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Space charges in metals during non-stationary heat flow

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Abstract
It is shown that during non-stationary heat flow in a metal the condition of charge neutrality inside the metal is violated by transient space charges which accompany the temperature relaxation. As expected for an effect of thermoelectricity, the magnitude of the space charges is small. It depends on a new parameter Q' which is related to, but different from the absolute thermopower. Both the case of an infinite system and that of a parallel plate with free boundaries are treated.

1. Introduction

It is not always appreciated that the condition of charge neutrality in metals only holds under certain conditions regarding the distribution of temperature inside a metallic body. These conditions are either a homogeneous temperature or a stationary inhomogeneous temperature distribution with heat flow. Under conditions of non-stationary heat flow, however, transient electrical space charges appear and charge neutrality is violated. This result lies at the heart

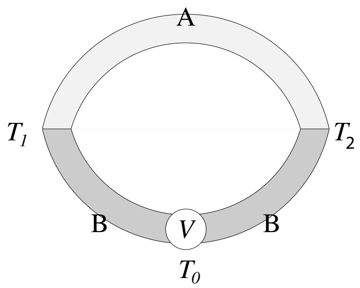

Figure 1. A thermoelectric circuit consisting of two metallic wires A and B. Wire B is interrupted by a voltmeter. In the stationary case, the points of contact of A and B are held at the different temperatures T_1 and T_2. The contacts to the voltmeter are assumed to be at the ambient temperature T_0. (Note that the position of the voltmeter is different from that in figure 13.1 of reference [3].)

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of thermoelectricity as can be seen by considering a thermoelectric circuit (figure 1): for stationary temperature gradients in the metallic wires A and B, the electrochemical potential measured by the voltmeter (which interrupts one of the wires) is purely electric and arises from electric charges located at the metal interfaces and surfaces of the circuit [1, 2]. When the external heat links are removed and the temperature gradients are allowed to relax via non-stationary heat flow, however, these charges turn into transient electric space charges.

It is the purpose of this paper to give a systematic derivation of these results on the basis of the established semiclassical theory of electron transport in metals [3]. The paper is organized as follows. In section 2 the semiclassical theory of electron transport with standard definitions is briefly reviewed. In section 3 the problem is treated for an infinite homogeneous metallic medium. Section 4 deals with the simplest case of a metallic system with boundaries, the infinitely extended parallel plate of finite thickness. In section 5 a short summary is given.

2. Constitutive equations

From a Boltzmann equation for the conduction electrons, the expressions for particle and heat current density $\vec{j}$ and $\vec{q}$ are derived as [3]

$$\vec{j} = -l_{11}(e\vec{E} + \vec{\nabla}\mu) - (l_{12}/T_0)\,\vec{\nabla}T \tag{2.1}$$

$$\vec{q} = -l_{21}(e\vec{E} + \vec{\nabla}\mu) - (l_{22}/T_0)\,\vec{\nabla}T \tag{2.2}$$

where l_{ij} $(i, j = 1, 2)$ are the elements of a symmetric 2×2 matrix of transport coefficients. $\vec{E}$ stands for the electric field, μ for the non-electric part of the chemical potential, T_0 for the global equilibrium temperature and $(-e)$ for the electronic charge. l_{11} is related to the static electrical conductivity σ by

$$l_{11}e^2 = \sigma. \tag{2.3}$$

The expressions are valid under the usual conditions for a hydrodynamic description, which require that spatial and temporal variations are slow compared with the mean free path and mean relaxation time of the conduction electrons. Under the condition of zero particle current

$$\vec{j} = 0 \tag{2.4}$$

one obtains Fourier's law for the heat current density:

$$\vec{q} = -\lambda\,\vec{\nabla}T \tag{2.5}$$

with the thermal conductivity λ given by

$$\lambda = (l_{22} - l_{12}^2/l_{11})/T_0 \tag{2.6}$$

and the expression for the thermoelectric field

$$\vec{E} + \vec{\nabla}\mu/e = Q\,\vec{\nabla}T \tag{2.7}$$

with the absolute thermopower (or Seebeck coefficient) Q given by

$$Q = -l_{12}/(l_{11}T_0 e). \tag{2.8}$$

The second term on the r.h.s. of the expression for λ is due to the contribution of the thermoelectric field (2.7) to the heat current (2.2). For time-dependent processes, the linear hydrodynamic equations of motion for the conduction electrons are the continuity equations for particle and heat current given by

$$\partial_t n + \vec{\nabla}\cdot\vec{j} = 0 \tag{2.9}$$

$$T_0\,\partial_t s + \vec{\nabla}\cdot\vec{q} = 0. \tag{2.10}$$

s is the electronic entropy density. Entropy production, i.e. by Joule heat, is neglected in our linear theory, since it depends quadratically on the deviations from equilibrium. Equations (2.9) and (2.10) are supplemented by Gauss's law

$$\vec{\nabla} \cdot \vec{E} = -e\, \delta n / \varepsilon_0 \tag{2.11}$$

where δn denotes the deviation of the electronic number density n from the constant equilibrium density n_0.

3. The initial-value problem for an infinite medium ('bulk')

Expanding μ and s as functions of n and T, we obtain from (2.9), (2.10), (2.11) the following coupled partial DEs for[1] $\delta n(\vec{r}, t)$ and $\delta T(\vec{r}, t)$:

$$\partial_t n = -\omega_\sigma (1 - \xi^2 \Delta)\, \delta n - \omega_\sigma \frac{\varepsilon_0}{e} Q' \,\Delta T \tag{3.1}$$

$$T_0 s_{|_n}\, \partial_t n + T_0 s_{|_T}\, \partial_t T = -(l_{12} e^2/\varepsilon_0)(1 - \xi^2 \Delta)\, \delta n + \lambda' \,\Delta T. \tag{3.2}$$

Here the following abbreviations are used: $\mu_{|_n}$, $\mu_{|_T}$, $s_{|_n}$, $s_{|_T}$ are the partial derivatives of μ and s with respect to n and T. Also,

$$\omega_\sigma = \sigma/\varepsilon_0. \tag{3.3}$$

ω_σ for metals is a high frequency of the order of 10^{16} s^{-1}. ξ is the electronic screening length defined by

$$\xi^2 = (\varepsilon_0/e^2)\mu_{|_n}. \tag{3.4}$$

For metals, ξ is of the order of the interatomic distance a_0. The appearance of a microscopic time $(1/\omega_\sigma)$ and length (ξ) for macroscopically prepared initial conditions (see below and section 4) is a characteristic feature of problems involving charge transport. The remaining abbreviations are

$$Q' = Q - \mu_{|_T}/e \tag{3.5}$$

$$\lambda' = l_{12}\mu_{|_T} + l_{22}/T_0. \tag{3.6}$$

As we shall see below, the quantity Q' has a direct physical meaning.

For given initial conditions $\delta n(\vec{r}, t = 0)$, $\delta T(\vec{r}, t = 0)$ the DEs (3.1) and (3.2) can be solved by Fourier–Laplace transformation. We determine the *initial conditions* for a situation in which particle currents are absent and stationary heat currents flow from heat sources to sinks described by a heat source density $h(\vec{r})$. Because condition (2.4) is valid for the initial condition, we can use (2.5) and (2.7) to calculate the Fourier transforms $\tilde{n}(\vec{k}, t = 0)$ and $\tilde{T}(\vec{k}, t = 0)$ of the initial values. From (2.7) together with Gauss's law (2.11) we find

$$\tilde{n}(\vec{k}, t = 0) = \frac{(\varepsilon_0/e) Q' k^2}{1 + \xi^2 k^2} \tilde{T}(\vec{k}, t = 0). \tag{3.7}$$

With

$$\vec{\nabla} \cdot \vec{q}(\vec{r}, t = 0) = h(\vec{r}) \tag{3.8}$$

using Fourier's law (2.5) we obtain

$$\tilde{T}(\vec{k}, t = 0) = \frac{\tilde{h}(\vec{k})}{\lambda k^2} \tag{3.9}$$

[1] Note that in all derivatives the deviations δn and δT from equilibrium may be replaced by the full values n and T.

which yields

$$\tilde{n}(\vec{k}, t = 0) = \frac{(\varepsilon_0/e)Q'}{\lambda(1 + \xi^2 k^2)}\tilde{h}(\vec{k}). \tag{3.10}$$

For a description on macroscopic length scales we can drop $\xi^2 k^2$ in comparison to unity. In a macroscopic description, therefore, the initial distribution of space charge is proportional to the heat source density:

$$-e\,\delta n(\vec{r}, t = 0) = -(\varepsilon_0 Q'/\lambda)h(\vec{r}). \tag{3.11}$$

The Fourier–Laplace transforms of equations (3.1), (3.2) read

$$(s + \omega_\sigma(1 + \xi^2 k^2))\hat{n}(\vec{k}, s) - \omega_\sigma \frac{\varepsilon_0}{e} Q' k^2 \hat{T}(\vec{k}, s) = \tilde{n}(\vec{k}, t = 0) \tag{3.12}$$

$$\begin{aligned} sT_0\big(s_{|_n}\hat{n}(\vec{k}, s) + s_{|_T}\hat{T}(\vec{k}, s)\big) + (l_{12}e^2/\varepsilon_0)(1 + \xi^2 k^2)\hat{n}(\vec{k}, s) + \lambda' k^2 \hat{T}(\vec{k}, s) \\ = T_0(s_{|_n}\tilde{n}(\vec{k}, t = 0) + s_{|_T}\tilde{T}(\vec{k}, t = 0)). \end{aligned} \tag{3.13}$$

If we solve these algebraic equations for the Fourier–Laplace transforms $\hat{n}(\vec{k}, s)$ and $\hat{T}(\vec{k}, s)$ of $\delta n(\vec{r}, t)$ and $\delta T(\vec{r}, t)$, we obtain expressions with two poles in the complex s-plane. For wavevectors $\vec{k}$ occurring in a macroscopic description, i.e. for

$$ka_0 \ll 1 \tag{3.14}$$

where a_0 is the mean interatomic distance, these poles correspond to very different timescales. One corresponds to a very high relaxation frequency of the order of ω_σ, which sets the timescale on which charge neutrality is established under isothermal conditions. In the k-range occurring in a macroscopic description, the other pole corresponds to a much lower relaxation frequency which depends on wavevector and is related to the heat conduction equation, as shown below. For a macroscopic description we are interested only in the behaviour of the solution on this longer timescale.

We have to restrict ourselves to such a macroscopic description, because the constitutive equations (2.1), (2.2) for the current densities $\vec{j}$ and $\vec{q}$ are not strictly valid for components of wavevectors of order a_0^{-1} and/or of frequencies of order ω_σ [4]. At such large wavevectors and high frequencies the transport coefficients l_{ij} themselves would depend on wavevector and frequency. Without an explicit model for this extra dependence, working out the solution on a short length scale corresponding to a_0 and a short timescale corresponding to ω_σ^{-1} would be of limited value. It is worth emphasizing, however, that we can determine the correct solution for small k and s, corresponding to long wavelengths and times, without knowledge of the form of the transport coefficients at large wavevectors and high frequencies.

We therefore proceed with the approximation of dropping terms s/ω_σ in comparison to unity everywhere in (3.12) and (3.13). In addition, we drop ξk in comparison to unity because of (3.14). This leads to

$$\hat{T}(\vec{k}, s) = \frac{(1 + [\alpha + \beta]k^2)\tilde{T}(\vec{k}, t = 0)}{s(1 + \alpha k^2) + [\lambda/(T_0 s_{|_T})]k^2} \tag{3.15}$$

where

$$\alpha = (\varepsilon_0 s_{|_n}/(e s_{|_T}))Q' \tag{3.16}$$

$$\beta = \varepsilon_0 Q Q'/s_{|_T}. \tag{3.17}$$

$|\alpha|$ and $|\beta|$ both have the dimension of length squared. With an order-of-magnitude estimate for the degenerate electron gas in a metal

$$s \sim nk_B T/T_F \tag{3.18}$$

$$Q, Q' \sim s/(ne) \tag{3.19}$$

where T_F is the Fermi temperature and k_B is Boltzmann's constant, we find with $n = a_0^{-3}$

$$|\alpha|, |\beta| \sim a_0^2 \frac{k_B T}{e^2/(\varepsilon_0 a_0)} \frac{T}{T_F} \ll a_0^2. \tag{3.20}$$

Consequently, in a macroscopic description the correction terms αk^2 and βk^2 may be safely neglected, and we arrive at the result

$$\hat{T}(\vec{k}, s) = \frac{\tilde{T}(\vec{k}, t = 0)}{s + [\lambda/(T_0 s_{|T})]k^2} \tag{3.21}$$

which corresponds exactly to the heat conduction equation

$$\partial_t T - a \nabla T = 0 \tag{3.22}$$

with thermal diffusivity $a = \lambda/(T_0 s_{|T})$, both with regard to the position and the residue of the pole. In other words: on the timescale of heat conduction on macroscopic length scales, the correct result for the solution $\delta T(\vec{r}, t)$ can be obtained from the heat conduction equation using the *full* initial value $\delta T(\vec{r}, t = 0)$.

The electric space charge $(-e)\,\delta n(r, t)$ accompanying heat conduction follows immediately from equation (3.1) if $\partial_t n$ is neglected in comparison to $\omega_\sigma\,\delta n$. On a macroscopic length scale we thus obtain the relation

$$-e\,\delta n(\vec{r}, t) = +\varepsilon_0 Q'\,\Delta T(\vec{r}, t). \tag{3.23}$$

This is a remarkable result: during temperature relaxation by heat conduction inside a metal, the condition of local charge neutrality is violated. The quantity Q' has a direct physical meaning since it determines the magnitude of the space charges.

It is worth pointing out that the validity of the heat conduction equation (3.22) is intimately connected with the existence of the space charges given by equation (3.23), although these are small. Using the equations of section 2 it is easy to show that under conditions of zero particle current (equation (2.4)) the heat conduction equation does not hold, despite the fact that Fourier's law (2.5) can be derived from this condition.

4. The parallel plate

It is of interest to study the same problem for a system with boundaries, at which electric charges are localized initially. We first derive the exact solution as it follows mathematically from the constitutive equations presented in section 2. For the reasons mentioned already in section 3 (following equations (3.12), (3.13)), only the small-wavevector and low-frequency components of this mathematical solution, which are relevant for a macroscopic description, are physically correct. Therefore, we are finally interested only in the macroscopic form of the solution. Since the solution to the mathematical problem is obtained as a Fourier series, the macroscopic form of the solution corresponds to a truncated Fourier series, where the components of short wavelength are suppressed.

The simplest case of such a system is the parallel metallic plate of thickness l and infinite horizontal extent. We assume that all variables depend only on the coordinate in the direction normal to the plate (z), which renders the problem one-dimensional. The equations of motion (2.9), (2.10) for this one-dimensional problem read

$$\partial_t n(z, t) + \partial_z j_z(z, t) = 0 \tag{4.1}$$

$$T_0\,\partial_t s(z, t) + \partial_z q_z(z, t) = 0 \tag{4.2}$$

complemented by Gauss's law

$$\partial_z E_z(z, t) = -e\,\delta n(z, t)/\varepsilon_0. \tag{4.3}$$

The boundary conditions are

$$j_z(0,t) = j_z(l,t) = q_z(0,t) = q_z(l,t) = 0 \tag{4.4}$$

and

$$E_z(0,t) = E_z(l,t) = 0. \tag{4.5}$$

The boundary conditions for E_z are due to the assumed overall charge neutrality of the plate, which gives zero electric field outside the plate.

The initial conditions for an initial situation of stationary heat flow across the electrically insulated plate are

$$j_z(z,t=0) = 0 \qquad \partial_z q_z(z,t=0) = 0. \tag{4.6}$$

From the first of these we derive, using expression (2.1) and Gauss's law (2.11), the equation

$$E_z(z,t=0) - \xi^2\,\partial_z^2 E_z(z,t=0) = Q'\,\partial_z T(z,t=0). \tag{4.7}$$

Since $j_z(z,t=0)=0$ implies $\partial_z j_z(z,t=0)=0$, taking this in combination with the second of the boundary conditions (4.6) we obtain the equations

$$\partial_z^2 T(z,t=0) = 0 \tag{4.8}$$

$$\delta n(z,t=0) - \xi^2\,\partial_z^2 n(z,t=0) = 0. \tag{4.9}$$

ξ^2 and Q' are given by (3.4) and (3.5). The solutions of these equations together with Gauss's law (4.3) and the boundary conditions (4.5) for E_z are

$$\delta T(z,t=0) = T'\cdot(z-l/2) \qquad T' = \text{constant} \tag{4.10}$$

$$\delta n(z,t=0) = \frac{\varepsilon_0}{e\xi} Q'T' \frac{\sinh[(z-l/2)/\xi]}{\cosh[l/(2\xi)]} \tag{4.11}$$

$$E_z(z,t=0) = Q'T'\left(1 - \frac{\cosh[(z-l/2)/\xi]}{\cosh[l/(2\xi)]}\right). \tag{4.12}$$

For illustration, the z-dependence of the initial charge density $(-e)\,\delta n$ and of the initial electric field E_z are plotted on a microscopic scale in figure 2. Because of the atomic scale of ξ and the limitation of the validity of the constitutive equations (2.1) and (2.2) mentioned above, this

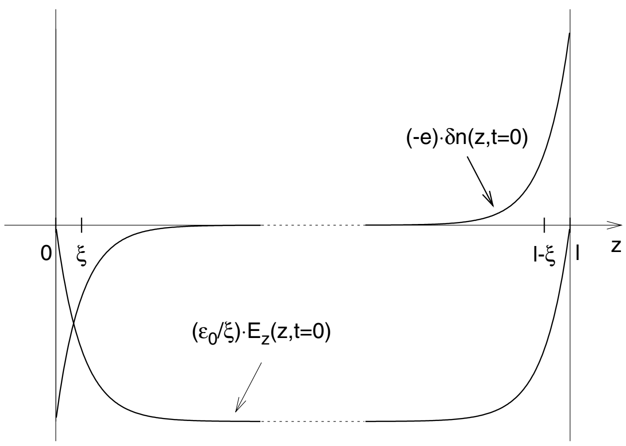

Figure 2. A plot of the initial conditions equations (4.11), (4.12) on a microscopic length scale for a plate of thickness l. For the two curves the same units are used. ($Q'T' < 0$.)

result is only qualitatively, not quantitatively, correct. For a plate of macroscopic thickness l the initial charge density is practically zero inside the plate, and the initial electrical field is practically constant, except for surface layers with a width of the order of ξ, which is of the order of the interatomic distance. On macroscopic length scales the initial charge density is a surface charge, and the initial electric field inside the plate is constant with a discontinuous drop to zero at the surfaces. As in the bulk (section 3), the initial charge density is located at the sources and sinks of the stationary initial heat flow, which are located at the surfaces.

It is convenient to solve the equations of motion (4.1), (4.2) for variables which obey homogeneous boundary conditions like equations (4.5) for E_z. A second variable obeying the same boundary conditions is found as

$$\tau(z,t) = \int_0^z \mathrm{d}z'\, \delta T(z',t). \tag{4.13}$$

The boundary condition

$$\tau(0,t) = 0 \tag{4.14a}$$

follows from this definition. The second boundary condition

$$\tau(l,t) = 0 \tag{4.14b}$$

is proved below. The equations of motion for $E_z(z,t)$ and $\tau(z,t)$ are obtained by integrating (4.1), (4.2) and (4.3) from $z' = 0$ to $z' = z$ using the boundary conditions (4.4) and (4.5). This results in

$$-\frac{\varepsilon_0}{e}\,\partial_t E_z(z,t) + j_z(z,t) = 0 \tag{4.15}$$

$$-\frac{\varepsilon_0}{e} T_0 s_{|n}\,\partial_t E_z(z,t) + T_0 s_{|T}\,\partial_t \tau(z,t) + q_z(z,t) = 0. \tag{4.16}$$

Setting $z = l$ in the second equation yields

$$\partial_t \tau(l,t) = 0. \tag{4.17}$$

Since $\tau(l, t = 0)$ is zero because of (4.10), the second boundary condition (4.14b) for τ is proven. With the explicit expressions (2.1), (2.2) for particle and heat current j_z and q_z inserted into the equations of motion (4.15), (4.16), these become

$$(\partial_t + \omega_\sigma(1 - \xi^2\,\partial_z^2))E_z(z,t) - \omega_\sigma Q'\,\partial_z^2 \tau(z,t) = 0 \tag{4.18}$$

$$((\varepsilon_0/e)T_0 s_{|n}\,\partial_t + e l_{12}(1 - \xi^2\,\partial_z^2))E_z(z,t) - (T_0 s_{|T}\,\partial_t - \lambda'\,\partial_z^2)\tau(z,t) = 0. \tag{4.19}$$

To solve this pair of partial DEs with homogeneous boundary conditions (4.5), (4.14a), (4.14b), we can apply Fourier's method, as is familiar from the problem of the vibrating string with fixed ends. Writing

$$E_z(z,t) = \sum_{n=1}^{\infty} E_z(k_n,t)\sin(k_n z) \tag{4.20a}$$

$$\tau(z,t) = \sum_{n=1}^{\infty} \tau(k_n,t)\sin(k_n z) \tag{4.20b}$$

with $k_n = n\pi/l$, $n = 1, 2, 3, \ldots$, we obtain the ordinary DEs for the time-dependent Fourier coefficients $E_z(k_n,t)$ and $\tau(k_n,t)$ as

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} + \omega_\sigma(1 + \xi^2 k_n^2)\right)E_z(k_n,t) + \omega_\sigma Q' k_n^2 \tau(k_n,t) = 0 \tag{4.21}$$

$$\left((\varepsilon_0/e)T_0 s_{|n}\frac{\mathrm{d}}{\mathrm{d}t} + e l_{12}(1 + \xi^2 k_n^2)\right)E_z(k_n,t) - \left(T_0 s_{|T}\frac{\mathrm{d}}{\mathrm{d}t} + \lambda' k_n^2\right)\tau(k_n,t) = 0. \tag{4.22}$$

Because of the symmetry of the initial conditions, only odd values of n occur. The initial-value problem for this pair of ordinary DEs can be solved by Laplace transformation. Arguing as in the bulk case, we proceed with the same approximation of dropping s/ω_σ and $\xi^2 k^2$ in comparison to unity. Using the relation for the initial conditions

$$E_z(k_n, t = 0) \approx -Q' k_n^2 \tau(k_n, 0) \tag{4.23}$$

which follows from (4.7), we find for the Laplace transform

$$\hat{\tau}(k_n, s) = \int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st} \tau(k_n, t) \tag{4.24}$$

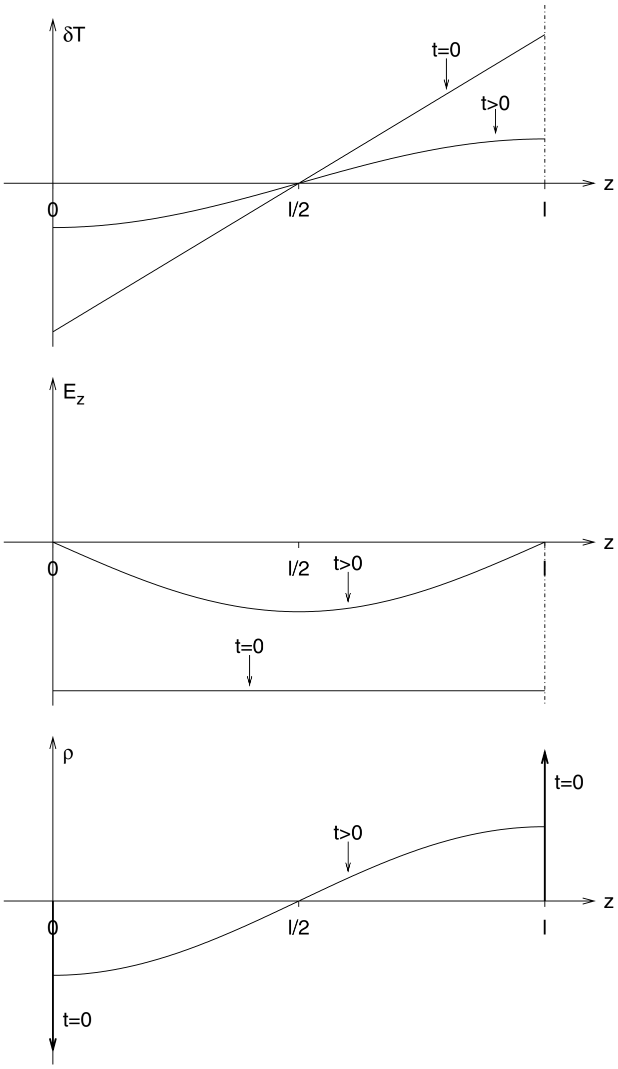

Figure 3. The temperature variation δT, electric field E_z and electric charge density $\rho = (-e)\,\delta n$ across an insulated parallel plate of thickness l with constant initial temperature gradient T' on a macroscopic scale. The times are $t = 0$ and a later time t where $a(\pi/l)^2 t = 1$ holds. $Q' < 0$. a is the thermal diffusivity. In the diagram for ρ the arrows at $z = 0$ and $z = l$ mark the initial surface charges (see also the text).

the result

$$\hat{\tau}(k_n, s) = \frac{\left(1 + [\alpha + \beta]k_n^2\right)\tau(k_n, t = 0)}{s(1 + \alpha k_n^2) + [\lambda/(T_0 s_{|T})]k_n^2} \tag{4.25}$$

with α and β given by (3.16), (3.17), which is analogous to (3.15). As argued in section 3, on a macroscopic length scale the correction terms αk_n^2 and βk_n^2 can be neglected, so $\tau(z, t)$ and its z-derivative $\delta T(z, t)$ obey the heat conduction equation (3.22). The electric field accompanying the time-dependent heat conduction is obtained from (4.18) in the same approximation as

$$E_z(z, t) = Q' \, \partial_z T(z, t) \tag{4.26}$$

which is analogous to the result (3.23). For a temperature gradient of 100 K cm^{-1} and $|Q'| = 10\ \mu$V K^{-1} this yields a weak electric field of only 1 mV cm^{-1}.

A qualitative illustration of the results for δT, E_z and the charge density $\rho = -e\,\delta n$ is shown in figure 3 on a macroscopic scale. At $t = 0$ the temperature gradient and electric field are constant across the plate. The initial charge density is given by two delta peaks located at the plate surfaces at $z = 0$ and $z = l$. The time $t > 0$ is chosen as $(a(\pi/l)^2)^{-1}$, where a is the thermal diffusivity. At this time, only the components with the smallest wavevector $k_1 = \pi/l$ are still appreciable. All components with larger wavevectors (k_n with $n \geqslant 3$) have already decayed. A distribution of space charge inside the plate has formed from what remains of the initial surface charges.

5. Summary

We have shown that the condition of charge neutrality inside a metal is transiently violated during non-stationary heat flow. The magnitude of the space charges, given by equation (3.23), is small, but their existence is necessary for the macroscopic heat conduction equation (3.22) to hold. A result of more mathematical interest is the applicability of Fourier's method to the plate problem with boundary conditions, for which the electric field and the integrated temperature (4.13) are conveniently chosen as dynamic variables.

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