

On pulse-like thermoelectric transport

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Abstract

A new type of thermoelectric transport is discussed, 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 the "off" times of the electric contacts, while maintaining continuously the thermal contacts. It is shown that such a non-equilibrium ideal thermal "engine" works cyclically with the same efficiency quotient as the ideal efficiency quotient of the thermoelectric devices operated in an equilibrium transport regime, but the electric flow and power are increased, as a consequence of concentrating the charge carriers on pulses of small spatial extent.

Transport in condensed matter proceeds by quasiparticles. Quasiparticles are elementary excitations possessing velocity (therefore momentum) and a finite lifetime τ . They obey either a Bose-Einstein distribution, 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 quasi-classical charge carriers (electrons and holes) in typical semiconductors. The electronic quasiparticles of a Fermi liquid possess the Fermi velocity \mathbf{v}_F , while the quasi-classical charge carriers in semiconductors have a thermal mean velocity $\bar{v} = \sqrt{T/m}$, where T is the temperature and m denotes an average effective mass. Transport along one direction, say x -direction, proceeds with an average transport velocity $v = \bar{v}/2$, or, respectively, $v = \bar{v}_F/2$, where \bar{v}_F denotes the spatial average of the Fermi velocity. The mean free path of the quasiparticles can also be represented as $\Lambda = v\tau$. Under these conditions, the local change $\partial n/\partial t + v\partial n/\partial x$ in the quasiparticle density $n(x, t)$ at position x and time t is given by the local imbalance $(1/2\tau)[n(x + \Lambda, t) + n(x - \Lambda, t) - 2n(x, t)]$ in the quasiparticle density,

$$\begin{aligned}\partial n/\partial t + v\partial n/\partial x &= (1/2\tau)[n(x + \Lambda, t) + n(x - \Lambda, t) - 2n(x, t)] = \\ &= \frac{1}{2}v\Lambda\partial^2 n/\partial x^2 ,\end{aligned}\tag{1}$$

which is the well-known diffusion equation. It describes a macroscopic, non-equilibrium transport (in contrast with the microscopic, 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. It is related to Boltzmann's kinetic equation (including changes in momentum), as well as to the master equation within the

quasi-classical description of the quasiparticles in condensed matter. 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, equation (1) has the well-known gaussian

$$n(x, t) = \frac{V\delta n}{\sqrt{2\pi v\Lambda t}} e^{-(x-vt)^2/2v\Lambda t} \quad (2)$$

as a solution. The gaussian pulse given by (2) may move as a whole with the transport velocity v , and has a spatial extension $l' = \sqrt{v\Lambda t}$ (in one direction); it flattens gradually on growing 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 (1) may be neglected, and we are left with the continuity equation whose solution is $V\delta n\delta(x - vt)$ 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 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 (2), whence one can see that the maximum value of the quasiparticle density is very close (up to $\sqrt{2/\pi} = 0.8$ a factor) 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 $V = 2l'$ 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 of a gaussian pulse, of course, where $V = l'$. Pulse-like thermoelectric transport has been discussed recently in various contexts.[1]

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 . 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 the statistical distribution and μ denotes the chemical potential. For electronic quasiparticles in metals $f(\mu, T) = [2/(2\pi\hbar)^3] \int d\mathbf{p} \cdot \{\exp[\varepsilon - \mu]/T] + 1\}^{-1}$, while $f(\mu, T) = [2/(2\pi\hbar)^3] \exp(\mu/T) \int d\mathbf{p} \cdot \exp(-\varepsilon/T)$ for Boltzmann's statistics of the charge carriers in semiconductors, where \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 temperature change. This change evolves in time and space according to equation (1), so that the quasiparticle density is given by the gaussian (2) 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 (2). The motion of the pulse as a whole is blocked in one direction by the sample wall, where the quasiparticles are continuously reflected, while its motion to 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 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 $\mathbf{q} = -cv\Lambda gradT = -K gradT$, 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 equilibrium 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.

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

$$U = -\frac{1}{e}[(\partial f/\partial T)/(\partial f/\partial\mu)]\delta T = Q\delta T \quad , \quad (3)$$

where $-e$ is the electron charge and $Q = -(1/e)[(\partial f/\partial T)/(\partial f/\partial\mu)]$ 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 (2). It corresponds to an electric field $-\text{grad}U = -Q\text{grad}T$, and therefore an electric flow (charge per unit area of the cross section and unit time) occurs inside the pulse, given by $\mathbf{j} = -\sigma Q\text{grad}T$, where σ denotes the electric conductivity; this is a well-known basic equation of the thermoelectricity (in the absence of external electric fields).[2] It is 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

$$j = -ev[\delta n(x) - \delta n(x + \delta x)] = ev\Lambda(\partial f/\partial T)(\partial T/\partial x) \quad , \quad (4)$$

hence the electric conductivity

$$\sigma = -ev\Lambda(\partial f/\partial T)/Q = e^2v\Lambda(\partial f/\partial\mu) \quad . \quad (5)$$

The electric power per unit volume is given by $-\text{grad}U \cdot \mathbf{j} = -Q\text{grad}T \cdot \mathbf{j} = j^2/\sigma$, which is the Joule-Lenz dissipated heat. Indeed, a voltage $U = Q\delta T$ 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 leads to another basic equation of the thermoelectricity $\mathbf{q} = QT\mathbf{j} - K\text{grad}T$, thermoconducted heat included.[2] 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 electric power of a pulse of extension l' is therefore $j^2/\sigma \cdot l' = Uj = -\sigma Q^2\delta T(\partial T/\partial x)$. The efficiency quotient of such a thermoelectric pulse is therefore straightforwardly obtained as

$$\eta = \frac{j^2/\sigma \cdot l'}{j^2/\sigma \cdot l' + QTj - K(\partial T/\partial x)} = \frac{\eta_c}{\eta_c + 1 + K/Q^2\sigma T} \quad , \quad (6)$$

where $\eta_c = \delta T/T$ is the Carnot efficiency quotient and $L = K/\sigma T$ is called usually 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". 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 $ZT = ZT'/(1 + ZT')$. As it is well-known[3] $L = \pi^2/3e^2$ for the electronic quasiparticles in metals, while $Q = -(\pi^2/6e)(T/\mu)$, such that $L \gg Q^2$ and ZT reduces to ZT' (and the efficiency quotient is very low). However, for electrons in typical semiconductors one obtains $L = (5/2e^2)(7/2 - \mu/T)$ and $Q = -(1/e)(3/2 - \mu/T)$, according to Boltzmann's distribution and classical transport theory,[4] 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. It is worthwhile mentioning here that the electronic heat capacity per unit volume for metals is given by[4] $c = (\pi^2/2\mu)nT$, and the electric conductivity is $\sigma = 3e^2v\Lambda n/2\mu$. Similarly, $c = (3n/2)(5/2 - \mu/T)$, $\sigma = e^2n\tau/m$, and $K = (5n\tau T/2m)(7/2 - \mu/T)$ (which agrees, up to minor numerical factors, with the representation $K = cv\Lambda$) for electronic charge carriers in semiconductors. It is worth stressing out that 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 well as for the classical, equilibrium 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 for the macroscopic pulse-like transport as well.

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 sample 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 , according to equations (1) and (2). This is a macroscopic, non-equilibrium, fast, pulse-like transport, taking place in the transient regime prior to establishing the thermal equilibrium along the whole length of the sample. The electric flow of such a pulse is given by

$$j = -e\delta n l' / t' = -ev\Lambda\delta n / l' = -ev\Lambda(\partial f / \partial T)\delta T / l' , \quad (7)$$

and one can see that it is identical with the electric flow of the microscopic transport as given by (4), as expected. During its "flight" through the external circuit such an electric pulse dissipates gradually the Joule-Lenz heat $-e\delta n l' Q \delta T$ (per unit area of the cross-section), until it reaches the cold end of the sample and compensates the positive ionic charges there; it is easy to see, by making use of (3) and (5), that the Joule-Lenz heat can be written as

$$-e\delta n l' Q \delta T = (j^2 / \sigma)(l'^3 / v\Lambda) , \quad (8)$$

where the electric flow is given by (7); hence the electric power of the pulse

$$P = j^2 / \sigma \cdot l' \quad (9)$$

(per unit area of the cross-section), as for the microscopic transport given in (6). 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 that the efficiency quotient of the pulse-like transport is the same as that given by (6) for the microscopic transport, as expected. After completing the "flight" through the external circuit the pulse is left with its internal heat $\delta E = cl'\delta T$ (the Peltier heat is transported from the hot

junction to the cold junction), and it must be "deflated" of this internal energy in order the device be operated cyclically. The time needed to extract this amount of heat is t' , *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 indeed ready for another operation. It follows that the thermal contacts must be maintained continuously during the operation of such pulse-like transport devices, 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 equilibrium regime would set up. Therefore, the electric contacts must be switched on and off periodically, with a certain frequency, and a certain duration of the "on" and the "off" times.

The "on" time is the "flight" time $t_0 = l_0/v$ of the pulse through the external circuit, where l_0 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 $\nu = 1/(t_0 + t') = v/(l_0 + l'^2/\Lambda)$, and it ranges between $\nu_0 = v/(l_0 + \Lambda) \simeq v/l_0$, corresponding to δ -pulses, and $\nu_1 = v/(l_0 + l^2/\Lambda)$, for pulses extending over the whole length l of the sample, where the equilibrium regime starts to set up. For reasonable values of l_0 the ratios $l^2/\Lambda l_0$ and $l'^2/\Lambda l_0$ acquire large values, so that one may write $\nu = v\Lambda/l'^2 = \nu_1(l/l')^2$, *i.e.* 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 t_0 in comparison with the "off" times t' , and to pulses of macroscopic extension l' . For $t_0 \geq t'$, *i.e.* $l_0 \geq l'^2/\Lambda$ the extension of the pulses starts to become microscopic. It is worth noting that during the "on" time the sample is not at equilibrium, and additional elastic waves are excited inside the sample, which takes over the heat excess, allowing thus a smooth flowing of heat. In addition, it is worth stressing out that the phonon thermoconduction is always present in the sample, as well as heat thermoconducted by other elementary excitations, which establishes in fact a small, uniform, continuous gradient of temperature along the sample. However, this equilibrium regime bears no relevance upon the pulses of the charge carriers as described herein, because the latter are not at equilibrium, and are practically decoupled from the rest of the sample.

The electric flow of the pulse-like transport, as given by either (4) or (7), can also be written as

$$j = j_{eq}(l/l') \quad , \quad (10)$$

where j_{eq} corresponds to the electric flow in the equilibrium-operated thermoelement, *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 pulse-like 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 Joule-Lenz dissipated heat per unit area of the cross-section and per time, *i.e.* the flux of electric power as given by (9), can be written as

$$P = P_{eq}(l/l') \quad , \quad (11)$$

i.e. the electric power produced by the pulse-operated thermoelements is higher, by the same factor l/l' , than the electric power of the same thermoelements operated at equilibrium. The Joule-Lenz heat as given by (8) is the total energy (per unit area of the cross-section) dissipated by a pulse during its "flight". Consequently, the average power produced by such a thermoelement operating cyclically is given by

$$\bar{P} = (j^2/\sigma)(l^3/v\Lambda) \cdot \frac{1}{t_0 + t'} = P_{eq}(l/l') \cdot \frac{1}{1 + \Lambda l_0/l'^2} \quad ; \quad (12)$$

one can see that for macroscopic pulses corresponding to short "on" times, *i.e.* for $\Lambda l_0/l'^2 \ll 1$, the average power is practically identical with the pulse power given by (11), $\bar{P} = P = P_{eq}(l/l')$, *i.e.* it is increased by the factor l/l' . In this case, the operating frequency $\nu = \nu_1(l/l')^2$ given above is proportional to the square of the electric power, *i.e.* $\nu \sim P^2$. In the opposite limit however, corresponding to microscopic pulses of extension Λ , the increase factor is controlled by the ratio l/l_0 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 $l' = \sqrt{\Lambda l_0}$, *i.e.* just for the border between microscopic and macroscopic pulses, as defined before.

For typical values $n = 10^{22}\text{cm}^{-3}$, $\mu = 1\text{eV}$ and $v = 10^5\text{m/s}$ in metals, and for room temperature $T = 300\text{K}$ and $\delta T = 100\text{K}$, one obtains a δ -pulse electric flow $j \simeq 10^7\text{A/cm}^2$, according to (7) ($\delta n = (\pi^2/4)(nT\delta T/\mu^2)$); making use of a typical mean free path value $\Lambda = 10^3\text{\AA}$ one obtains an equilibrium flow $j_{eq} \simeq 10^3\text{A/cm}^2$ for a sample length $l = 1\text{mm}$. The voltage is $U \simeq 4 \cdot 10^{-4}\text{V}$ (thermopower coefficient $Q \simeq 4 \cdot 10^{-6}\text{V/K}$); the electric power of the pulse is therefore $P \simeq 4\text{kw/cm}^2$, in comparison with the equilibrium power $P_{eq} \simeq 0.4\text{w/cm}^2$. For a pulse of length $l' = l/2$ the power is $P \simeq \bar{P} \simeq 0.8\text{w/cm}^2$, and the operating frequency $\nu \simeq 40\text{kHz}$, with a very short "on" time ($t_0 \simeq 10^{-8}\text{s}$ for $l_0 = 1\text{mm}$). For electrons in semiconductors we may take $n = 10^{17}\text{cm}^{-3}$ and $v = 10^4\text{m/s}$ as an illustrative example; one obtains $\mu/T = -5.7$ ($\mu/T = \ln[n(2\pi\hbar^2/mT)/2]$) and an electric flow $j \simeq 4 \cdot 10^4\text{A/cm}^2$ for a δ -pulse ($\delta n = n(3/2 - \mu/T)\delta T/T$), for the same temperature values; the voltage is $U \simeq 6 \cdot 10^{-2}\text{V}$ ($Q \simeq 6 \cdot 10^{-4}\text{V/K}$), and the electric power $P \simeq 2.4\text{kw/cm}^2$. For a mean free path $\Lambda = 100\text{\AA}$ one obtains $j_{eq} \simeq 0.4\text{A/cm}^2$ for a sample length $l = 1\text{mm}$ and an equilibrium power $P_{eq} \simeq 2.4 \cdot 10^{-2}\text{w/cm}^2$. For a pulse of extension $l' = l/2$ the operating frequency is approximately $\nu \simeq 0.4\text{kHz}$ and the electric power $P \simeq \bar{P} \simeq 4.8 \cdot 10^{-2}\text{w/cm}^2$; the "on" time is $t_0 \simeq 10^{-7}\text{s}$ (for $l_0 = 1\text{mm}$).

In conclusion, a new type of thermoelectric transport has been described herein, which proceeds by pulses of charge carriers. It is a macroscopic, non-equilibrium, fast, transient regime transport, which diminishes the effects of thermal diffusion. This pulse-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 the "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 pulse-like transport than for equilibrium transport, as a consequence of concentrating the charge carriers on pulses of small spatial extent. Such a pulse-like operating thermoelectric device works cyclically, with an ideal efficiency quotient equal with the ideal efficiency quotient of the equilibrium operated thermoelements. Therefore, it is a high power thermoelectric converter.

References

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