

Ultrafast thermoelectric conduction

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Abstract

An ultrafast process of thermoelectric conduction is described, whose increased performance is realized by minimizing the effects of thermal dissipation. A pulse-operating regime of such "cold" thermoelectric devices is also described.

Recently, new ideas have been advanced in order to increase the proficiency of the thermoelectric devices.[1] Usually, such devices consist of an alternate sequence of p - n -semiconducting junctions, subjected to an alternate sequence of temperature differentials, such as to create a serial battery of thermoelectric generators. The performance of the power supply output is improved by a switching-contactors system. While operating such switching electric contactors it has been noticed that the power output may greatly be increased for short, and ultra-short, pulses. Indeed, as it is well-known, the thermoelectric (Seebeck) effect, which produces a driving voltage (thermopower) due to a temperature differential, is compensated in time by the electrothermal (Peltier) effect, which generates an opposite temperature differential as a consequence of the voltage. Both effects are controlled by the relaxation of the electric-charge carriers, leading to the thermalization of the small, external disturbances, according to the principle of the thermal equilibrium. However, an ultrafast thermoelectric conduction may diminish the thermoconduction and the heat dissipation for very short times, leading thus to an increased proficiency of the thermoelectric devices. It is worth emphasizing that the efficiency quotient of the conversion of the thermal energy into electric energy is not increased in such devices, but a continuous pulse operation with an increased electric output provides obvious benefits for users. The transient, non-stationary regime of such an ultrafast process of thermoelectric conduction is described in the present paper.

Let $n(\varepsilon) = [\exp[(\varepsilon - \mu)/T] + 1]^{-1}$ be the Fermi-Dirac distribution of the charge carriers with the Fermi level (chemical potential) μ at temperature T . A local change δT in the temperature gives rise to a change

$$\begin{aligned} \delta n_T &= -\frac{2}{(2\pi\hbar)^3} \int d\mathbf{p} \cdot (\partial n / \partial \varepsilon) [(\varepsilon - \mu)/T] \delta T = \\ &= -\frac{1}{\pi^2 \hbar^3} \int d\varepsilon \cdot (p^2/v)(\varepsilon - \mu)(\partial n / \partial \varepsilon)(\delta T/T) \end{aligned} \quad (1)$$

in the electron density, where $\mathbf{v} = \partial \varepsilon / \partial \mathbf{p} = \mathbf{p}/m$ is the quasi-particle velocity, and m is the quasi-particle effective mass; for practical purposes m may be taken as the bare electron mass,

and \hbar denotes Planck's constant. According to the theory of the slightly inhomogeneous electron liquid[2] the chemical potential μ may be taken as $\mu = p_F^2/2m$, where p_F is the Fermi momentum of a spherical Fermi surface. Integrating by parts in (1) and making use of the Fermi-Dirac integrals

$$\int d\varepsilon \cdot n(\varepsilon)f(\varepsilon) = \int_0^\mu d\varepsilon \cdot f(\varepsilon) + \frac{\pi^2}{6}T^2f'(\mu) + \dots \quad (2)$$

for $T/\mu \ll 1$ one obtains

$$\delta n_T = \frac{\pi^2}{4} \bar{n} \frac{T\delta T}{\mu^2} \quad , \quad (3)$$

where $\bar{n} = p_F^3/3\pi^2\hbar^3$ is the electron concentration. The result may be generalized for non-spherical Fermi surfaces, and it may also be derived for relatively small concentrations of charge carriers, where equation (2) must be corrected. The numerical computations are carried out here as for electrons in simple metals; the general behaviour of the results and the ensuing physical picture do not differ qualitatively for various other practical situations.

The chemical potential undergoes a change $\delta\mu$, given by

$$\delta n_\mu = -\frac{2}{(2\pi\hbar)^3} \int d\mathbf{p} \cdot (\partial n/\partial\varepsilon)\delta\mu = \frac{3}{2}\bar{n}\frac{\delta\mu}{\mu} \quad , \quad (4)$$

such as to preserve the number of electrons. Therefore,

$$\delta n_T + \delta n_\mu = 0 \quad , \quad (5)$$

and

$$\delta\mu = -\frac{\pi^2}{6} \frac{T}{\mu} \delta T \quad . \quad (6)$$

The change $\delta\mu$ in the chemical potential is equivalent with a change $-\delta\mu$ in the energy levels; therefore, an electric potential U appears, such as

$$-eU = -\delta\mu = \frac{\pi^2}{6} \frac{T}{\mu} \delta T \quad , \quad (7)$$

or

$$U = -\frac{\pi^2}{6} \frac{T}{e\mu} \delta T \quad , \quad (8)$$

where $-e$ is the electron charge. This is the origin of the thermoelectric effect, and $Q = -(\pi^2/6e)(T/\mu)$ in $U = Q\delta T$ above is the thermopower.[3] The change in energy per unit volume is

$$\delta E = c\delta T = (\pi^2/2\mu)\bar{n}T\delta T \quad , \quad (9)$$

where $c = (\pi^2/2\mu)\bar{n}T$ is the heat capacity of the electrons (per unit volume).

The excited (quasi-) electrons in number of $\delta n = \delta n_T = -\delta n_\mu$ (per unit volume) move along the x -axis with the (average) velocity $v_0 = v_F \overline{\cos\theta} = v_F/2$, where $v_F = p_F/m$ is the Fermi velocity; here, we leave aside the finite-size and other geometric effects of the sample. The electronic quasi-particles have a finite lifetime τ , as due, for instance, to the electron-electron and electron-phonon interaction; during this short time τ they move along the mean free path Λ , so that their density $n(x, t)$ changes according to

$$n(x, t + \tau) - n(x, t) = n(x - \Lambda, t) - n(x, t) \quad ; \quad (10)$$

or, as long as $\tau \ll t$ and $\Lambda \ll x$,

$$\frac{\partial n}{\partial t} = -v_0 \frac{\partial n}{\partial x} ; \quad (11)$$

this is the continuity equation, and $j = v_0 n$ is the density of the particle flow; its general solution is

$$n = f(x - v_0 t) ; \quad (12)$$

for the initial condition $n(x, t = 0) = V \delta n \delta(x)$, where V denotes the volume of the local heating, one obtains $f(x) = V \delta n \delta(x)$, so that

$$n(x, t) = V \delta n \delta(x - v_0 t) ; \quad (13)$$

the original perturbation propagates along the sample with the velocity v_0 . The electric flux is therefore

$$I_0 = -e v_0 A \delta n , \quad (14)$$

where A is the area of the cross-section of the sample. Making use of (3) and (8) one may write Ohm's law for the electric resistance as

$$R = U/I_0 = \frac{4}{3} \frac{\mu}{e^2 v_F \bar{n}} \frac{1}{A} ; \quad (15)$$

since $\mu/v_F \bar{n} = (3\pi^2/2)\hbar^3/p_F^2$ one obtains also

$$R = \frac{h}{e^2} (\pi a_e^2/A) , \quad (16)$$

where $a_e = 1/k_F$ is the average inter-particle separation, $k_F = \hbar/p_F$ being the Fermi wavevector; it follows that the conductivity $R^{-1} = (e^2/h) \times$ number of current lines, hence the quanta e^2/h for electric conductivity. It is worth emphasizing that the formation of a δ -pulse through local heating is a highly idealized situation, the volume V in (13) being given by $V = A l_0$, where $l_0 \sim \Lambda$ is a length of the order of the mean free path.

It is worthwhile estimating the efficiency of this ultrafast thermoelectric conduction. According to the above equations the electric energy is given by

$$E = U I_0 t = \frac{\pi^4}{24} \bar{n} V \frac{(T \delta T)^2}{\mu^3} , \quad (17)$$

while the heat δE is given by (9); it follows the efficiency quotient

$$\eta = E/\delta E = \frac{\pi^2}{12} \frac{T^2}{\mu^2} \eta_C , \quad (18)$$

where $\eta_C = \delta T/T$ is the Carnot quotient. One can see that η is much smaller than η_C , since $T/\mu \ll 1$; the thermoelectric conduction is indeed a second-order effect, in the sense that both the voltage and the number of charge carriers are proportional to δT , so that the electric power goes like $(\delta T)^2$, in contrast with the heat given by (9) which is a first-order effect (and which is transported by thermal conduction); while the main part of the heat is spent for thermal disorder only a small fraction of it is spent in the thermoelectric conduction. For typical values $\mu \sim 1\text{eV}$ ($v_F \sim 10^5\text{m/s}$), $A \sim 1\text{cm}^2$, $\delta T \sim 100\text{K}$ and room temperature T one obtains a rather small voltage $U \sim 10^{-4}\text{V}$, according to (8), but a high electric flux $I_0 \sim 10^7\text{A}$ (from (14)), *i.e.* an electric power of the order of $\sim 1\text{kw}$. It is worth emphasizing that the electric flow as given by I_0 in (14) does not depend essentially on the electron concentration. We also note that the efficiency quotient derived

above for an ideal δ -pulse is the same as the efficiency quotient corresponding to thermoelectric conduction at thermal equilibrium.

The lifetime τ_e of the electronic quasi-particles due to the electron-electron collisions may be represented as[2]

$$1/\tau_e \simeq \frac{1}{\hbar} B^2 \frac{\rho^3}{\bar{n}} T^2 \quad , \quad (19)$$

where $B \simeq 4\pi e^2/k_F^2$ and $\rho = mp_F/\pi^2\hbar^3$ is the density of states at the Fermi level; making use of the atomic units Bohr radius $a_H = \hbar^2/me^2 = 0.53\text{\AA}$ and $e^2/a_H = 27.2\text{eV}$, one gets

$$1/\tau_e \simeq (a_e^4/27.2) \cdot 10^7 T^2 \quad , \quad (20)$$

and for typical electronic densities at room temperature one obtains $1/\tau_e \simeq 10^{12}\text{s}^{-1}$; the corresponding mean free path is $\Lambda \sim 10^{-7}\text{m} = 10^3\text{\AA}$. The electronic quasi-particle lifetime τ_{e-ph} caused by the electron-(acoustic) phonon collisions is given by[4]

$$1/\tau_{e-ph} \simeq \frac{1}{\hbar} T/F = \frac{1}{\hbar} (m/M)(\mu/\omega_D)^2 T \quad , \quad (21)$$

where M is the atomic mass and ω_D is the Debye frequency; for typical parameter values one gets $F \sim 10 - 100$ and

$$1/\tau_{e-ph} \simeq 10^{9-10} T \quad , \quad (22)$$

which gives $1/\tau_{e-ph} \sim 10^{11-12}\text{s}^{-1}$ at room temperature. As one can see, it is comparable with the electron-electron lifetime, so that one may take $\tau \sim 10^{12}\text{s}^{-1}$ for the lifetime of the electronic quasi-particles, and the mean free path $\Lambda \sim 10^{-7}\text{m} = 10^3\text{\AA}$ as given above. A more accurate comparison of the numerical factors in (20) and (22) shows that at room temperature the temperature dependence of the transport coefficients is usually dominated by the electron-phonon interaction.

It follows from the above considerations that the δ -pulse corresponding to the thermoelectric flux I_0 given by (14) is transported without dissipation over the length l of the sample with the velocity $v_0 = v_F/2$; the time of flight is therefore $t_0 = 2l/v_F$; for $l = 1\text{mm}$, for instance, one obtains $t_0 \simeq 2 \cdot 10^{-8}\text{s}$, *i.e.* a frequency $\nu_0 = 1/t_0 \simeq 50\text{MHz}$. However, for longer times it begins to appear the dissipation of the electric flow, as due to the diffusion of the charge carriers. Indeed, already for an open circuit the electrons bounce on the ends of the sample, giving rise to thermal dissipation; similarly, for a continuous operation in short circuit the electrons move repeatedly along the sample. For a motion proceeding in both directions equation (10) becomes

$$n(x, t + \tau) - n(x, t) = n(x + \Lambda, t) + n(x - \Lambda, t) - 2n(x, t) \quad , \quad (23)$$

or

$$\frac{\partial n}{\partial t} = \Lambda v_0 \frac{\partial^2 n}{\partial x^2} \quad , \quad (24)$$

which is the diffusion equation. It is worth emphasizing in this context the statistical nature of equations (10) and (23), as $1/\tau$ is the quasi-particle probability, and Λ stands therefore for a dissipation length.[5] For the same initial condition $n(x, t = 0) = V\delta n\delta(x)$ as the one used in (11) one may write for (24) the Fourier representation

$$n(x, t) = V\delta n \frac{1}{2\pi} \int dk \cdot e^{-ikx - \Lambda v_0 k^2 t} \quad ; \quad (25)$$

the integral can easily be estimated as

$$n(x, t) = V\delta n \frac{1}{\sqrt{4\pi\Lambda v_0 t}} e^{-x^2/4\Lambda v_0 t} \quad , \quad (26)$$

which is the well-known solution of the diffusion equation. Similarly, equation (10) becomes for longer times

$$\frac{\partial n}{\partial t} = -v_0 \frac{\partial n}{\partial x} + \frac{1}{2}\Lambda v_0 \frac{\partial^2 n}{\partial x^2} \quad , \quad (27)$$

whose solution is

$$n(x, t) = V\delta n \frac{1}{\sqrt{2\pi\Lambda v_0 t}} e^{-(x-v_0 t)^2/2\Lambda v_0 t} \quad ; \quad (28)$$

one can see that the peak of the charge carriers flattens gradually over a distance $\Delta x = 2\sqrt{\Lambda v_0 t}$, while moving with the velocity v_0 ; the electric flux

$$I = -e \int dx \cdot v_0 \frac{\partial n}{\partial x} \quad (29)$$

vanishes in the limit of the long times. For shorter times the electric flux is diminished to $I \sim I_0 l_0 / \sqrt{2\pi\Lambda v_0 t}$, where l_0 ($\sim \Lambda$) is the original width of the ideal δ -pulse. The time after which the dissipation effect prevails upon the propagation is of the order of $t_1 \sim l^2 / \Lambda v_0 \sim t_0 (l/\Lambda)$, corresponding to $\Delta x \sim l$; for $l = 1\text{mm}$ and $t_0 \simeq 2 \cdot 10^{-8}\text{s}$ given above, and for the diffusion length $\Lambda \sim 10^3 \text{\AA}$, one obtains $t_1 \simeq 10^4 t_0 \simeq 2 \cdot 10^{-4}\text{s}$, corresponding to a frequency $\nu_1 \simeq 5\text{kHz}$. For any pulse-operating regime of frequency ν in the range $\nu_1 - \nu_0$, *i.e.* $\nu_1 < \nu < \nu_0$, the electric flux is of the order of I given above, diminishing gradually for lower frequencies; for frequencies below the lower bound ν_1 the electric flux diminishes drastically, and the equilibrium-transport regime is reached. Of course, the finite duration of the electric contacts has the same damping effect.

The ideal pulse-operating regime described above is therefore limited by the extent of the local heating, over which the heat dissipation acts. Let us assume that the local heating takes place over a length l' , such as $\Lambda \ll l' \ll l$; then, the heat $cl'\Delta T$ (per unit area) supplied for a temperature variation ΔT is given by $K(\Delta T/l')t'$, where $K \simeq cv_F\Lambda$ is the electron thermoconductivity,[3] and t' is the time needed for this process; consequently, $cl'\Delta T = K(\Delta T/l')t'$, hence $t' = (1/v_F)l'^2/\Lambda$ (which is independent of the temperature difference). The pulse formed over the distance l' moves with the velocity v_0 , so that the "flight" time is $t = (l - l')/v_0 \sim t_0$. One can see that the time t' needed for the formation of the pulse is much longer than the flight time (by the factor $l'^2/l\Lambda$). For an optimal operation the electric contacts should be maintained a duration t , and interrupted a duration t' (while the thermal contacts must be maintained a time t' , *i.e.* practically all the time). The operating frequency is therefore $\nu = 1/(t + t') \simeq \nu_0(\Lambda l/l'^2)$, and one can see that the ideal case $\nu = \nu_0$ is not attained, except for a "microscopic engine" where $l' \sim \Lambda$ (the equality $\Lambda l = l'^2$ is difficult to be satisfied in practice; in fact, in order to preserve the width of the pulse during its flight through the sample the condition $\Lambda l \ll l'^2$ must be satisfied, which is equivalent to $\nu \ll \nu_0$ and $t \ll t'$). The frequency ν can also be written as $\nu = \nu_1(l/l')^2$, where $\nu_1 = \nu_0\Lambda/l$ has been introduced above as the lower limit of the operating frequency. For the typical values given before ($\nu_1 = 5\text{kHz}$) and a reasonable ratio $l'/l \sim 1/2$ one obtains approximately $\nu \sim 20\text{kHz}$. The density of the charge carriers in the pulse formed at one end of the sample is given by (26) where now the volume V is given by $V = Al'$. The electric flux is of the order of I_0 , and the electric energy is $E(l'/\Lambda)$, where E is given by (17) (corresponding to $V \sim A\Lambda$). One can see that it increased in the same proportion as heat increased, so that the efficiency quotient given by (18) is left unchanged. However, the electric power is referred to the time $t' = (1/v_F)l'^2/\Lambda$ needed for

formation of the pulse (as well as for its full relaxation), so that it is decreased by the factor l'/Λ , and the electric flux

$$I \sim I_0(\Lambda/l') \quad (30)$$

is also reduced to the same extent. One can see that the ideal situation is approached for heating lengths l' as short as possible. For $l'/l \sim 1/2$ and for the typical values given above the electric flux is reduced to $I \sim 10^3 \text{A}$. It is also worth noting that the extent of the pulse is now $\Delta x \sim \sqrt{\Lambda v_0 t'} = l'$, as expected, and t' is precisely the time needed for formation of a pulse tail $\sqrt{\Lambda v_F t'}$ of the order of l' , *i.e.* $t' \sim (1/v_F)l'^2/\Lambda$.

In general, the high-performance device operation requires high-quality electric contacts, a sharply-defined operating pulse frequency ν , obeying as close as possible the contact interruption $t' = (1/v_F)l'^2/\Lambda$ and contact duration $t = (l-l')/v_0$, good thermal isolation and contacts; the latter are necessary since the thermal conduction is always present (including that due to the phonon transport), and a decrease of temperature as abrupt as possible must be ensured over short distances l' . Under the conditions described above the heat injection into the sample is an equilibrium process, its rate being of the order of $v_F(\Lambda/l')$ (while the heating time is $t' = (1/v_F)l'^2/\Lambda$). A similar rate holds for the lattice heat, where the Fermi velocity is replaced by the sound velocity v_s . Usually, after heat dissipation is fully developed, a stationary drop of temperature is realized over the sample length, of a small, constant gradient, which is the usual circumstance under which the transport experiments (like thermoconduction, electric conduction) are performed.[3] In contrast to the situation described here (which is a non-stationary, transient, and non-equilibrium one), such cases correspond to a stationary, equilibrium transport.

It is worth noting that for equilibrium transport the electric conductivity σ is given by $I = \sigma UA/l$ and the thermoconductivity K is defined through $\partial\delta E/\partial t = KA\delta T/l$; the electric power is therefore $P_e = UI = \sigma Q^2 A(\delta T)^2/l$, where $Q = U/\delta T$ is the thermopower, while the caloric power is $P_{cal} = \partial\delta E/\partial t$; one can write therefore the efficiency quotient as

$$\eta = \frac{T\sigma}{K}Q^2\eta_C ; \quad (31)$$

the ratio $K/T\sigma = L$ is the Lorenz number, which is independent of temperature, according to Wiedemann-Franz law; for ideal conditions $L = \pi^2/3e^2$; making use of the thermopower $Q = -(\pi^2/6e)(T/\mu)$ given by (8) the efficiency quotient above becomes $\eta = (\pi^2/12)(T/\mu)^2\eta_C$, as that given by (18).

Finally, the electric flux through the sample at equilibrium is given by $I \sim I_0(\Theta/T)^2$ or $I \sim I_0(\Theta^2/T(T + \Theta_2))$ at room temperatures, as corresponding to electron-electron or electron-electron plus electron-phonon relaxation processes, where the scale temperatures are typically $\Theta \sim 1\text{K}$ (for 1cm^2 an area of the cross-section) and $\Theta_2 \sim 10^2\text{K}$; both I_0 and the voltage U are the same as those computed above;[3] one can see that the equilibrium processes reduce the electric flow by a factor of $\sim 10^5$ at least, leading to $I \sim 10^2\text{A}$ for the typical sample employed here. It corresponds very closely to a reduction factor of the order Λ/d ($\Theta^2 \sim 1/d$), where d is the mean transverse size of the sample ($d \sim 1\text{cm}$), and stands for the local heating length l' introduced above. As long as this length d is replaced by the much shorter length l' , through the pulse-operating regime described here, the performance of such devices is much improved. In this difference resides the distinction between the equilibrium thermoelectric conduction employed in the usually operated thermoelectric devices and the non-equilibrium thermoelectric transport in the fast pulse-operating devices.

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