditions we can make it more explicit.

3.5. Equilibrium

The system is in equilibrium when $\Delta = 0$ and all $E_k = 0$. Consider the probability measure $\rho_{\beta,\mu}$ defined as

$$\rho_{\beta,\mu}(\eta) = \frac{1}{Z} \exp\left(\beta\mu \sum_x \eta(x)\right) \exp\left[-\beta \sum_{k=1}^N \sum_{e \in \mathcal{E}_k} e \eta(k, e)\right]. \tag{3.5}$$

That is a product measure but it is not (in general) homogeneous. It is a stationary reversible measure for the equilibrium dynamics. Its single cell marginal is given by the Fermi–Dirac distribution, for $e \in \mathcal{E}_k$,

$$\rho_{\beta,\mu}(\eta(k, e) = 1) = \frac{1}{e^{\beta(e-\mu)} + 1}. \quad (3.6)$$

That corresponds to the grand canonical set-up. Except when we add sources and sinks for the particles ($a_k \neq 0$), the total number of particles is conserved in the dynamics as defined above.

Being in steady equilibrium implies ignoring the difference between thermodynamic past and future and on average there is no net transport nor dissipation.

3.6. Simplification

The simplest version is obtained by taking $\mathcal{E}^1 = \{e_1\}$ and $\mathcal{E}^2 = \{e_2\}$ singletons. There is then one energy level per cell, $n_1 = n_2 = 1$, and we may just as well put $e_2 - e_1 = e$. We also put $a_k = 0 = E_k$ for all k (canonical set-up without external field). In the bulk of each of the wires we now only have symmetric hopping and at the two ends of the wires (we are now talking about the bonds $(M, M+1)$ and $(N, 1)$), there are thermal transitions:

$$\eta \rightarrow T_M \eta, \quad \text{at rate} \quad \exp[(\beta + \Delta)e(\eta(M) - \eta(M+1))/2]$$

through which the occupations are exchanged over the bond $(M, M+1)$ and

$$\eta \rightarrow T_N \eta, \quad \text{at rate} \quad \exp[-\beta e(\eta(N) - \eta(1))/2]$$

through which occupations are exchanged over the bond $(N, 1)$. We see that it formally corresponds to the toy model for heat transport of section 2 with $2M = N$ and $\beta_A = \beta$, $\beta_B = \beta + \Delta$ at the junctions. In that way, the model system of section 2 has two possible physical interpretations, one as consisting of M cells each with two energy levels, the other as a couple of two wires each of length M and each with one energy level per cell. In that last interpretation, the heat current in Fourier's law (defined in (2.3)) is in fact a particle current through the *upper* wire, caused by the different temperatures $\beta_A \neq \beta_B$ at the junctions and so provides the simplest illustration of a Seebeck effect. To see the Peltier effect, we take $\Delta = 0$ (equal bath temperatures) but some $E_k > 0$. A particle current arises through the ring and energy of magnitude e gets dissipated at the junctions.

4. Currents and dissipation

4.1. Local particle and heat currents

The basic physical quantities in the phenomenon are energy and particle number. The electric or particle current consists of particles hopping to nearest-neighbour sites. We fix a path $\omega = (\eta_0, \dots, \eta_\tau)$ in which each change (at a random time) corresponds to one of the transitions described in section 3.3.

The net particle current (integrated over a time-interval $[0, \tau]$) from energy level e at cell k to energy level e' at cell $k+1$ equals

$$J^k(e, e')(\omega) \equiv \sum_t [\eta_t(k, e) - \eta_t(k+1, e')] \quad (4.1)$$

for $e \in \mathcal{E}_k, e' \in \mathcal{E}_{k+1}$. The sum in the right-hand side of (4.1) is over all jump times t ; the moments at which the trajectory ω changes states. Here and in what follows, all times in the sums are $t = t^-$, right before the jump. So (4.1) is a sum of +1's and -1's according to

whether the particle jumps from (k, e) to $(k + 1, e')$ or oppositely; the jump is counted at the time of the transition. When the bond $(k, k + 1)$ is in the bulk of the wires ($k \neq M, N$), then only transitions between levels of the same energy are possible and the net number of particles jumping forward equals

$$J^k(e, e)(\omega) = J^{e,k}(\omega) \equiv \sum_t [\eta_t(k, e) - \eta_t(k + 1, e)].$$

We call

$$J_E^k \equiv \sum_{e \in \mathcal{E}_k, e' \in \mathcal{E}_{k+1}} J^k(e, e') \quad (4.2)$$

the variable electric current over the bond $(k, k + 1)$.

Secondly, energy is transported. Over the bond $(k, k + 1)$ in the bulk the time-integrated energy current equals

$$J_H^k \equiv \sum_{e \in \mathcal{E}_k} e J^{k,e}.$$

At each junction $k = M, N$, there is a local heat exchange with the environment, commonly called the Peltier heat (counted positive for a heat transfer *into* the environment), here variable and equal to

$$J_P^k \equiv \sum_{e \in \mathcal{E}_k, e' \in \mathcal{E}_{k+1}} (e - e') J^k(e, e').$$

4.2. Conservation laws

In a configuration η ,

$$U_k(\eta) \equiv \sum_{e \in \mathcal{E}_k} e \eta(k, e), \quad N_k(\eta) \equiv \sum_{e \in \mathcal{E}_k} \eta(k, e)$$

are the energy and the particle number at cell k , respectively. These change. We fix again a trajectory $\omega = (\eta_0, \dots, \eta_\tau)$. For $k - 1, k \neq M, N$

$$U_k(\eta_\tau) - U_k(\eta_0) = J_H^{k-1}(\omega) - J_H^k(\omega). \quad (4.3)$$

At the junctions $k = M, N$,

$$U_k(\eta_\tau) + U_{k+1}(\eta_\tau) - U_k(\eta_0) - U_{k+1}(\eta_0) = J_H^{k-1}(\omega) - J_H^{k+1}(\omega) - J_P^k(\omega). \quad (4.4)$$

Similar relations hold for particle conservation. In particular,

$$N_k(\eta_\tau) - N_k(\eta_0) = J_E^{k-1} - J_E^k. \quad (4.5)$$

As a consequence, the steady-state average defines the particle current

$$J_E \equiv \langle J_E^k \rangle$$

independent of k .

In the steady state (4.4) can be rewritten as

$$\langle J_H^{k-1} \rangle = \langle J_P^k \rangle + \langle J_H^{k+1} \rangle$$

with, from (4.3), $\langle J_H^k \rangle = J_1$ constant for $k = 1, \dots, M - 1$ and $\langle J_H^k \rangle = J_2$ constant for $k = M + 1, \dots, N - 1$. Therefore, denoting the Peltier heat at junction $(M, M + 1)$ with $J_B \equiv \langle J_P^M \rangle$ and at junction $(N, 1)$ with $J_A \equiv \langle J_P^N \rangle$, we have

$$J_1 = J_B + J_2, \quad J_A + J_B = 0. \quad (4.6)$$

4.3. Heat dissipation

The first law of thermodynamics

$$dU = -dQ + dW \quad (4.7)$$

with dQ the dissipated heat and dW the work done on the system can be applied to our model by identifying the proper currents. The total energy of the system

$$U = \sum_{k=1}^N U_k$$

is not globally conserved, see (4.4). The Joule heat is the (electrical) work done

$$W_k \equiv E_k J_E^k$$

over the bond $(k, k + 1)$. As a result, for a path $\omega = (\eta_0, \dots, \eta_\tau)$ the variable dissipated heat over a time interval $[0, \tau]$ is

$$Q(\omega) \equiv \sum_{k=1}^N E_k J_E^k(\omega) + \sum_{k=M,N} J_P^k(\omega).$$

Since each bond $(k, k + 1)$ is assumed attached to a large heat bath, we get that as a function of the system's history the total change of entropy in the environment equals

$$S(\omega) \equiv \sum_{k=1}^N \beta E_k J_E^k(\omega) + \beta J_P^N(\omega) + (\beta + \Delta) J_P^M. \quad (4.8)$$

5. Entropy production

5.1. Driving forces and mean entropy production rate

There are in fact two driving sources of nonequilibrium: one is the temperature gradient and the other is the electric field. The temperature gradient is installed by putting different temperatures at the junctions. The electric field models the presence of an external electric field or more simply, of a battery and the installation of an electric potential.

In steady-state average, the steady entropy current equals the mean entropy production

$$\langle S \rangle = \beta \sum_k E_k \langle J_E^k \rangle + (\beta + \Delta) J_B + \beta J_A \quad (5.1)$$

as obtained from (4.8). Writing

$$\beta \equiv \frac{1}{N} \sum_k E_k, \quad \nabla T \equiv \frac{1}{N} \left(\frac{1}{\beta + \Delta} - \frac{1}{\beta} \right) \quad (5.2)$$

and using the conservation law (4.6), we have

$$\frac{1}{N} \langle S \rangle = \beta [\beta J_E - \nabla T J_S] \quad (5.3)$$

for the entropy source strength per unit length of the wire. The driving forces are clearly visible: β is the gradient of electric potential and ∇T is the temperature gradient. $J_S \equiv (\beta + \Delta) J_B$ is the entropy flux into the reservoir controlling the junction at inverse temperature $\beta + \Delta$.

The mean entropy production rate σ over a time interval $[0, \tau]$ is defined as

$$\sigma_\tau \equiv \sigma \equiv \frac{1}{\tau} \int S(\omega) dP_\rho^\tau(\omega) = \frac{1}{\tau} \langle S \rangle \quad (5.4)$$

and can of course be rewritten from (5.3). We have the fundamental result that it is positive: when not in equilibrium $\sigma > 0$. That can be seen as follows. We compute

$$R \equiv \log \frac{dP_\rho^\tau}{dP_\rho^\tau \Theta} \quad (5.5)$$

where Θ is the dynamical time reversal: $\Theta\omega = (\eta_{\tau-t})_{t=0}^\tau$. Then, by construction,

$$\int dP_\rho^\tau(\omega) e^{-R(\omega)} = 1$$

and hence,

$$\int dP_\rho^\tau(\omega) R(\omega) \geq 0 \quad (5.6)$$

and is non-zero whenever $R(\omega)$ is not constant (with, P_ρ^τ , probability one). The hypothesis ‘not in equilibrium’ refers exactly to that breaking of time-reversal invariance. The computation of R is an application of the Girsanov formula for Markov jump processes, see, e.g., the appendix in [4]. It is easy to check from section 3.4 that

$$R(\omega) = S(\omega) - \log \rho(\eta_\tau) + \log \rho(\eta_0) \quad (5.7)$$

and hence the steady-state expectations of R and of S coincide. As a result, (5.6) implies the positivity of (5.4).

5.2. Fluctuations

Consider again (4.8):

$$S = S(E, \Delta) \equiv S_0 + \sum_k E_k J_E^k + \Delta J_P^M, \quad S_0 \equiv \beta(J_P^N + J_P^M). \quad (5.8)$$

In equilibrium $E_k = \Delta = 0$ and always $\langle S_0 \rangle = 0$. The dissipation (5.8) is a fluctuating quantity and we can consider its generating function

$$F_\tau(z) \equiv \langle e^{-zS} \rangle.$$

Clearly $S\Theta = -S$ so that by combining (5.5) and (5.7), we get

$$F_\tau(z) = \int \exp(-(1-z)S(\omega)) \frac{\rho(\eta_\tau)}{\rho(\eta_0)} dP_\rho^\tau(\omega).$$

From assumption (3.4) and for real z that implies the fluctuation symmetry

$$p(z) = p(1-z), \quad p(z) \equiv - \lim_{\tau \rightarrow +\infty} \frac{1}{\tau} \log F_\tau(z). \quad (5.9)$$

We can however look in somewhat greater detail to the fluctuations as they arise from the local currents.

Given numbers $\gamma^k(e, e')$, we write

$$\vec{\gamma} \cdot \vec{J} \equiv \sum_{k=1}^N \sum_{e \in \mathcal{E}_k, e' \in \mathcal{E}_{k+1}} \gamma^k(e, e') J^k(e, e').$$

For example, with $\gamma^k(e, e') = \varphi^k(e, e') \equiv E_k + (e - e')\beta^k$, $\vec{\varphi} \cdot \vec{J} = S$ the entropy current. If we take $\gamma^k(e, e') = \varphi_0^k(e, e') \equiv (e - e')\beta$, then $\vec{\varphi}_0 \cdot \vec{J} = S_0$ the equilibrium value defined in (5.8).

Consider now the following generating function for the fluctuations of the currents

$$p(\vec{\gamma}, \vec{\varphi}) \equiv - \lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \left[\int dP_\rho^\tau(\omega) e^{-\vec{\gamma} \cdot \vec{J}(\omega)} \right]. \quad (5.10)$$

The second argument of p (the dependence on $\vec{\varphi}$) comes of course from the dependence of the steady-state law $= dP_\rho^\tau$ on the driving parameters. The limit exists for the relevant choices of $(\gamma^k(e - e'))$ via an application of the Perron–Frobenius theorem, see, e.g., [8]. Moreover,

$$p(\vec{\gamma}, \vec{\varphi}) = p(\vec{\varphi} - \vec{\varphi}_0 - \vec{\gamma}, \vec{\varphi}). \quad (5.11)$$

To see it, we start again from the definition (5.5) for R and observe that for all functions f ,

$$\int dP_\rho^\tau(\omega) f(\Theta\omega) = \int dP_\rho^\tau(\omega) e^{-R(\omega)} f(\omega). \quad (5.12)$$

We substitute $f = \exp \vec{\gamma} \cdot \vec{J}$ and use first that $J^k(e, e')(\Theta\omega) = -J^k(e, e')(\omega)$, the antisymmetry under time reversal of the variable currents. On the other hand, $R = S - \log \rho(\eta_\tau) + \log \rho(\eta_0)$ with

$$S = (\vec{\varphi} - \vec{\varphi}_0) \cdot \vec{J} + S_0$$

given in (4.8) or in (5.8) where, as follows from (4.3) and (4.4), the equilibrium value

$$S_0(\omega) = \vec{\varphi}_0 \cdot \vec{J}(\omega) = \beta[U(\eta_\tau) - U(\eta_0)]$$

equals the total change of energy.

For that choice of f

$$C \int dP_\rho^\tau \exp(-(\vec{\varphi} - \vec{\varphi}_0) \cdot \vec{J}) f \leq \int dP_\rho^\tau e^{-R} f \leq \frac{1}{C} \int dP_\rho^\tau \exp(-(\vec{\varphi} - \vec{\varphi}_0) \cdot \vec{J}) f \quad (5.13)$$

where we used again (3.4). We conclude that after taking the logarithm and dividing by $\tau \uparrow +\infty$, R can be substituted with $(\vec{\varphi} - \vec{\varphi}_0) \cdot \vec{J}$ in (5.12) and the identity (5.11) follows immediately.

6. Linear response regime

6.1. Green–Kubo relations

The steady state average will from now on be decorated by the field $\vec{\varphi}$ to indicate its dependence on the driving: $\langle \cdot \rangle = \langle \cdot \rangle_{\vec{\varphi}}$. For the equilibrium values $\vec{\varphi}_0$, we write $\langle \cdot \rangle_{\vec{\varphi}_0} = \langle \cdot \rangle_0$. A general couple of energy values $e \in \mathcal{E}_k$, $e' \in \mathcal{E}_{k+1}$ is denoted by $\alpha = (e, e')$, $J^k(e, e') = J_\alpha^k$, $\varphi^k(e, e') = \varphi^k(\alpha)$. In particular, for all α and k ,

$$\langle J_\alpha^k \rangle_0 = 0$$

is the zeroth-order contribution to the steady currents. The Green–Kubo relations want to give details about the linear order in $\vec{\varphi}$ around $\vec{\varphi}_0$:

$$\langle J_\alpha^k \rangle_{\vec{\varphi}} = \sum_{\delta, \ell} L_{\alpha, k; \delta, \ell} (\varphi^\ell(\delta) - \varphi_0^\ell(\delta))$$

up to higher order terms, with

$$L_{\alpha, k; \delta, \ell} \equiv \frac{\partial}{\partial \varphi^\ell(\delta)} \langle J_\alpha^k \rangle_{\vec{\varphi}=\vec{\varphi}_0} \quad (6.1)$$

linear transport coefficients.

The following Green–Kubo relation follows directly from (5.11):

$$L_{\alpha, k; \delta, \ell} = \frac{1}{2} \lim_{\tau \uparrow +\infty} \frac{1}{\tau} \langle J_\alpha^k J_\delta^\ell \rangle_0 \quad (6.2)$$

where one should remember that the currents J_α^k are extensive in τ . Deriving (6.2) proceeds by differentiating the left- and right-hand sides of (5.11). With the notation

$$C_\alpha^k g(\vec{\gamma}, \vec{\varphi}) \equiv \frac{\partial}{\partial \gamma_\alpha^k} g(\vec{\gamma}, \vec{\varphi}) \quad (6.3)$$

$$D_\alpha^k g(\vec{\gamma}, \vec{\varphi}) \equiv \frac{\partial}{\partial \varphi^k(\alpha)} g(\vec{\gamma}, \vec{\varphi}) \quad (6.4)$$

and under the condition that the function p in (5.10) is smooth, we have in fact

$$D_\delta^\ell C_\alpha^k p(0, 0) = -\frac{1}{2} C_\delta^\ell C_\alpha^k p(0, 0) \quad (6.5)$$

which implies (6.2). The reasoning above is a detailed reproduction of what was observed before, e.g., in [7–9], to derive fluctuation–dissipation relations from the fluctuation symmetry (5.11). One observes that the Green–Kubo relations (6.2) immediately imply the Onsager reciprocity

$$L_{\alpha,k;\delta,\ell} = L_{\delta,\ell;\alpha,k}. \quad (6.6)$$

6.2. Reproducing the phenomenological behaviour

The above Green–Kubo relations (6.2) are the most detailed forms of linear response relations. We connect them now with the standard experimental set-up for the situation of the different thermoelectric effects.

The basic equation is (5.3). Though we did not start from a balance equation for the ‘close to equilibrium entropy of the system’, (5.3) reproduces exactly equation (61) in chapter XIII of [2]. The next thing is to linearize the currents J_S and J_E around $\nabla T = \beta = 0$. For that we have the Green–Kubo relations. We can indeed either work from the previous section or, more directly, use (5.12) which says that

$$\langle J \rangle = \frac{1}{2} \langle J(1 - e^{-R}) \rangle \quad (6.7)$$

for functions J that are antisymmetric under time reversal, $J\Theta = -J$, like currents.

We specify to the case where just one of the bonds, pick $(k, k + 1)$, carries an electric field $E_k = EN$ (proportional to the length of the wire), all others being exactly zero. That corresponds to the situation where locally in the wire some external electric power is applied to particles that do not interact besides exclusion. This may seem unrealistic but it keeps things manageable and we expect the results to be equivalent to a more realistic description. We then have, up to linear order in E and Δ ,

$$\lim_{\tau} \frac{1}{\tau} J_S = \lim_{\tau} \frac{1}{\tau} \left[\frac{\beta(\beta + \Delta)EN}{2} \langle J_P^M J_E^k \rangle_0 + \frac{\Delta(\beta + \Delta)}{2} \langle (J_P^M)^2 \rangle_0 \right]. \quad (6.8)$$

Rewriting that for $j_s \equiv \lim_{\tau} J_S/N\tau$ (per unit length and per unit time)

$$j_s = -L_{11}\nabla T + L_{12}E \quad (6.9)$$

with

$$L_{11} \equiv \frac{\beta}{2} \lim_{\tau} \frac{1}{\tau} \langle (J_P^M)^2 \rangle_0, \quad L_{12} \equiv \frac{\beta(\beta + \Delta)}{2} \lim_{\tau} \frac{1}{\tau} \langle J_P^M J_E^k \rangle_0. \quad (6.10)$$

In the same way,

$$\lim_{\tau} \frac{1}{\tau} J_E = \lim_{\tau} \frac{1}{\tau} \left[\frac{\beta EN}{2} \langle (J_E^k)^2 \rangle_0 + \frac{\Delta}{2} \langle J_E^k J_P^M \rangle_0 \right] \quad (6.11)$$

so that for $j_E \equiv \lim_{\tau} J_E / N\tau$,

$$j_E = -L_{21}\nabla T + L_{22}E \quad (6.12)$$

with

$$L_{22} \equiv \frac{\beta}{2} \lim_{\tau} \frac{1}{\tau} \langle (J_E^k)^2 \rangle_0, \quad L_{21} \equiv \frac{\beta(\beta + \Delta)}{2} \lim_{\tau} \frac{1}{\tau} \langle J_P^M J_E^k \rangle_0. \quad (6.13)$$

The Onsager relation $L_{12} = L_{21}$ is apparent and hence, if we write the standard form

$$j_S = -\lambda\beta\nabla T + \pi\beta j_E, \quad E = -v\nabla T + Rj_E \quad (6.14)$$

we get $\lambda\beta \equiv L_{11} - L_{21}L_{12}/L_{22}$ for heat conductivity λ , $R \equiv 1/L_{22}$ is a resistivity, and the coefficients $\pi\beta \equiv L_{12}/L_{22}$ and $v = -L_{21}/L_{22}$ verify the second Thomson relation

$$v = -\pi\beta.$$

The coefficient v is called the differential thermoelectric power and $\pi\beta$ is the entropy current per electric current when temperatures are equal, see [2].

6.2.1. Seebeck effect. That is the effect of so-called thermoelectric power that can be measured via a thermocouple. We have two different metals with junctions at temperatures T and $T + \epsilon$ in two heat reservoirs. The point is that the temperature difference $\epsilon \neq 0$ generates by itself an electromotive force. In other words, we can counterbalance by a non-zero electric field E and still have zero electric current. It can be measured in various ways, either by inserting condenser plates in one of the metals and seeing a potential difference or by inserting a battery in one of the metals and measure the voltage necessary to cancel the electric current.

The simplest realization in our model is again the one of section 2. Instead of thinking of one wire (with M cells each consisting of two energy levels) we can think of two different wires (each with M cells containing one energy level). What we have called the energy current in (2.3) now becomes the electric or particle current. We have $\beta_A = \beta$, $\beta_B = \beta + \Delta$. We insert an electric field of strength NE at the bond $(N, 1)$ (the B junction). The differential thermoelectric power or Seebeck coefficient can now be computed by first solving for E the equation

$$NE\beta_B + \beta_B e = \beta e \quad (6.15)$$

which cancels the particle current and then putting $v = -E/\nabla T$, cf (6.14). One easily finds that now

$$v = -e\beta. \quad (6.16)$$

6.2.2. Peltier effect. The Peltier effect is the production/absorption of heat at the junctions by the presence of an electric current across. Even without establishing a temperature difference, one generates a heat flow. The electric current is generated by an electric field or by an established electro-chemical gradient. To say it differently, to maintain a uniform and constant temperature throughout the system, absorption of heat from the reservoir is necessary. That is the Peltier effect used, for example, to cool an external device.

Let us again look at the toy model described in section 2. By definition, $\pi\beta$ is the isothermal entropy flux per unit electric current. Since the energy dissipation into the reservoir at inverse temperature β equals e , we get $\pi\beta = e\beta$. Comparing with (6.16), we see again $\pi\beta = -v$, the second Thomson relation.

In the general model particle current and heat current are not proportional and there is no simple analogue to (6.15). Fortunately, the Onsager relation gives $v = -\pi\beta$ automatically.

7. Beyond linear order, final remarks

Despite their general appearance, fluctuation relations like (5.9), (5.11) or (6.7) are not sufficient to build a systematic perturbation theory for the physical currents beyond linear order. The reason is that, for say the second-order term in a current, we need to know the linear order for a time-symmetric observable (the square of the current) and that information is absent from the fluctuation relations. There are however alternatives. Instead of going through general procedures, we outline here how for the model at hand one can compute higher order corrections to (6.9) and (6.12). The more systematic expansion will be the part of another manuscript.

As is clear from section 4, all steady-state averages of the form $\langle J \rangle$ (where J is some current) can be computed from the steady-state average of the particle current $J^{e,k}$ over a bond $(k, k + 1)$ in the bulk. That is directly clear from (4.5) for the electric current $J = J_E^k$ but it also includes $J = J_P^M$ the Peltier current as we can see from (4.4). We thus only need to consider one bond $(k, k + 1)$ and one energy level $e \in \mathcal{E}_k$ and estimate

$$\langle J^{e,k} \rangle.$$

We consider the case where we take a symmetric exclusion hopping process in the bulk of each line, i.e., $E_k = 0$ for $k \neq M, N$. Due to the symmetric exclusion the occupation profile on energy level e is linear and the steady-state particle current on that level is exactly given by the difference between the corresponding occupations at the two junctions in the same sense as (2.3). More precisely, for $k = 1, \dots, M - 1$

$$\langle J^{e,k} \rangle = \frac{\text{Prob}[\eta(e, 1) = 1] - \text{Prob}[\eta(e, M) = 1]}{M - 1}$$

and similarly for the other bulk bonds. Hence, all boils down to getting an expression for the occupations

$$\text{Prob}[\eta(e, k) = 1], \quad e \in \mathcal{E}_k, k = 1, M, M + 1, N.$$

To proceed we can take the same strategy as in (2.3)–(2.5) and suppose that M, N are sufficiently large so that the occupation numbers are given by the Fermi–Dirac equilibrium distributions. The driving parameters are present in these occupations through the different temperatures at the junctions and/or through the shifting of the energy levels by the presence of a local electric field. We do not continue giving the details of the computation but it should be clear that the computation is most pleasant in the grand-canonical ensemble where the occupations and hence all currents can be straightforwardly computed to any given order.

Acknowledgment

We are very grateful to Karel Netočný for initial conception and conversations that started us out on the model.

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