

A pulse thermoelectric machine

M. Apostol

Department of Theoretical Physics, Institute of Atomic Physics,

Magurele-Bucharest MG-6, POBox MG-35, Romania

email: apoma@theory.nipne.ro

Abstract

A new type 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 non-equilibrium ideal thermal "machine" 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. The machine is reversible, in the sense that it can operate either as a thermoelectric generator or as an electrothermal cooler.

1 Theoretical background

1.1 Reference to prior work

[001] The pulse thermoelectric machine described herein is based on work previously published in M. Nedelcu, *PhD Thesis*, Polytechnical Institute, Bucharest, Romania (2001); M. Apostol and M. Nedelcu, *J. Optoelect. & Adv. Materials*, **3** 125 (2001); M. Apostol and M. Nedelcu, *Proceedings of the 20th International Conference on Thermoelectrics*, Beijing, June (2001), p. 42; M. Apostol, *J. Theor. Phys.* **69** 55 (2001); *ibid*, **81** 173 (2002). The physical principles of the pulse thermoelectric transport can be found in M. Apostol, *Transport Theory*, **apoma**, Magurele Bucharest (2001) and M. Apostol, *The Electron Liquid*, **apoma**, Magurele Bucharest (2000).

1.2 Related work

[002] W. C. White, *Elect. Engng.*, N. Y., **70** 589 (1951); A. D. Reich, unpublished, *Internal Reports to the Borg-Warner Research Center*, Des Plaines, Il, USA (1960); K. Landecker and A. W. Findlay, *Solid-State Electronics* **3** 239 (1961); R. J. Buist and P. G. Lau, *The 15th International Conference on Thermoelectrics*, Pasadena, California, March (1996); G. Jeffrey Snyder, Jean-Pierre Fleurial, Thierry Caillat, Ronggui Yang and Gang Chen, *J. Appl. Phys.* **92** 1564 (2002) (see also V. P. Babin and E. K. Iordanishvili, *Sov. Phys.-Tech. Phys.* **14** 293 (1969)); J. M. Schroeder, *ENTELEC News*, Winter 1999, p.7 (US Patent 5 393 350 (1995)); J. Stockholm, private communication (2001); U. S. Ghoshal, US Patents 5 867 990 (1999), 6 065 293 (2000); L. E. Bell, US Patent 0108381 A1 (2002).

1.3 Physical description

[003] Quasiparticles. 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 (dilute electron liquid). The electronic quasiparticles of a Fermi liquid possess the Fermi velocity v_F , while the quasi-classical charge carriers in semiconductors have a mean thermal 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 $\Lambda = v\tau$.

[004] Einstein's kinetic equation. 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. Its general form is derived from Einstein's work on diffusion, and may be called Einstein's kinetic equation.

[005] Gaussian pulse. 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

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

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 $2l'\bar{\delta n}$ (for a unit area of the cross-section), where $\bar{\delta n}$ is the average quasiparticle density; on the other hand, the maximum value of the density in the gaussian peak is $V\delta n/\sqrt{2\pi}l' = \sqrt{2/\pi}\bar{\delta n}$ 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 $V = 2l'$ (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 of a gaussian pulse, of course, where $V = l'$. Pulse-like thermoelectric transport has been discussed recently in various contexts.

[006] Thermal pulse. 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.

[007] Heat flow. Such 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 $\mathbf{q} = -cv\Lambda \text{grad}T = -K \text{grad}T$, 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 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.

[008] Thermopower. 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

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

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).

[009] Electric flow. The voltage U 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).

[010] Electric conductivity. 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

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

hence the electric conductivity

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

[011] Joule-Lenz dissipated heat and Peltier heat. 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. 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.

[012] Efficiency quotient. 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

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

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

[013] Figure of merit. 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 $L = \pi^2/3e^2$ 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, 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 $c = (\pi^2/2\mu)nT$, 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.

[014] Thermoelectricity of pulses. 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, whereby a pulse is viewed as a whole. Indeed, 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. Such an electric pulse dissipates gradually the Joule-Lenz heat $-e\delta n l' Q\delta T$ (per unit area of the cross-section); it is easy to see, by making use of (3) and (5), that the Joule-Lenz heat can also 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 the efficiency quotient of the pulse-like transport is the same as that given by (6) 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 stressing out that the electric flow of the pulse-like transport, as given either by (4) or (7), can also be written as

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

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 dissipated Joule-Lenz heat per unit area of the cross-section and per time, *i.e.* the flow of electric power as given by (9), can be written as

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

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. It is easy to see that the equilibrium power $P_{eq} = j_{eq}^2 / \sigma \cdot l$ (per unit area of the cross-section) can also be written as $P_{eq} = \sigma U^2 / l$, which is $P_{eq} = U^2 / r$, where r is the internal electric resistance.

[015] 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 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. 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

$$j_e = -e\delta n l'/(l'/v) = -ev\delta n = j(t'/l')v = j(\tau_{off}/\tau_{on})(l_e/l') , \quad (12)$$

where (7) has been used. The electric flow does not conserve, as the transport is discontinuous. 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 (8) is the energy delivered into the external circuit. The (discontinuous) momentous power delivered into the external circuit is $E_{el}/(l'/v) = (\tau_{off}/\tau_{on})(l_e/l'^2)P_{eq}$, where (11) has been used. It is less relevant; less relevant also is an average external power over the on-time, $E_{el}/\tau_{on} = (\tau_{off}/\tau_{on})(l/l')P_{eq}$. 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 the machine be operated cyclically. 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 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 $f = 1/T$, where $T = \tau_{off} + \tau_{on} = \tau_{off} + l_e/v$, and a certain duration of the on- and off- times.

[016] Pulse frequency. As 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 equilibrium 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.* 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 macroscopic extension l' . For $t_{on} \geq t'$, *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 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.

[017] Power delivered into the external circuit. The Joule-Lenz heat E_{el} 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

$$\bar{P} = (j^2/\sigma)(l'^3/v\Lambda) \cdot \frac{1}{\tau_{on} + \tau_{off}} = P_{eq}(l/l') \cdot \frac{1}{1 + \Lambda l_e/l'^2} , \quad (13)$$

where (10) and (11) 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 (11), $\bar{P} = P = P_{eq}(l/l')$, *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

$$\bar{P}^{max} = \frac{1}{2} \frac{l}{\sqrt{\Lambda l_e}} P_{eq} ; \quad (14)$$

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 $P_{dc} = U^2/4r = P_{eq}/4$, corresponding to a load electric resistance equal to the internal resistance in an equilibrium (drift current) operating regime. One obtains therefore $\bar{P}^{max} = 2(l/\sqrt{\Lambda l_e})P_{dc}$. The optimal power in the pulse operating regime as given by (14) is higher than the equilibrium power, so the pulse thermoelectric machine is therefore superior to an equilibrium one.

[018] Frequency dependence. The external power given by (13) can also be written as

$$\bar{P} = P_{eq}(l/l') \cdot \frac{\tau_{off}}{\tau_{on} + \tau_{off}} = \frac{l}{\sqrt{v\Lambda}} \sqrt{f(1 - \tau_{on}f)} P_{eq} , \quad (15)$$

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 $\tau_{on} = l_e/v$ equation (15) gives also a characteristic dependence of the external power on the load resistance $\sim l_e$.

[019] Numerical estimates. 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 an optimal pulse length $l' = l/10$ the power is $P \simeq 4\text{w/cm}^2$, the maximal power is $\bar{P}^{max} \sim 2\text{w/cm}^2$, *i.e.* an increase factor 5, and the operating frequency $f \simeq 500\text{kHz}$, with a very short on-time ($\tau_{on} \simeq 10^{-6}\text{s}$ for $l_e = 10\text{cm}$). 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 optimal extension $l' = l/30$ the operating frequency is approximately $f \simeq 50\text{kHz}$, the electric power $P \simeq 0.72\text{w/cm}^2$, and the maximal power is $\bar{P}^{max} \sim 0.36\text{w/cm}^2$, *i.e.* an increase factor 15; the on-time is $\tau_{on} \simeq 10^{-5}\text{s}$ (for $l_e = 10\text{cm}$).

[020] Conclusion. 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 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 operating thermoelements. Therefore, it is an high power thermoelectric converter.

[021] Final remarks. The thermoelectric machine described herein is an ideal machine, intended to illustrate the physical principles of a new type of thermoelectric transport, which may be termed the pulse transport. In practice, there are several technical issues which must be addressed, in order to get the increasing performance of this new type of thermoelectric device. First, 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 pulse machine is equal to the ideal efficiency coefficient of the machine operating in a continuous, equilibrium, regime, the technical efficiency may be increased for the pulse machine, as a result of the very basic principle of the pulse transport, which is the diminution of dissipation. Another important issue related to the pulse machine 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 pulse machine, so way is therefore open for employing new classes of thermoelectric materials in pulse machines.

1.4 Claims

[022] A new type of transport in condensed matter, which may be termed the pulse transport, as based on the kinetics of the quasiparticles and elementary excitations.

[023] Identification of Einstein's kinetic equation as the starting point of the pulse transport.

[024] Quantitative estimation of the characteristic parameters both of the classical and pulse transport, both for metals and semiconductors.

[025] Revisiting the classical thermoconduction theory and pointing out a new, more appropriate, concept of "figure of merit".

[026] Description of the cyclic working of the pulse thermoelectric machine, with a superior performance, as due to the pulse concentration of charge, limitation of the diffusion and diminution of the dissipation.

[027] Establishing the equations for the optimal operation of the pulse thermoelectric machine, including the efficiency coefficient.

[028] Establishing the reversible character of the pulse thermoelectric machine, which may also work as a electrothermal pulse cooling machine.

1.5 List of figures

Fig 1. Heating a thermoelectric sample

Fig 2. Diffusion limits the free transport

Fig 3. Pulse and thermoelectric "condenser"

Fig 4. Discharge of the "condenser"

Fig 5. "Deflating" the pulse, ready for a new operation

Fig 6. Diffusion of a gaussian pulse

Fig 7. Equilibrium regime

Fig 8. A thermoelectric gaussian pulse

Fig 9. Building up a gaussian pulse in a thermoelectric "condenser"

Fig 10. Discharging a gaussian pulse in the thermoelectric "condenser"

Fig 11. "Deflating" the pulse while buiding up a new one

newpage

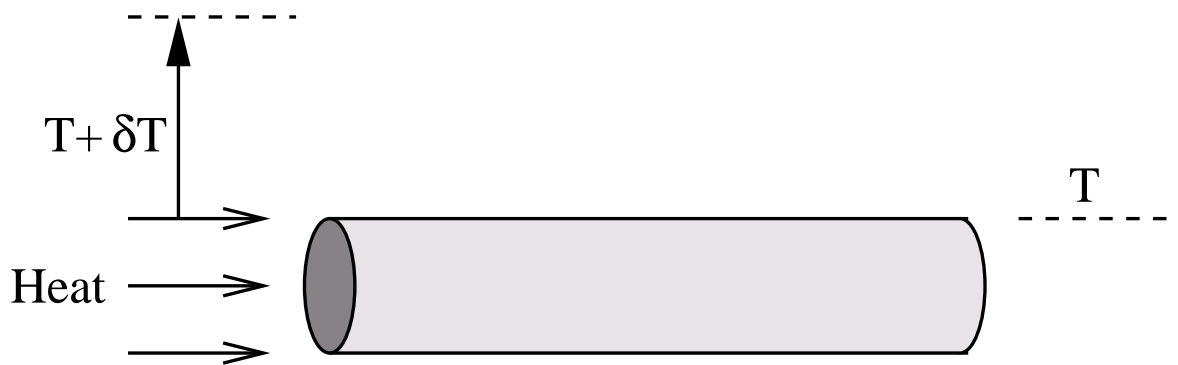


Figure 1: Heating a thermoelectric sample

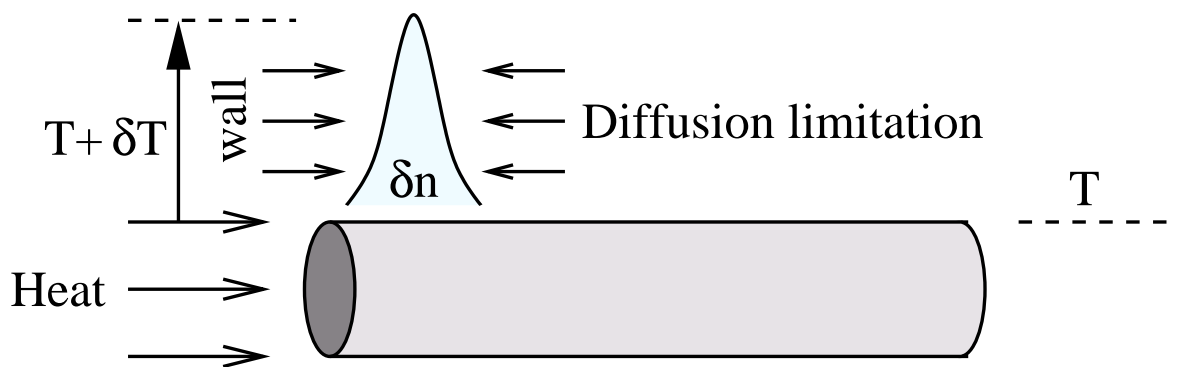


Figure 2: Diffusion limits the free transport

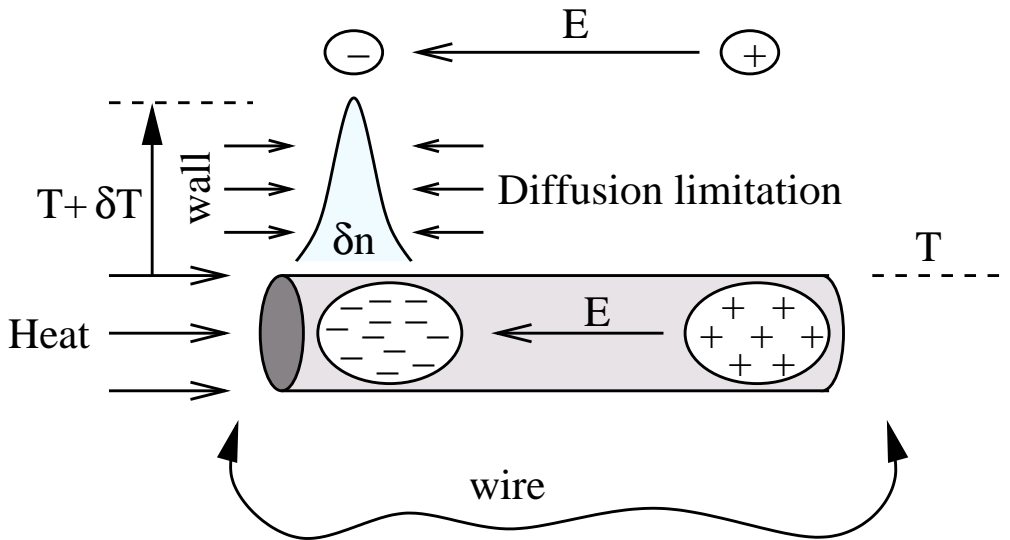


Figure 3: Pulse and thermoelectric "condenser"

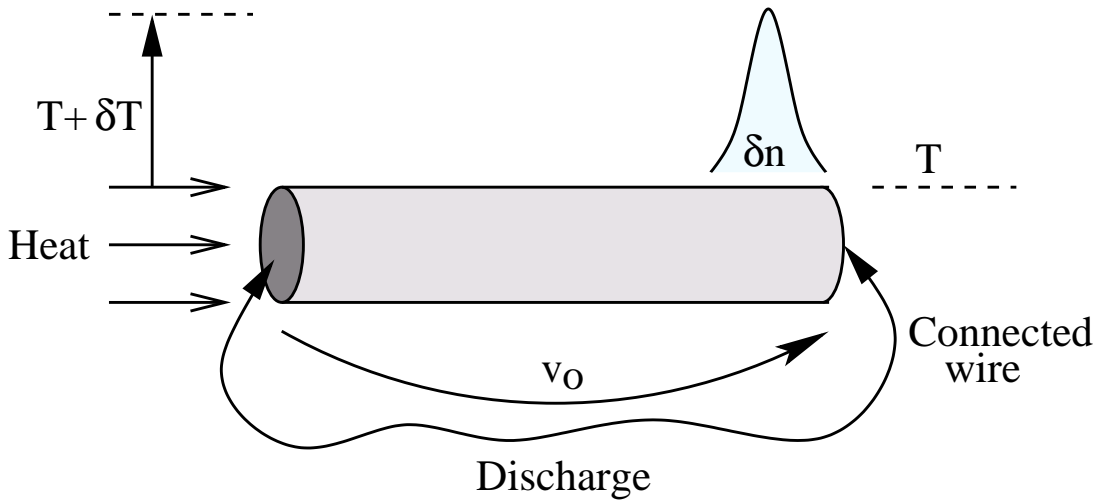


Figure 4: Discharge of the "condenser"

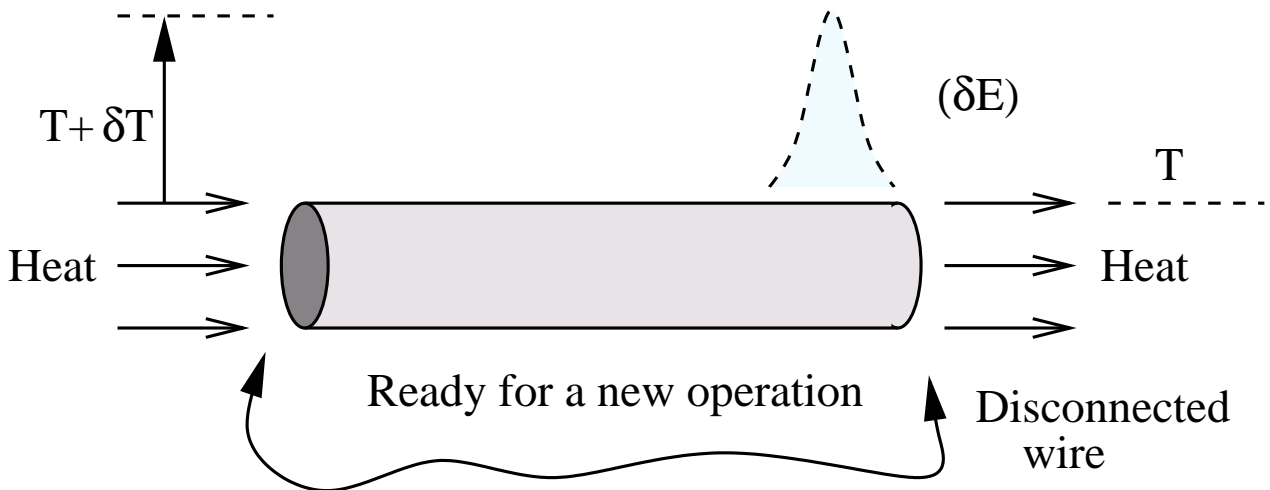


Figure 5: "Deflating" the pulse, ready for a new operation

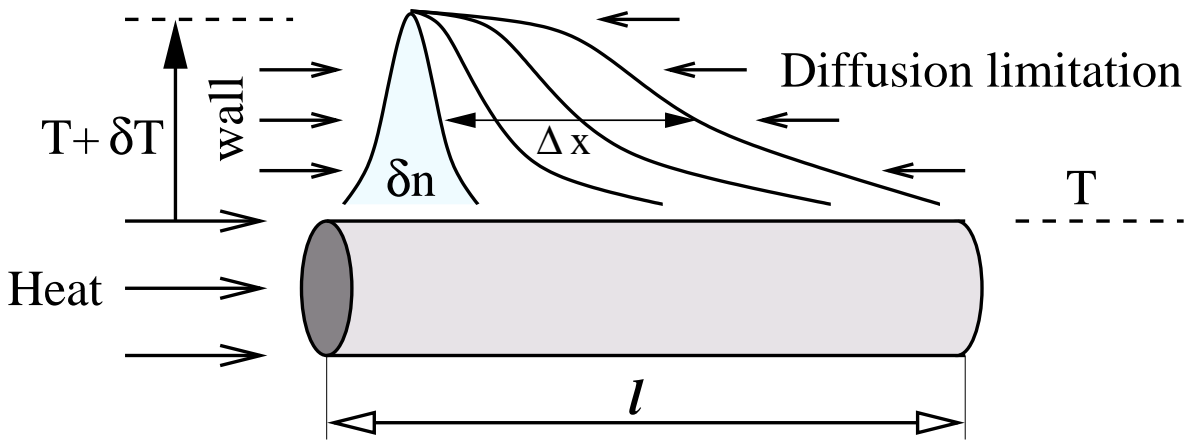


Figure 6: Diffusion of a gaussian pulse

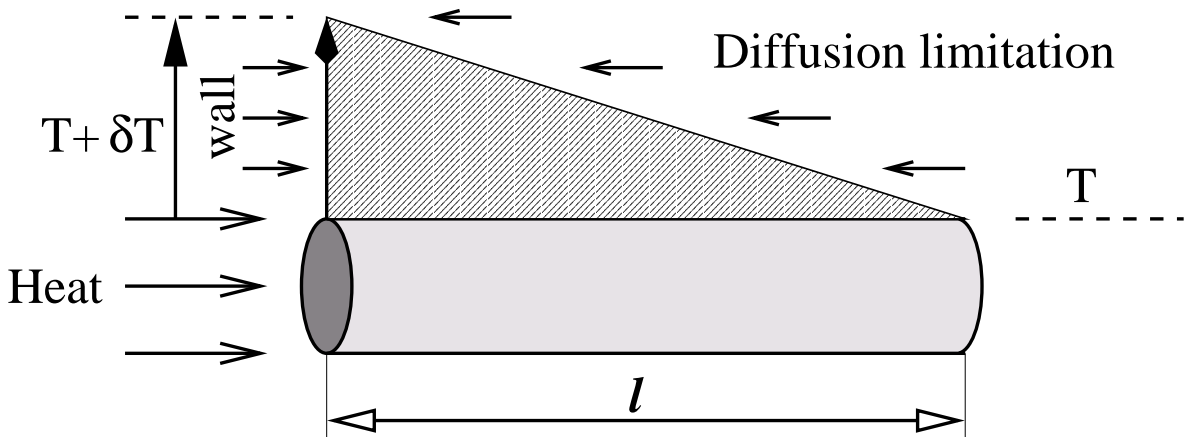


Figure 7: Equilibrium regime

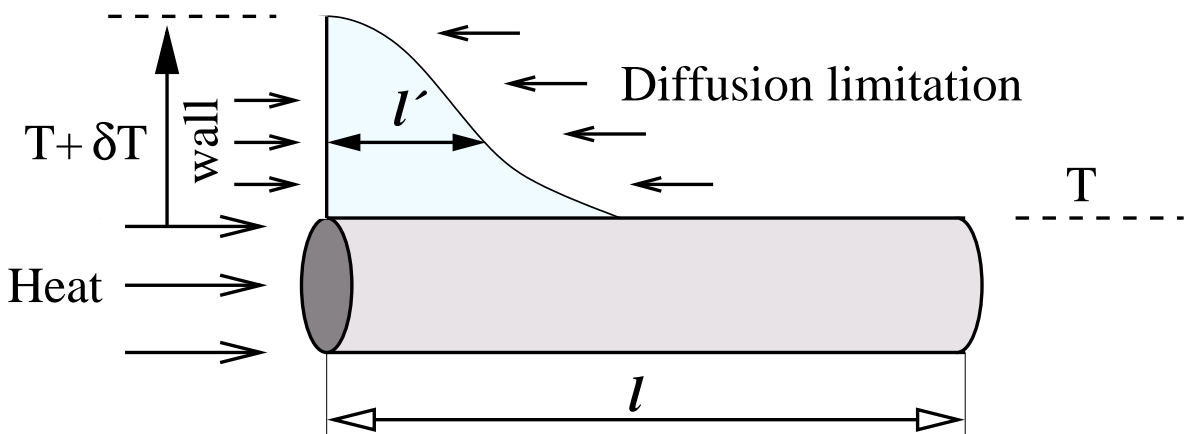


Figure 8: A thermoelectric gaussian pulse

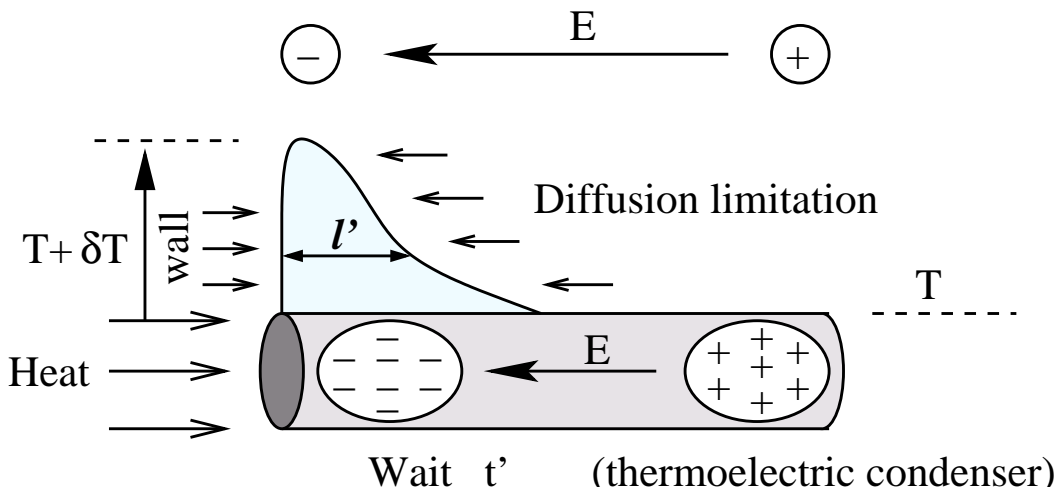


Figure 9: Building up a gaussian pulse in a thermoelectric "condenser"

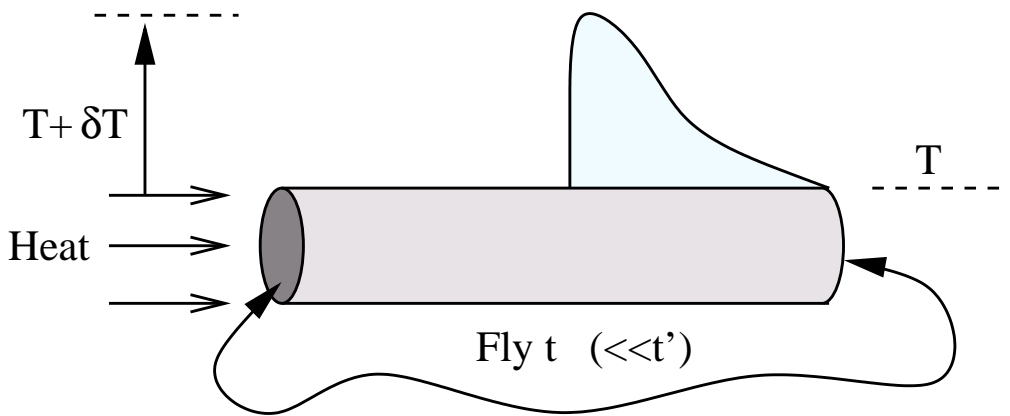


Figure 10: Discharging a gaussian pulse in the thermoelectric "condenser"

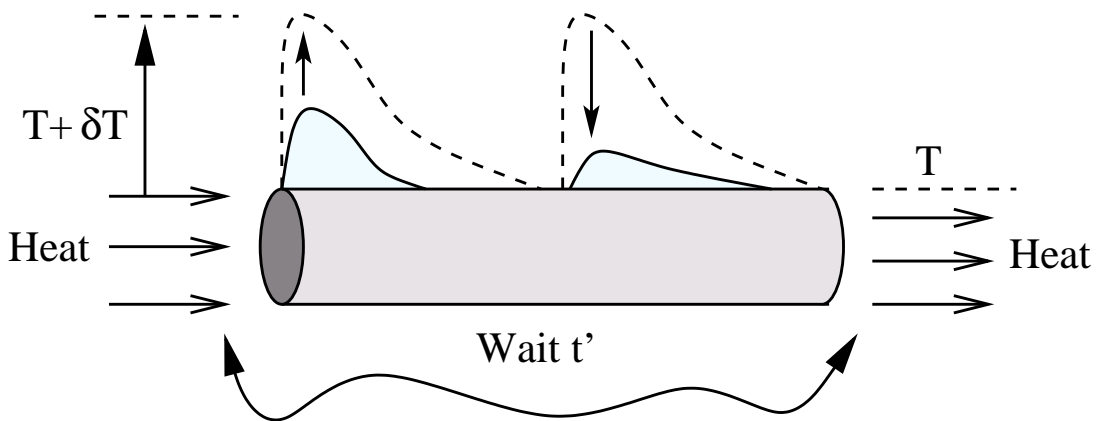


Figure 11: "Deflating" the pulse while buiding up a new one