Pulsed thermoelectricity

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A special mechanism of thermoelectric transport is described, consisting of pulses of charge carriers which "fly" periodically through the external circuit from the hot end of the sample to the cold end, with a determined duration of the "on" and "off" times of the electric contacts, while maintaining continuously the thermal contacts. It is shown that such a "resonant" ideal thermogenerator may work cyclically, with the same efficiency quotient as the ideal efficiency quotient of the thermoelectric devices operated in the usual stationary transport regime but the electric flow and power are increased, as a consequence of the concentration of the charge carriers on pulses of small spatial extent. The process is reversible, in the sense that it can be operated either as a thermoelectric generator or as an electrothermal cooler. © *2010 American Institute of Physics.*
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I. INTRODUCTION

It is well known that the classical way of operating the thermoelectric circuits consists of establishing small and continuous temperature and voltage gradients along a thermoelectric sample, while maintaining the local thermodynamic equilibrium. The sample is assumed to be homogeneous on the macroscopic scale, as for a stable thermodynamical phase. The physics and technology of the classical thermoelectricity is described in great detail in reference treatises, textbooks, or handbooks, as those given in Refs. 1–3. The electric flow **j** and heat flow **q**, i.e., the electric charge and, respectively, heat flowing across the unit area of the cross-section per unit time, are given by the basic equations of the thermoelectricity[4]

$$\mathbf{j} = \sigma\mathbf{E} - \sigma Q \, grad T, \tag{1}$$

and

$$\mathbf{q} = \varphi\mathbf{j} + QT\mathbf{j} - K \, grad T, \tag{2}$$

where σ is the electric conductivity, **E** is the external electric field, Q is the thermopower, T is the temperature, φ is the electric potential ($\mathbf{E} = -grad\varphi$), and K denotes the thermoconductivity. The gradient may be specialized to the x-direction, i.e., $grad = \partial/\partial x$. One can see from Eq. (1) that a temperature gradient gives rise to an electric field $\mathbf{E} = -Q \, grad T$, controlled by the Seebeck thermopower coefficient Q; this is the Seebeck effect. By Eq. (2), the continuity of the flows across a junction leads to a released heat $-\Delta Q \cdot T\mathbf{j} = \Pi\mathbf{j} = -\Delta(K \, grad T)$ per unit time and per unit area of the junction, which is the Peltier effect, and $\Pi = -T\Delta Q$ denotes the Peltier coefficient. One can already notice from Eqs. (1) and (2) that high values of Q and σ and low values of K are desirable. Unfortunately, high values of electronic properties like σ and Q are usually related to a high K, which lowers the effectiveness of the thermoelectric devices.

There have been long and sustained efforts along the years to improve upon the performances of the thermoelectric devices. In this respect, a few recent works are given in Refs. 5–8. Particular emphasis is being given to designing of new materials and devices, with high efficiency, engineering functionally graded materials, segmented or cascades devices, or assessing the compatibility of thermoelectric materials.[9–13] Thermoelectric thin films, nanocomposites and nanostructured materials can enhance the efficiency,[14–18] presumably by interface reflection of heat (which may not impede upon the electrical conductivity),[19] or by highly-peaked electron density of states, as in low-dimensional materials.[20–22] The inherent limitations of the classical mode of operating the thermoelectric devices originate in the small, continuous temperature gradient superimposed along the whole length of the sample. This circumstance brings about both small currents and heat flows, on one hand, and may increase appreciably the risk of heat loss through a spatially-extended dissipation, on the other. In particular, the undesired effects of a high thermoconductivity are enhanced by a continuous temperature gradient extending over the whole length of the sample. We put forward here a different mechanism of thermoelectric transport, based on pulses of heat and current, which may circumvent, to some extent, the aforementioned limitations. It leads to high electric pulses "flying" periodically through the external circuit. The objectives of the pulse thermoelectric device are to increase the delivered electric flow and power, by concentrating the charge carriers on pulses of small spatial extent. A former, preliminary, description of this pulsed thermoelectric transport was given in Refs. 23–25. We refer here to some other works, given in Refs. 26–30, which may bear some relevance on the ideas described here.

II. BASIC THEORETICAL INGREDIENTS

Usually, the transport in condensed matter proceeds by quasiparticles.[31] As it is well-known, quasiparticles are elementary excitations possessing velocity (momentum) and a finite lifetime τ. They obey either a Bose–Einstein distribu-

tion, like phonons (with a vanishing chemical potential), or a Fermi distribution, as for electronic quasiparticles of the Fermi liquid in metals, or Boltzmann's distribution, as for the quasiclassical charge carriers (electrons and holes) in typical semiconductors. We adopt here a simple, general picture of this type of entities. For instance, we may assume that the electronic quasiparticles of a Fermi liquid possess the Fermi velocity $\mathbf{v}_F$, while the quasiclassical charge carriers in semiconductors have a mean thermal velocity $\bar{v} = \sqrt{T/m}$, where T is the temperature and m denotes a mean effective mass. It is easy to see (by averaging over the solid angle) that the transport along one direction, say the positive x-direction, proceeds with a mean transport velocity $v = \bar{v}/2$, or, respectively, $v = \bar{v}_F/2$, where $\bar{v}_F$ denotes the average of the Fermi velocity (which may be anisotropic). The mean free path of the quasiparticles can be represented as $\Lambda = v\tau$.

Under these conditions the local change $\partial n/\partial t + v_0 \partial n/\partial x$ in the quasiparticle density $n(x,t)$ at position x and time t, where v_0 is a transport velocity, is given by the local imbalance $(1/2\tau)[n(x+\Lambda,t)+n(x-\Lambda,t)-2n(x,t)]$ in the quasiparticle density,

$$\partial n/\partial t + v_0 \, \partial n/\partial x = (1/2\tau)[n(x+\Lambda,t) + n(x-\Lambda,t)$$
$$- 2n(x,t)] = \frac{1}{2}v\Lambda \partial^2 n/\partial x^2. \qquad (3)$$

This is the well-known diffusion equation. It describes a macroscopic, nonequilibrium transport (in contrast with the local-equilibrium transport), for densities varying slowly over large distances and long times in comparison with the quasiparticle mean free path and, respectively, lifetime. It may also be generalized to an anisotropic spatial transport, and applies also to fluctuations (with the fluctuating time and length instead of quasiparticle lifetime and, respectively, mean free path), describing the approach to equilibrium. In this form, Eq. (3) has been used by Einstein in his classical analysis of the Brownian motion.

For an initial δ-condition $n(x,t=0)=V\delta n \delta(x)$, where V is the original volume of the δ-peak and δn is the quasiparticle density in the δ-peak, Eq. (3) has the well-known Gaussian solution

$$n(x,t) = \frac{V\delta n}{\sqrt{2\pi v\Lambda t}}e^{-(x-v_0 t)^2/2v\Lambda t}. \qquad (4)$$

The Gaussian pulse given by Eq. (4) may move as a whole with the transport velocity v_0, and has a spatial extension

$$l' = \sqrt{v\Lambda t} \qquad (5)$$

(in one direction). This is taken as the pulse length. As one can see, it goes like the square root of the product of velocity by mean free path by the duration, as it well known. $n(x,t)$ flattens gradually on increasing the time, and vanishes in the limit of an infinite duration; in the opposite limit of a very short time the Gaussian pulse reduces to the original δ-pulse, as expected. Indeed, for very short times and distances the diffusion term in Eq. (3) may be neglected, and we are left with the continuity equation whose solution is $V\delta n \delta(x-v_0 t)$ for the original $V\delta n \delta(x)$ peak. The total number of quasiparticles in the Gaussian peak is $V\delta n$, and it may be represented
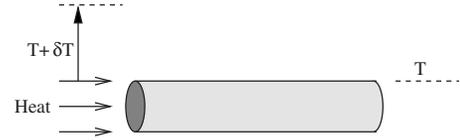

FIG. 1. Heating a thermoelectric sample.

as $2l'\overline{\delta n}$ (for a unit area of the cross-section), where $\overline{\delta n}$ is the average quasiparticle density; on the other hand, the maximum value of the density in the Gaussian peak is $V\delta n/\sqrt{2\pi l'} = \sqrt{2/\pi}\overline{\delta n}$ from Eq. (4), whence one can see that the maximum value of the quasiparticle density is very close (up to a factor of $\sqrt{2/\pi}=0.8$) to the average quasiparticle density. Therefore, one may take, with a good approximation, $V\delta n$ for the total number of quasiparticles in a Gaussian peak, where $V=2l'$ (for unit area of the cross-section) and δn is the maximum value of the quasiparticle density; this is identical with the representation of the δ-pulse, and it holds also for half a Gaussian pulse, of course, where $V=l'$.

III. THERMAL AND CHARGE PULSES

Let a homogeneous conducting sample of length l and uniform cross-section, at temperature T, be uniformly heated at one end, such as to rise locally its temperature by the small amount δT, as shown in Fig. 1. We may neglect the small changes in volume, or pressure, and write $n=f(\mu,T)$ for the concentration n of the quasiparticles at equilibrium, where f is the integral over statistical distributions and μ denotes the chemical potential. As it is well known, for electronic quasiparticles in metals $f(\mu,T)=[2/(2\pi\hbar)^3]\int d\mathbf{p}\cdot\{\exp[(\varepsilon-\mu)/T]+1\}^{-1}$, i.e., the Fermi–Dirac distribution, while $f(\mu,T)=[2/(2\pi\hbar)^3]\exp(\mu/T)\int d\mathbf{p}\cdot\exp(-\varepsilon/T)$ is the Boltzmann distribution of the charge carriers in semiconductors; $\mathbf{p}$ denotes the quasiparticle momentum and $\varepsilon=\mathbf{p}^2/2m$ is the quasiparticle energy (for a spherical Fermi surface). At constant chemical potential the quasiparticle density changes by $\delta n = (\partial f/\partial T)\delta T$, as a consequence of the change in temperature. This change evolves in time and space according to Eq. (3), so the quasiparticle density is given by the Gaussian in Eq. (4) for $\delta n=(\partial f/\partial T)\delta T$. The number of quasiparticles in the Gaussian pulse increases in proportion of the extension l' of the pulse ($l' < l$), and, similarly, the temperature drop broadens in the same proportion, by continuously absorbing heat from the external source. It follows that both the quasiparticle density $\delta n(x,t)$ and the temperature drop $\delta T(x,t)$ can be represented by a Gaussian of the form given by Eq. (2). The motion of the pulse as a whole is blocked in one direction by the sample end-wall, where the quasiparticles are continuously reflected, while its motion in the opposite direction along the sample is limited by diffusion; along this direction the pulse only broadens gradually by diffusion, which is a much slower process than the transport motion. Consequently, the pulse is in fact half of a Gaussian pulse with its peak just on the hot end of the sample. Such a Gaussian pulse is shown in Fig. 2.

Everywhere in the present paper we use, for the sake of the numerical illustration, a set of typical values for the basic physical quantities. For instance, we take the density n
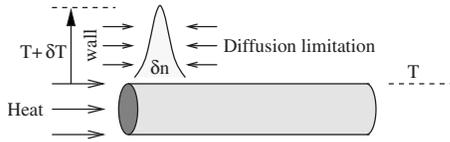
FIG. 2. Diffusion limits the free transport.

FIG. 4. Stationary regime.

$=10^{22}$ cm^{-3} for electrons in metals and the chemical potential $\mu=1$ eV. We take $v=10^5$ m/s for the Fermi velocity and $\Lambda=10^3$ Å for the electronic mean free path (at room temperature). We denote by $t'=\tau_{off}$ the time t in Eq. (5) needed to build up the pulse. From Eq. (5) we get $l' =10^5\tau_{off}^{1/2}$ μm (microns) for the spatial extension of the pulse, which is much smaller than the sample length l for sufficiently small τ_{off}. Its limiting value is of the order of the mean free path Λ. For instance, for $\tau_{off}=10^{-6}$ s we get $l' =100$ μm. For semiconductors we take $n=10^{17}$ cm^{-3} as a typical value, corresponding to a chemical potential given by $\mu/T\simeq-5.7$ (this is easily derived from the Boltzmann distribution given above). In semiconductors we use $v=10^4$ m/s for velocity and $\Lambda=10^2$ Å (at room temperature) for the mean free path. The spatial extent of the pulse is given by Eq. (5) as $l'=10^4\tau_{off}^{1/2}$ μm. For $\tau_{off}=10^{-6}$ s the spatial extent is $l'=10$ μm. All these are typical figures for metals and, respectively, semiconductors, which we use here in order to get illustrative numerical estimations.

IV. HEAT AND ELECTRIC FLOWS

A thermal pulse needs a time t' to build up, according to $l'=\sqrt{v\Lambda t'}$, hence $t'=l'^2/v\Lambda$. During this time a heat flow (heat per unit area of the cross-section and per unit time) $q =cl'\delta T/t'=cv\Lambda(\delta T/l')$ is absorbed, where c is the heat capacity per unit volume; this heat flow may be represented as $\mathbf{q}=-cv\Lambda\,\mathrm{grad}T=-K\,\mathrm{grad}T$, where $K=cv\Lambda$ is a well-known representation for the thermoconductivity. Similarly, one can say that the heat flux (heat per unit area of the cross-section) absorbed by a Gaussian pulse of extension l' is $\delta E =(Kl'/v\Lambda)\delta T$. In the limit of the δ-pulses, whose spatial extension is of the order of the mean free path Λ, it reduces to $\delta E=(K/v)\delta T$, and one can see, as expected, that heat absorbed by a pulse is proportional to its extension. In the opposite limit of a pulse as broad as the length of the sample, i.e., $l'=l$, the stationary transport regime starts to set up, where a small, uniform, continuous gradient of quasiparticle density and temperature extends over the whole length of the sample. This is valid both for charge carriers and for phonons, and the phonon thermoconductivity (as well as the thermoconductivity of other quasiparticles) must be added to the thermoconductivity K of the charge carriers given above. The diffusion of a Gaussian pulse is shown in Fig. 3, the
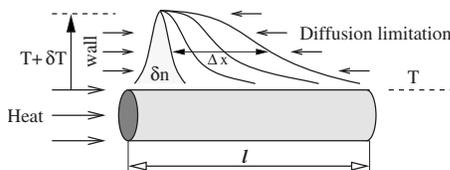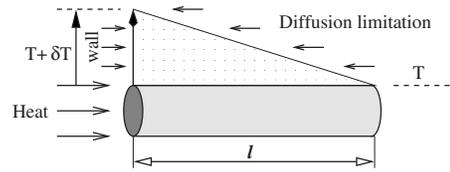
stationary transport is shown schematically in Fig. 4, and the pulse used in the pulsed mode of operation is shown in Fig. 5. For our models of metals and semiconductors used here (defined by the statistical distributions given above) it is easy to derive the heat capacity c and the thermoconductivity K.[32] Although these expressions are not relevant for the subsequent discussion we note them here for the sake of a more detailed information. The heat capacity per unit volume is $c=\pi^2nT/2\mu$ for metals (Fermi liquids) and $c=(3/2)(5/2 -\mu/T)n$ for semiconductors. The thermoconductivity can be represented as $K=\pi^2nv\Lambda T/2\mu$ for metals and $K =(5n\Lambda T/2mv)(7/2-\mu/T)$ for semiconductors. These expressions agree with $K=cv\Lambda$ up to some minor numerical factors.

Heat δE absorbed by the pulse is its internal thermal energy, due to the thermal excitations of the quasiparticles. For instance, it is due to the particle–hole excitations of the electronic quasiparticles in a Fermi liquid. Apart from this energy, the electronic quasiparticles in a pulse possess also single-particle energy, arising from the change in the chemical potential. Indeed, in order to preserve the charge neutrality of the sample, a change $(\partial f/\partial\mu)\delta\mu$ occurs in the quasiparticle density at the cold end of the sample, such as $(\partial f/\partial T)\delta T+(\partial f/\partial\mu)\delta\mu=0$; it follows that a voltage drop U appears at the hot end of the sample, with respect to the rest of the sample, such as $-eU=-\delta\mu$, or

$$U = -\frac{1}{e}[(\partial f/\partial T)/(\partial f/\partial\mu)]\delta T = Q\delta T, \tag{6}$$

where $-e$ is the electron charge and $Q=-(1/e) \times[(\partial f/\partial T)/(\partial f/\partial\mu)]$ is the well-known Seebeck thermopower coefficient. One can see easily that Q acquires negative values for electrons. The voltage U has the same spatial dependence as the temperature drop and the quasiparticle density, i.e., the Gaussian given by Eq. (4). Again, making use of the statistical distribution functions, it is easy to compute the thermopower. For metals $Q=-(\pi^2/6e)(T/\mu)$, while for semiconductors $Q=-(1/e)(3/2-\mu/T)$. One can see easily that the thermopower coefficient Q is much higher for semiconductors than for metals, as it is well known (typical values for semiconductors are of the order of 200 μV/K).
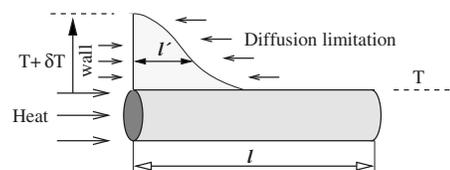

FIG. 3. Diffusion of a Gaussian pulse.

FIG. 5. A thermoelectric Gaussian half-pulse.

The voltage U corresponds to an electric field $-gradU = -QgradT$, and therefore an electric flow (charge per unit area of the cross-section and unit time) occurs inside the pulse, given by $\mathbf{j} = -\sigma QgradT$, where σ denotes the electric conductivity; this is a well-known basic equation of the thermoelectricity (in the absence of external electric fields). It is worth noting the opposite flow of the electrons with respect to the temperature gradient as well as the high current density for pulses due to $gradT = \delta T/l'$ (not $\delta T/l; l' \ll l$).

It is also worth noting that j is the electric flow inside the pulse, as given by the microscopic transport of the charge carriers. It can also be written as

$$j = -ev[\delta n(x) - \delta n(x + \delta x)] = ev\Lambda(\partial f/\partial T)(\partial T/\partial x), \quad (7)$$

hence the electric conductivity

$$\sigma = -ev\Lambda(\partial f/\partial T)/Q = e^2 v\Lambda(\partial f/\partial \mu). \quad (8)$$

This is a well-known representation for the electric conductivity, where $\partial f/\partial \mu \sim n/mv^2$. Making use of the statistical distributions given afore, we get $\sigma = 3e^2 nv\Lambda/2\mu$ for metals and $\sigma = e^2 nv\Lambda/mv^2$ for semiconductors. Using the thermoconductivities computed above, we can obtain the Lorenz number defined as $L = K/\sigma T$. It is given by $L = \pi^2/3e^2$ for metals and $L = (5/2e^2)(7/2 - \mu/T)$ for semiconductors, as it is well known.

The electric power per unit volume is given by $-gradU \cdot \mathbf{j} = -QgradT \cdot \mathbf{j} = j^2/\sigma$, which is the Joule–Lenz dissipated heat. Indeed, a voltage drop $U = Q\delta T$ implies an electric potential $\varphi = QT$, and therefore a heat flow $\mathbf{q} = QT\mathbf{j}$; this is the Peltier heat electrically transported (or the electrothermal Peltier heat), which is included in the basic Eq. (2) of the thermoelectricity ($\mathbf{q} = QT\mathbf{j} - KgradT$). From $q = QTj$ one gets easily the dissipated heat per unit volume and unit time $-\partial q/\partial x = -Qj(\partial T/\partial x) = j^2/\sigma$, i.e., the Joule–Lenz dissipated heat. The Peltier heat $q = QTj$ is worth noted: if we are going to get high currents in the pulsed transport we get a high Peltier cooling by reversing the mode of operation.

The electric power of a pulse of extension l' is therefore $j^2/\sigma \cdot l' = Uj = -\sigma Q^2 \delta T(\partial T/\partial x)$ (per unit area of the cross-section). The efficiency quotient of such a thermoelectric pulse is obtained by dividing the electric power $j^2/\sigma \cdot l' = -\sigma Q^2 \delta T(\partial T/\partial x)$ to the sum of this electric power, the Peltier heat QTj and the thermoconducted heat $-K(\partial T/\partial x)$, using $j = = -\sigma QgradT$ and dividing both the numerator and the denominator by $\sigma Q^2 T(\partial T/\partial x)$. The result was obtained in Ref. 33. We get straightforwardly

$$\eta = \frac{j^2/\sigma l'}{j^2/\sigma l' + QTj - K(\partial T/\partial x)} = \frac{\eta_c}{\eta_c + 1 + K/Q^2 \sigma T}, \quad (9)$$

where $\eta_c = \delta T/T$ is the Carnot efficiency quotient and $L = K/\sigma T$ is the Lorenz number.

The efficiency quotient can also be written as $\eta = \eta_c/(\eta_c + 1/ZT)$, where $ZT = Q^2/(L + Q^2)$ is a "figure of merit." This generalized figure of merit has been recently discussed in a broader context of thermoelectric transport.[33] One can see that the figure of merit introduced here can never exceed unity, and it is related to the usual figure of merit $ZT' = Q^2/L$ by $ZT = ZT'/(1 + ZT')$. Since $L = \pi^2/3e^2$ and $Q = -(\pi^2/6e)(T/\mu)$ for the electronic quasiparticles in

metals, we have $L \gg Q^2$, and ZT reduces to ZT'; as it is well known the efficiency quotient is very low in this case. On the contrary, for electrons in typical semiconductors one obtains $L = (5/2e^2)(7/2 - \mu/T)$ and $Q = -(1/e)(3/2 - \mu/T)$, as noted above, so that L and Q^2 are comparable; for large values of the ratio $-\mu/T$ the figure of merit ZT approaches unity, and the efficiency quotient is increased. On the other hand, however, the Joule–Lenz heat is drastically diminished, as a consequence of the low electric conductivity of the dilute gas of charge carriers in typical semiconductors, as it is also well known.

It is worth noting that the efficiency quotient derived above for pulses is the same as for an ideal stationary thermoelectric transport.[33]

V. THERMOELECTRICITY OF PULSES

The efficiency quotient, as well as the electric flow, the electric power, and the basic equations of the thermoelectricity are derived above for the internal, microscopic transport inside pulses. As expected, they agree (are practically identical) with the corresponding quantities of the classical, stationary transport, where a small, uniform, continuous gradient of temperature and quasiparticle density extends over the whole length of the sample. One can also say that this microscopic transport holds for pulses at rest. It is easy to see, however, that these equations hold also for the macroscopic pulselike transport as well, whereby a pulse is viewed as a whole. Indeed, the electric flow of such a pulse is given by

$$j = -e\delta nl'/t' = -ev\Lambda\delta n/l' = -ev\Lambda(\partial f/\partial T)\delta T/l', \quad (10)$$

and one can see that it is identical with the electric flow of the microscopic transport as given by Eq. (7). Such an electric pulse dissipates gradually the Joule–Lenz heat $-e\delta nl'Q\delta T$ (per unit area of the cross-section); it is easy to see, by making use of Eqs. (6) and (8), that the Joule–Lenz heat can also be written as

$$-e\delta nl'Q\delta T = (j^2/\sigma)(l'^3/v\Lambda), \quad (11)$$

where the electric flow is given by Eq. (10); hence, making use of Eq. (5), the electric power of the pulse is

$$P = j^2/\sigma l', \quad (12)$$

(per unit area of the cross-section), as for the microscopic transport used in Eq. (9). Similarly, the flow of the Peltier heat is QTj and the flow of the thermoconducted heat is $K\delta T/l' = -K(\partial T/\partial x)$, so the efficiency quotient of the pulselike transport is the same as that given by Eq. (9) for the microscopic transport, as expected. All these flows, as well as the electric power, last for a time t', i.e., the time during which the pulse is built up at the hot end of the sample. In addition, the pulse contains also its internal heat $\delta E = cl'\delta T$. It is worth emphasizing that the electric flow of the pulselike transport, as given either by Eq. (7) or Eq. (10), can also be written as

$$j = j_s(l/l'), \quad (13)$$

where j_s corresponds to the electric flow in the stationary transport, i.e., to the pulse extending over the whole length

of the sample ($l'=l$). One can see that the electric flow is increased in the pulselike transport by the ratio l/l' of the sample length to the pulse extension, as expected. This increase originates in the concentration of the charge carriers on small spatial extensions of narrow pulses. Similarly, the dissipated Joule–Lenz heat per unit area of the cross-section and per time, i.e., the flow of electric power as given by Eq. (12), can be written as

$$P = P_s(l/l'), \tag{14}$$

i.e., the electric power produced by the pulse transport is higher, by the same factor l/l', than the corresponding electric power delivered in the stationary transport. It is easy to see that the stationary power $P_s=j_s^2/\sigma l$ (per unit area of the cross-section) can also be written as $P_s=\sigma U^2/l$, which is $P_s=U^2/r$, where r is the internal electric resistance, as expected.

VI. FLYING PULSES

A thermoelectric sample with a charge pulse built up at the hot end evokes an electric "condenser," and, like any other condenser, such a "thermoelectric condenser" can be "discharged" by switching on the electric contacts to the external circuit. Under these circumstances the (ideal) sample end-wall does not block anymore the motion of the charge carriers, and the pulse "flies" through the external circuit as a whole, with the transport velocity $v_0=v$, according to Eqs. (3) and (4). This is a macroscopic, nonstationary, fast, pulsed-like transport, taking place in the transient regime prior to establishing the extension of the pulse along the whole length of the sample. In order to allow a smooth "fly," the cross-section of the external circuit must be equal to, or greater than, the cross-section of the sample (and, of course, the contacts are assumed to be perfect). The flying of the pulse through the external circuit of length l_e takes an on-time $\tau_{on}=l_e/v$. On the other side, the time t' needed to build up a pulse at the hot end of the sample is an off-time, $\tau_{off}=t'$. In addition, it is worth noting that such a flying pulse does not obey Ohm's law, as the transport is discontinuous. The electric charge conserves, so the external (local) electric flow is

$$j_e = -e\,\delta n l'/(l'/v) = -ev\,\delta n = j(t'/l')v = j(\tau_{off}/\tau_{on})(l_e/l'), \tag{15}$$

where Eq. (10) has been used. The energy conserves, i.e., the electric energy $E_{el}=-e\,\delta n l'Q\,\delta T$ (per unit area of the cross-section) as given by Eq. (11) is the energy delivered into the external circuit. The (discontinuous) momentous power de-
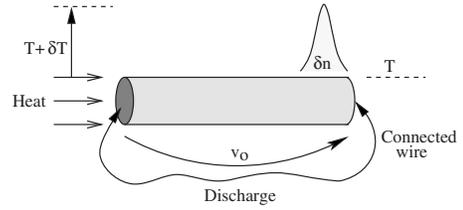

FIG. 6. Pulse and thermoelectric condenser.

FIG. 7. Discharge of the "condenser."

livered into the external circuit is $E_{el}/(l'/v)=(\tau_{off}/\tau_{on})\times(ll_e/l'^2)P_s$, where Eq. (14) has been used. It is less relevant; less relevant also is the external power averaged over the on-time, $E_{el}/\tau_{on}=(\tau_{off}/\tau_{on})(l/l')P_s$. While flying through the external circuit the pulse dissipates therefore gradually the Joule–Lenz heat E_{el}, and gives away the Peltier heat (the Peltier heat is transported from the hot junction to the cold junction), until it reaches the cold end of the sample and compensates the positive ionic charges there. After completing its "flight" through the external circuit the pulse is left with its internal heat $\delta E=cl'\,\delta T$, and it must be "deflated" of this internal energy in order to have a cyclic process. The time needed to extract this amount of heat is $t'=\tau_{off}$, i.e., precisely the time during which an identical pulse is built up at the hot end of the sample, such that, after this duration, the thermoelectric sample is ready for another operation. It follows that the thermal contacts should be maintained continuously during the operation of such a pulsed-like transport, while the electric contacts must be switched off once the pulse arrived at the cold end of the sample; otherwise, the pulse would move continuously through the entire circuit and the stationary regime would set up. Therefore, the electric contacts must be switched on and off periodically, with a certain frequency $f=1/(\tau_{off}+\tau_{on})$, where $\tau_{on}=l_e/v$, and a certain duration of the on- and off-times. The building of the pulse at the hot end is shown in Fig. 6, the flying pulse is shown in Fig. 7 and the deflating of the pulse at the cold end is shown in Fig. 8.

As it was said above, the on-time is the flight time $\tau_{on}=l_e/v$ of the pulse through the external circuit, where l_e is the length of the external circuit. The off-time, or the waiting time, is the time $t'=l'^2/v\Lambda$ needed for building up a pulse of length l' at the hot end of the sample (and for "deflating" a similar pulse of its internal heat at the cold end of the sample). The operating frequency is therefore $f=1/(\tau_{on}+\tau_{off})=v/(l_e+l'^2/\Lambda)$, and it ranges between $f_0=v/(l_e+\Lambda)\simeq v/l_e$, corresponding to δ-pulses, and $f_1=v/(l_e+l'^2/\Lambda)$, for pulses extending over the whole length l of the sample, where the stationary transport regime begins to set up. For reasonable values of l_e, the ratios $l^2/\Lambda l_e$ and $l'^2/\Lambda l_e$ acquire large values, so that one may write $f=v\Lambda/l'^2=f_1(l/l')^2$, i.e.,
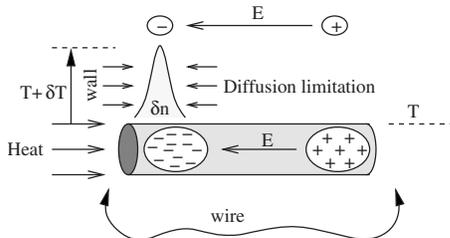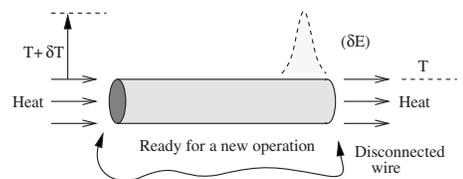

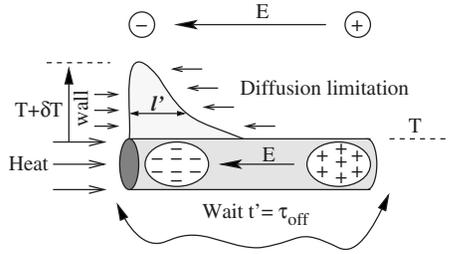FIG. 8. Deflating the pulse, ready for another operation.

FIG. 9. Building up a Gaussian pulse in a thermoelectric condenser.

the operating frequency is quadratic in the ratio l/l' of the sample length l to the pulse extension l'. This corresponds to very short on-times τ_{on} in comparison with the off-times $\tau_{off} = t'$, and to pulses of large extension l'. For $\tau_{on} \geq t'$, i.e., $l_e \geq l'^2/\Lambda$ the extension of the pulses starts to become microscopic. It is worth noting that during the on-time the sample is not at local equilibrium, and additional elastic waves may be excited inside the sample, which takes over the heat excess, allowing thus the flowing of heat. In addition, the phonon thermoconduction may be present in the sample, as well as heat thermoconducted by other elementary excitations, which may tend to establish in fact a small, uniform, continuous gradient of temperature along the sample. However, this local-equilibrium regime bears no relevance upon the pulses of the charge carriers as described herein, because the latter are not at local equilibrium, and are practically decoupled from the rest of the sample.

VII. POWER DELIVERED INTO THE EXTERNAL CIRCUIT

The Joule–Lenz heat E_{el} as given by Eq. (11) is the total energy (per unit area of the cross-section) dissipated by a pulse during its flight. Consequently, the average power produced in such a pulsed transport operated cyclically is given by

$$\bar{P} = (j^2/\sigma)(l'^3/v\Lambda)\frac{1}{\tau_{on} + \tau_{off}} = P_s(l/l')\frac{1}{1 + \Lambda l_e/l'^2}, \quad (16)$$

where Eqs. (13) and (14) have been used. One can see that for macroscopic pulses, corresponding to short on-times, i.e., for $\Lambda l_e/l'^2 \ll 1$, the average power is practically identical with the pulse power given by Eq. (14), $\bar{P} = P = P_s(l/l')$, i.e., it is increased by the factor l/l'. In this case, the operating frequency $f = f_1(l/l')^2$ given above is proportional to the square of the electric power, i.e., $f \sim P^2$. In the opposite limit however, corresponding to microscopic pulses of extension Λ, the increase factor is controlled by the ratio l/l_e of the sample length to the length of the external circuit (which may be higher than unity very well). In both cases the average power is increased in comparison with the equilibrium-operated thermoelements. The maximum value of the average power is obtained for $l' = \sqrt{\Lambda l_e}$, i.e., just for the border between microscopic and macroscopic pulses, as defined before. It is given by

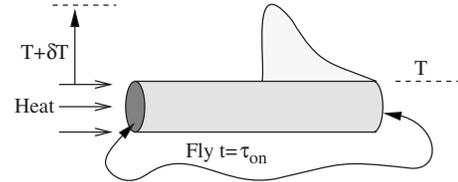$$\bar{P}^{max} = \frac{1}{2}\frac{l}{\sqrt{\Lambda l_e}}P_s; \quad (17)$$

FIG. 10. Discharging a Gaussian pulse in the thermoelectric condenser.

it corresponds to an optimal $\tau_{off} = l_e/v = \tau_{on}$ (ratio $\tau_{on}/\tau_{off} = 1$) and an optimal frequency $f = v/2l_e$. It is perhaps more convenient to refer the power to the maximal power $P_{dc} = U^2/4r = P_s/4$, corresponding to a load electric resistance equal to the internal resistance in a stationary operating regime (drift current). One obtains therefore $\bar{P}^{max} = 2(l/\sqrt{\Lambda l_e})P_{dc}$. The optimal power in the pulsed-operating regime as given by Eq. (17) is much higher than the stationary power.

The external power given by Eq. (16) can also be written as

$$\bar{P} = P_s(l/l')\frac{\tau_{off}}{\tau_{on} + \tau_{off}} = \frac{l}{\sqrt{v\Lambda}}\sqrt{f(1 - \tau_{on}f)}P_s, \quad (18)$$

where $\tau_{on} = l_e/v$ and $(1 + l^2/\Lambda l_e)^{-1} < \tau_{on}f < (1 + \Lambda/l_e)^{-1}$. It has a maximum value at the optimal frequency $f = 1/2\tau_{on}$ given before, and a characteristic frequency dependence. Making use of $\tau_{on} = l_e/v$, Eq. (18) gives also a characteristic dependence of the external power on the load resistance $\sim l_e$.

The pulsed-operating mode of the thermoelectric transport is shown in Figs. 9–11. Finally, we give here some numerical estimates. For typical values $n = 10^{22}$ cm^{-3}, $\mu = 1$ eV, and $v = 10^5$ m/s in metals, and for room temperature $T = 300$ K and $\delta T = 100$ K one obtains a δ-pulse electric flow $j \simeq 10^7$ A/cm^2, according to Eq. (10). Indeed, it is easy to see, making use of the Fermi–Dirac distribution, that the variation in the charge density is given by $\delta n = (\pi^2/4) \times (nT\delta T/\mu^2)$.[32] Making use of a typical mean free path value $\Lambda \simeq 10^3$ Å one obtains a stationary flow $j_s \simeq 10^3$ A/cm^2 for a sample length $l = 1$ mm. The voltage is $U \simeq 4 \times 10^{-4}$ V (thermopower coefficient $Q = -(\pi^2/6e)(T/\mu) \simeq 4 \times 10^{-6}$ V/K). The electric power of the pulse is therefore $P \simeq 4$ kW/cm^2, in comparison with the stationary power $P_s \simeq 0.4$ W/cm^2, which implies a factor 10^4. For an optimal pulse length $l' = l/10$ the current is $j = 10^4$ A/cm^2, the power is $P \simeq 4$ W/cm^2 and the maximal power is $\bar{P}^{max} \sim 2$ W/cm^2 for an operating frequency $f \simeq 500$ kHz, with a very short on-time ($\tau_{on} \simeq 10^{-6}$ s and $l_e = 10$ cm). This implies an increase factor 5 in comparison with the stationary regime ($P_s \simeq 0.4$ W/cm^2).

For electrons in semiconductors we may take $n = 10^{17}$ cm^{-3} and $v = 10^4$ m/s as an illustrative example; one
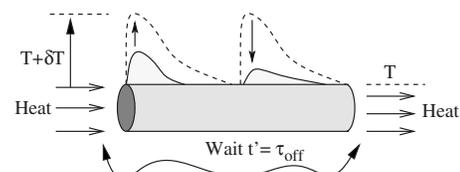

FIG. 11. Deflating the pulse while building up another.

obtains $\mu/T = -5.7$ ($\mu/T = \ln[n(2\pi\hbar^2/mT)^{3/2}/2]$ from the Boltzmann distribution,[32]) and an electric flow $j \simeq 4 \times 10^4$ A/cm^2 for a δ-pulse ($\delta n = n(3/2 - \mu/T)\delta T/T$, similarly, from the Boltzmann distribution[32]), for the same temperature values as those used above; the voltage is $U \simeq 6 \times 10^{-2}$V($Q \simeq 6 \times 10^{-4}$ V/K), and the electric power $P \simeq 2.4$ kW/cm^2. For a mean free path $\Lambda = 100$ Å one obtains $j_s \simeq 0.4$ A/cm^2 for a sample length $l = 1$ mm and a stationary power $P_s \simeq 2.4 \times 10^{-2}$ W/cm^2. The increase factor is 10^5. For a pulse of optimal extension $l' = l/30$, the operating frequency is approximately $f \simeq 50$ kHz, the current is $j = 12$ A/cm^2, the electric power $P \simeq 0.72$ W/cm^2, and the maximal power is $\bar{P}^{max} \sim 0.36$ W/cm^2; the on-time is $\tau_{on} \simeq 10^{-5}$ s (for $l_e = 10$ cm). Comparing $\bar{P}^{max} \sim 0.36$ W/cm^2 with $P_s \simeq 2.4 \times 10^{-2}$ W/cm^2 we can see an increase factor 15.

VIII. CONCLUSIONS

In conclusion, a mechanism of thermoelectric transport has been described here, which proceeds by pulses of charge carriers. It is a macroscopic, cyclic, nonstationary, fast, transient regime transport, which may diminish the effects of a spatially-extended thermal diffusion. This pulsed-like transport regime is operated by periodically switching on and off the electric contacts, while maintaining continuously the thermal contacts. The operating frequency is determined, as well as the on- and off-times, as functions of the nature of the sample, the extension of the pulses and the length of the external circuit. The electric flow and power are higher for pulsed-like transport than for stationary, classical transport, as a consequence of concentrating the charge carriers on pulses of small spatial extent. Such a pulsed-like transport may be operated cyclically, with an ideal efficiency quotient equal with the ideal efficiency quotient of the stationary transport. It may open the possibility of a practical realization of a high-power thermoelectric converter. High values of thermopower Q and conductivity σ are desirable but low values of thermoconductivity K are not critical.

Of course, the pulsed transport described here is an ideal process, intended to illustrate the physical principles of another type of thermoelectric transport. As regards practical purposes, there are several technical issues which must be addressed, in order to get the increasing performance of this type of thermoelectric transport. Among these, we may say that the contacts, both electric and thermal, must be as good as possible, in order to minimize the loss. In this respect, although the ideal efficiency coefficient of the pulsed transport is equal to the ideal efficiency coefficient of the stationary, continuous regime, the technical efficiency may be increased for the former because the pulsed transport reduces the risk of heat loss due to spatially-extended dissipation along the whole length of the sample. Another important issue related to the pulsed transport is the extraction of the electric energy delivered into the external circuit. At high frequencies, the transport proceeds mainly by impedance, and most of the energy may reside in the electromagnetic field of the reactances, so the usual Joule–Lenz effect is diminished, in fact. Finally, one may also note that the material

parameters which decrease usually the efficiency of a classical thermoelement are not critical anymore for a pulsed transport, so way may therefore be open for employing new classes of thermoelectric materials in pulsed transport.

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