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The Benedicks effect: Nonlocal electron transport in metals

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The Benedicks effect is the voltage difference between two points in a solid that are at the same temperature. A nonzero value may be obtained if the temperature profile between the points is asymmetric. We derive the nonlocal transport theory of a metal from the Boltzmann equation, and use the results to discuss the Benedicks effect. The nonlocal theory is needed whenever the electron mean free path has the same size as variations in the gradients of the voltage, temperature, or chemical potential.

I. INTRODUCTION

Electron transport is inherently nonlocal. The electrons arrive at a point having brought their energy from some place else. Usually a local theory is adequate for transport, since the mean free path of the electrons is usually short compared with spatial variations in the temperature, voltage, or density.[1-3] However, laser heating of materials can produce transient heat pulses with very large thermal gradients.[4] In this case, the nonlocal theory is required.

The Benedicks effect[5] is the voltage difference between two points in a solid which are at the same temperature. It is related to thermoelectric phenomena, where a voltage difference may exist between two points which are at different temperatures.[6] The Benedicks effect was observed long ago in semiconductors.[7] The effects are expected to be much smaller in metals.[8] Recent experiments observed a voltage along a metal surface with an oscillatory temperature profile. It was suggested that this voltage was caused by the Benedicks effect.[9] Here we provide a theory of the Benedicks effect. We show that the phenomenon is caused by the nonlocal nature of the electron transport. We prove several theorems regarding the occurrence of the effect.

Recently we shared in deriving a theory of nonlocal heat transport for insulators where the heat is carried by phonons.[10-12] Here the relevant experiments were in silicon, in which large thermal gradients were produced by laser annealing.[4] Now we wish to extend this theory to include nonlocal transport in metals. We calculate the nonlocal transport of the electrical conductivity, the Seebeck coefficient, and the thermal conductivity. The derivation is somewhat similar to our earlier theory of heat transport by phonons.

The local version of our transport equations are[13]

$$\mathbf{J}=-\frac{\sigma}{e}(\nabla\mu-S\nabla T)\ , \tag{1}$$

$$\mathbf{J}_Q=\frac{\sigma ST}{e}\nabla\mu-\kappa\nabla T\ . \tag{2}$$

The linear transport coefficients are electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (κ). Gradients in the temperature (T) and chemical potential (μ) provide the driving forces. These local equations require modification whenever the electron mean free path (MFP) is long compared with the distance scale of variations in the driving forces.

This paper was inspired by the recent theory in Ref. 9. These authors consider the case of large thermal gradients and discuss the *nonlinear* thermoelectric response. While this phenomena is certainly nonlinear, we think the important aspect of the phenomena is its *nonlocal* character. Boltzmann's equation for electrons is solved exactly, and exact expressions are provided for the transport coefficients. All coefficients are nonlocal. The nonlinear solution of Ref. 9 is an approximate solution which we obtain as the first two terms in a series expansion of our result. However, our nonlocal solution is obtained in closed form, without the need for a series expansion.

II. NONLOCAL THERMOELECTRIC CURRENT

Consider a metal with a temperature distribution $T(z)$. We solve for the heat and electrical currents generated by this temperature distribution. Although we are describing a transient process, we initially ignore the temporal response of the electron distribution. Instead, we consider the spatial response by examining the Boltzmann equation for the electron distribution

$$\mathbf{v}_k\cdot\nabla n_k(z)=-\frac{n_k-n_{k0}}{\tau}\ , \tag{3}$$

$$n_{k0}=\frac{1}{e^{\xi_k/k_BT(z)}+1}\ , \tag{4}$$

$$\xi_k=\frac{k^2}{2m}-\mu(z)\ . \tag{5}$$

The chemical potential μ depends upon temperature, and so it also depends upon position.

We want to find the actual distribution of electrons $n_k(z)$ in terms of the equilibrium distribution n_{k0} which depends upon position z through the local temperature $T(z)$. We have assumed a relaxation-time approximation for the scattering term. Since we work at high temperatures, this approximation is valid. We also assume that the temperature profile varies in only one dimension. This approximation, which applies to many experimental situations, permits an exact solution to Boltzmann's equation in terms of nonlocal response. The theory can be expanded to transport in more than one dimension by following the procedure of Ref. 12. We also assume that the material is homogeneous, so that the only variation in z is caused by variations in the temperature.

Equation (1) can be solved following the steps used by Mahan and Claro.[10–12] The symbol $\nu = \cos\theta$, where θ is the angle between $\mathbf{k}$ and $\hat{\mathbf{z}}$. For $\nu > 0$ one has

$$n_k(z) = \int_{-\infty}^{z} dz' \frac{1}{\nu l(z')} n_{k0}(z') \exp\left[-\int_{z'}^{z} dz'' \frac{1}{\nu l(z'')} \right] , \tag{6}$$

while for $\nu < 0$ one has

$$n_k(z) = -\int_{z}^{\infty} dz' \frac{1}{\nu l(z')} n_{k0}(z') \exp\left[\int_{z}^{z'} dz'' \frac{1}{\nu l(z'')} \right] . \tag{7}$$

The mean free path of the electron is $l(z) = v_k \tau(k,z)$, where the lifetime depends upon position if it depends upon temperature. The possible forms for the MFP are discussed below.

The electrical current is obtained by integrating over the wave vector:

$$\mathbf{J}(z) = 2e \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_k n_k(z) , \tag{8}$$

$$J_z(z) = \frac{e\hbar}{2\pi^2 m} \int_{-1}^{1} d\nu\, \nu \int dk\, k^3 n_k(z) . \tag{9}$$

The integrals for $\nu > 0$ are treated separately from $\nu < 0$. In fact the latter are handled by changing variables to $\nu \rightarrow -\nu$. The above expression for the current is changed by an integration by parts:

$$J_z(z) = \frac{e\hbar}{2\pi^2 m} \int_0^1 d\nu\, \nu I(z,\nu) , \tag{10}$$

$$I(z,\nu) = -\int dk\, k^3 \int_{-\infty}^{\infty} dz' \frac{\partial n_{k0}(z')}{\partial z'} \times \exp\left[-\left| \int_{z'}^{z} dz'' \frac{1}{\nu l(z'')} \right| \right] . \tag{11}$$

The result is simplified by first doing the integral over the electron wave vector k. First we must evaluate the derivative:

$$\frac{\partial n_{k0}}{\partial z'} = \frac{1}{(e^{\beta\xi}+1)(e^{-\beta\xi}+1)} \left[\frac{\xi}{k_B T^2} \frac{\partial T}{\partial z'} + \beta \frac{\partial \mu}{\partial z'} \right] , \tag{12}$$

$$\frac{\partial \mu}{\partial z'} = \frac{\partial \mu}{\partial T} \frac{\partial T}{\partial z'} = -\frac{\pi^2 k_B^2}{12\mu} \frac{\partial T^2}{\partial z'} , \tag{13}$$

where $\beta = 1/k_B T$. Both terms on the right in Eq. (12) make a similar contribution to the final answer. However, the term $\partial\mu/\partial z'$ does not contribute to the thermoelectric response. Instead, it contributes to the nonlocal electrical conductivity due to spatially varying chemical potentials. These effects include electric fields, density gradients, and temperature gradients. These effects are considered below. Now we consider only the first term in Eq. (12).

Another feature of the wave-vector integrals is that the electron free path l will usually depend upon the wave vector. We write the exponential factor in (11) as $\exp[-f(k)] \approx \exp[-f(k_F) - \alpha\xi/\mu]$, where $\alpha = 0.5 k_F \partial f/\partial k$. The integration variable is changed to ξ, so the $\mathbf{k}$ integral has the form

$$\frac{\beta}{T} \int d\xi\, \xi \frac{(\mu+\xi)(1-\alpha\xi/\mu)}{(e^{\beta\xi}+1)(e^{-\beta\xi}+1)} \frac{\partial T}{\partial z} = \frac{\pi^2}{6} k_B^2 (1-\alpha) \frac{\partial [T(z)]^2}{\partial z} . \tag{14}$$

All of these terms are collected to produce the final result for the integral over the wave vector:

$$\int dk\, k^3 \frac{\partial n_{k0}}{\partial z'} = \frac{\pi^2 m^2 k_B^2}{3\hbar^4} (1-\alpha) \frac{\partial [T(z')]^2}{\partial z'} , \tag{15}$$

$$I(z,\nu) = -\frac{\pi^2 m^2 k_B^2}{3\hbar^4} \int_{-\infty}^{\infty} dz' [1-\alpha(z,z')] \frac{\partial [T(z')]^2}{\partial z'} e^{-f} , \tag{16}$$

$$f = \left| \int_{z'}^{z} dz'' \frac{1}{\nu l(z'')} \right| . \tag{17}$$

Equations (10) and (16) represent our general result.

First we wish to show that this result reduces to familiar expressions in the limit of a local response. We assume that variations of temperature $T(z)$ are slow compared with the MFP l, so that the temperature can be removed from the integral. We also use the fact that the quantity α is just the derivative of the argument in the exponent. The factor $(1-\alpha)$ can be rewritten as $1+(k_F/2)\partial/\partial k_F$ are removed from the integral. The only k dependence of the integral is in the MFP l in the term f. In the limit of slow spatial variation in the temperature, we find

$$I = \frac{2\pi^2 k_B^2}{3\hbar^4} \frac{\partial T^2(z)}{\partial z} \left[\left[1 + \frac{k}{2} \frac{\partial}{\partial k} \right] \nu l(k) \right]_{k=k_F} , \tag{18}$$

$$J_z = \frac{emk_B^2 l(k_F)}{9\hbar^2} \frac{\partial T^2(z)}{\partial z} \left[1 + \frac{\partial \ln[l(k)]}{\partial \ln\xi} \right]_{\xi=0} . \tag{19}$$

The advantage of using logarithm derivatives is that one can ignore all constants. The MFP can be related to the electrical conductivity $l(k) \sim \sigma(k)/k^2$, which shows that the factor in parentheses is $\partial\ln[\sigma(\mu)]/\partial\ln(\mu)$. The standard definition of the Seebeck coefficient S if found from $\mathbf{J} = \sigma S \nabla T/e$, where σ is the electrical conductivity. Thus we derive

$$S = \frac{\pi^2 k_B^2 T}{3eE_F} \frac{\partial \ln[\sigma(\mu)]}{\partial \ln(\mu)} . \tag{20}$$

This expression is called the Mott formula[3,14,15] for the thermopower of a metal. It is the standard result, which relates the Seebeck coefficient to the logarithmic derivative of the electrical conductivity with respect to the chemical potential. Our nonlocal theory reduces to this expression in the limit that the local theory is valid, which occurs when the spatial variations in the temperature are small compared with the size of the electron MFP.

Next we consider possible situations where the nonlocal theory is required. The first case is where the temperature profile is periodic in space. Then $[T(z)]^2$ is also periodic, which we represent by a series in $\cos(2\pi nz/a)$, where a is the period. Then all of the integrals can be done analytically, with the result ($\theta_n \equiv 2\pi nl/a$):

$$[T(z)]^2 = T_0^2 + \sum_n s_n \cos(2\pi nz/a) , \tag{21}$$

$$J_z(z) = \frac{emk_B^2}{3\hbar^3}\left[1+\frac{k_F}{2}\frac{\partial}{\partial k_F}\right] \times \left[\sum_n \frac{s_n}{\theta_n}\left[1-\frac{1}{\theta_n}\tan^{-1}(\theta_n)\right]\sin(2\pi nz/a)\right] . \tag{22}$$

Obviously the current is also periodic. The derivative with respect to k_F operates on the MFP $l(k_F)$.

The second case is when the MFP is limited by electron-phonon interaction. This scattering dominates in pure metals at high temperatures. Then the MFP is given in terms of the transport form of the electron-phonon coupling constant λ_t:

$$l(z) = \frac{\hbar v_F}{2\pi\lambda_t k_B T(z)} . \tag{23}$$

When the MFP depends upon position, the factor in the exponent has to be evaluated numerically. It has the form

$$\frac{1}{\nu l} = \gamma_k T , \tag{24}$$

$$\gamma_k = \frac{2\pi\lambda_t k_B}{\nu\hbar v_F} . \tag{25}$$

An estimate of the size of nonlocal effects can be obtained by some manipulations on the integral in (16). For $z > z'$ we write the factor as

$$T(z')\exp\left[-\gamma_k \int_{z'}^{z} dz'' T(z'')\right] = \frac{1}{\gamma_k}\frac{\partial}{\partial z'}\exp\left[-\gamma_k \int_{z'}^{z} dz'' T(z'')\right] . \tag{26}$$

The integral can now be written as

$$I' = \frac{2}{\gamma_k}\left[\int_{-\infty}^{z} dz' - \int_{z}^{\infty} dz'\right]\frac{\partial T(z')}{\partial z'}\frac{\partial}{\partial z'}e^{-f} . \tag{27}$$

The minus sign between the two integrals occurs because of the absolute-magnitude symbols in the definition of f. Next, we integrate by parts:

$$I' = \frac{2}{\gamma_k}\frac{\partial T(z)}{\partial z} - \frac{1}{\gamma_k}\left[\int_{-\infty}^{z} dz' - \int_{z}^{\infty}\right]\frac{\partial^2 T(z')}{\partial z'^2}e^{-f} . \tag{28}$$

The first term on the right is identical to the local theory of thermoelectricity. The other terms contribute to the nonlocal theory. The size of these additional terms may be estimated by expanding the exponent in a Taylor series:

$$T(z'') = T(z) + (z''-z)\frac{\partial T(z)}{\partial z} + \cdots , \tag{29}$$

$$f = T(z)|z-z'| - \operatorname{sgn}(z-z')\frac{1}{2}\frac{\partial T(z)}{\partial z}(z'-z)^2 + \cdots , \tag{30}$$

$$e^{-f} \approx e^{-\gamma_k T(z)|z'-z|}\left[1+\operatorname{sgn}(z-z')\frac{1}{2}\frac{\partial T(z)}{\partial z} \times (z'-z)^2 + \cdots\right] , \tag{31}$$

$$I' \approx \frac{2}{\gamma_k}\frac{\partial T(z)}{\partial z}\left[1+\frac{\nu^2 l^2}{T}\frac{\partial^2 T(z)}{\partial z^2} + \cdots\right] . \tag{32}$$

Thus the local theory is valid whenever

$$\frac{l^2}{T}\frac{\partial^2 T}{\partial z^2} \ll 1 . \tag{33}$$

This criteria applies to the case of the electron-phonon interaction at high temperatures. The important point is that the validity of the local theory does not rely upon whether the first derivative $\partial T/\partial z$ is large or small. Instead, the local theory is valid as long as the variations of the *second* derivative are small compared to the size of the MFP. The local theory is valid even if $l\,\partial T/\partial z$ is large. Also note that the correction terms are nonlinear. This expansion rederives the nonlinear term of Ref. 9. However, if this term is large enough to be important, then one should use the nonlocal theory which gives an exact evaluation of all contributions.

III. NONLOCAL ELECTRICAL CONDUCTIVITY

Here we solve for the nonlocal electrical conductivity. We evaluate the contribution of the second term in (12). In the local limit, it will give the first term on the right in Eq. (1). The integral I is

$$I = -\frac{2m^2}{\hbar^4}\int_{-\infty}^{\infty} dz'\beta\frac{\partial\mu}{\partial z'}e^{-f}\int d\xi\frac{(\xi+\mu)(1-\alpha\xi/\mu)}{(e^{\beta\xi}+1)(e^{-\beta\xi}+1)} , \tag{34}$$

$$I = -\frac{m^2}{\hbar^4}\int_{-\infty}^{\infty} dz'\frac{\partial\mu^2}{\partial z'}e^{-f} . \tag{35}$$

The quantity α is in a term which is smaller by the ratio $(k_B T/E_F)^2$ and is neglected. The term in α only contributes significantly to the nonlocal thermoelectric current. The result for the current is

$$J_z = -\frac{em}{2\pi^2\hbar^3}\int_0^1 d\nu\,\nu \int_{-\infty}^{\infty} dz' \frac{\partial \mu^2(z')}{\partial z'} e^{-f} . \tag{36}$$

This integral is our basic result for the nonlocal conductivity. In the local limit we obtain the first term in (1), where the expression for the electrical conductivity is $\sigma = e^2 n_0 \tau / m$.

Ziman[3] and Chambers[16] considered nonlocal electrical conduction in metals. Their theory was derived for the anomalous skin effect, where the ac electric field penetrates only a small distance into the surface of a metal. Their theory differs from ours in that they considered only linear response, while our nonlocal theory is also nonlinear.

IV. HEAT CURRENTS

The heat current is evaluated from the expression

$$\mathbf{J}_Q = 2\int \frac{d^3k}{(2\pi)^3} \mathbf{v}_k \xi_k n_k(\mathbf{r}) . \tag{37}$$

This formula is similar to (8). The factor of e is missing, and it has an additional factor of the particle energy ξ_k in the integrand. There are other terms in the heat current, but they are unimportant in metals.

There are two terms in this expression, which correspond to the two terms in (2). The first contributes another formula for the nonlinear thermoelectric effect. The second is the nonlocal thermal conductivity. The derivation of these two terms is similar to the derivations of the preceding sections. One first integrates by parts. The derivative of the occupation number is given in (12). The first term on the right in (12) gives the result for the thermal conductivity. We find

$$J_{Qz} = -\frac{mk_B^2}{6\hbar^3}\int_0^1 d\nu\,\nu \int_{-\infty}^{\infty} dz' \mu(z') \frac{\partial T^2(z')}{\partial z'} e^{-f} . \tag{38}$$

The local limit of this expression is given by the standard result that $J_{Qz} = -\kappa\,\partial T/\partial z$, where the thermal conductivity is given by the Wiedemann-Franz law

$$\kappa = \frac{\pi^2 \sigma k_B^2 T}{3e^2} . \tag{39}$$

The nonlocal thermal conductivity depends upon the local values of the temperature, and also the local values of the chemical potential.

The second term on the right in (12) gives the thermoelectric contribution to the heat current. We find

$$J_{Qz} = -\frac{mk_B^2}{3\hbar^3}\left[1 + \frac{k}{2}\frac{\partial}{\partial k}\right]_{k=k_F} \times \int_0^1 d\nu\,\nu \int_{-\infty}^{\infty} dz' T^2(z') \frac{\partial \mu(z')}{\partial z'} e^{-f} . \tag{40}$$

This expression has the factor of $(1-\alpha)$ which again has been changed to a factor with a derivative with respect to wave vector. This factor always enters the thermopower. The integral dz' again contains the factors of $T^2(z')$ and $\mu(z')$ which were found in the integral for the thermal conductivity. However, here the derivative is taken on the chemical potential rather than on the temperature. In the limit that the local theory is valid, this expression reduces to the first term on the right in (2), where the Seebeck coefficient is given again by the Mott formula (20).

Again one can derive the conditions for the local theory to be valid. At high temperature, one finds again a criterion similar to (33). The local theory is valid for the thermal conductivity whenever

$$\frac{l^2}{\mu T}\frac{\partial}{\partial z}\left[\mu \frac{\partial T}{\partial z}\right] \ll 1 . \tag{41}$$

The local theory is valid for the thermoelectric contribution to the heat current whenever

$$\frac{l^2}{\mu T}\frac{\partial}{\partial z}\left[T \frac{\partial \mu}{\partial z}\right] \ll 1 . \tag{42}$$

In both of these cases, the nonlocal theory is required when either the temperature or the chemical potential varies rapidly with position.

V. THE BENEDICKS EFFECT

The Benedicks effect[5] is the dc voltage in a solid which exists between two points which are at the same temperature. A nonzero voltage may be observed if the temperature profile $T(z)$ between these two points is asymmetric. It has been observed in semiconductors. However, in metals the voltage is expected to be small. One way to obtain a larger voltage is to have a periodic array of asymmetric temperature variations. One possible profile is shown in Fig. 1. If the periodic temperature distribution is symmetric about a maximum point, then there is no voltage. A voltage comes about because of asymmetry in the periodic distribution. Recently, a voltage has been observed in metals which have a periodic temperature distribution. It has been suggested that this is caused by the Benedicks effect.[9]

The Benedicks effect is predicted by our nonlocal theory. Here we discuss the conditions under which it is observed. We show that there are three requirements in order to observe it. (i) The first was already stated above, namely, the periodic distribution is asymmetric about a maximum point. (ii) The second condition is that the electron MFP must depend upon temperature. No effect is observed for a MFP which is a constant. (iii) The third condition is that the electron MFP must depend upon the wave vector of the electron. All of these requirements are discussed below.

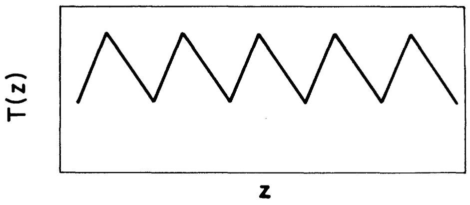

FIG. 1. An example of a periodic but asymmetrical temperature variation, which would show a Benedicks effect.

The most general periodic distribution, with a spatial period of a, is given below. We also give the series for the square of the function, which enters into the integral for the nonlocal current. It is convenient to introduce the wave vector $k_n \equiv 2\pi n/a$. The temperature and chemical potential can be expressed as

$$T(z)=T_0+\sum_n [t_n \cos(k_n z)+s_n \sin(k_n z)] , \tag{43}$$

$$T^2(z)=T_1^2+\sum_n [T_n \cos(k_n z)+S_n \sin(k_n z)] , \tag{44}$$

$$T_1^2=T_0^2+\tfrac{1}{2}\sum_n (t_n^2+s_n^2) , \tag{45}$$

$$\mu^2(z)=\mu_0^2+C_1 z+\sum_n [U_n \cos(k_n z)+V_n \sin(k_n z)] . \tag{46}$$

One condition for the observation of this effect is that both sets of coefficients (t_n, s_n) in the temperature series must have some nonzero values. This is the requirement that the distribution be asymmetric about a maximum in the periodic distribution. We do not provide here the simple trigometric relations between (t_n, s_n) and (T_n, S_n).

We have included a similar series for the chemical potential. Obviously, if the temperature distribution is periodic, then so is the chemical potential. The object of the derivation is to see whether the oscillating components of the temperature distribution can provide a nonzero value for the linear coefficient C_1.

We use (10) and (16) for the nonlinear thermoelectric coefficient $J_z^{(T)}$, plus (36) for the nonlocal electrical current $J^{(E)}$, to generalize (1):

$$J_z=J^{(E)}+J^{(T)} , \tag{47}$$

$$J^{(E)}=-j_E\int_0^1 d\nu\, \nu \int_{-\infty}^{\infty} dz' \frac{\partial \mu^2(z')}{\partial z'} e^{-f} , \tag{48}$$

$$J^{(T)}=-j_T\int_0^1 d\nu\, \nu \int_{-\infty}^{\infty} dz' \frac{\partial T^2(z')}{\partial z'} e^{-f} , \tag{49}$$

$$j_E=\frac{em}{2\pi^2\hbar^3} , \tag{50}$$

$$j_T=\frac{emk_B^2}{6\hbar^3}\left[1+\frac{k_F}{2}\frac{\partial}{\partial k_F}\right] . \tag{51}$$

It is convenient to rewrite (47) as

$$J_z=-j_E\int_0^1 d\nu\, \nu \int_{-\infty}^{\infty} dz' \frac{\partial}{\partial z'}[\mu^2(z')+bT^2(z')L]e^{-f} , \tag{52}$$

$$b=\frac{\pi^2 k_B^2}{3} , \tag{53}$$

$$L\equiv 1+\frac{k_F}{2}\frac{\partial}{\partial k_F} . \tag{54}$$

This expression will form the basis for the remainder of our discussion. In a one-dimensional system, the equation of continuity for a static system requires $\partial J_z/\partial z=0$. We also assume that the ends are insulated, so that no current can flow. This is the same as $J_z=0$. Both conditions are satisfied, since if $J=0$ for all values of z, then the derivative is also zero. Thus we must have that the two currents $J^{(E)}$ and $J^{(T)}$ are equal and opposite. The periodic distribution in temperature will provide contributions to $J^{(T)}$. These contributions are set equal to $-J^{(E)}$, which determines the chemical potential.

We begin our discussion by proving two theorems. The first theorem is that the Benedicks effect is zero if the MFP l is a constant, independent of position. In homogeneous systems this assumption is equivalent to assuming the resistivity is independent of temperature. The exponential factor $f=|z-z'|/(\nu l)$, and the integrals above can be evaluated analytically. The result is similar to (21), as a series in $\theta_n \equiv 2\pi n l/a$:

$$J^{(T)}=-2j_T\sum_n \frac{1}{\theta_n}\left[1-\frac{\tan^{-1}\theta_n}{\theta_n}\right] \times [S_n \cos(k_n z)-T_n \sin(k_n z)] , \tag{55}$$

$$C_1=0 . \tag{56}$$

Here the thermoelectric current is periodic, and there is no dc component. There is no Benedicks effect. We have proved that there is no Benedicks effect when the electron mean free path is independent of position in the solid. For homogeneous systems, this assumption is equivalent to the condition that the MFP does not depend upon temperature. The only other assumption which we made in this proof is that Boltzmann's equation (1) is valid. We solved this equation exactly in obtaining our proof of no Benedicks effect. This form of the Boltzmann equation is approximate. A better equation is the quantum Boltzmann equation which is valid for electrons which are not good quasiparticles. We have not tried to solve this equation for this problem.

The second theorem is that the Benedicks effect is zero if the electron MFP is independent of the Fermi wave vector k_F. That is, there is no dc voltage if the derivative factor L is replaced by unity in (52). Since we just proved that there is no effect if the MFP is independent of position, we must now assume that it does depend upon position. Thus we express the exponential factor as

$$f=\frac{1}{\nu}\left|\int_{z'}^{z} dz'' F(z'')\right| \approx \frac{1}{\nu}\left|F(z)(z-z')+\frac{1}{2}\frac{\partial F(z)}{\partial z}(z-z')^2+\cdots\right| , \tag{57}$$

$$G(z)\equiv \mu^2+bT^2 , \tag{58}$$

$$0=\int_0^1 d\nu\, \nu \int_{-\infty}^{\infty} dz' \frac{\partial G(z')}{\partial z'} e^{-f} . \tag{59}$$

Change the integration variable to $s\equiv|z-z'|F(z)/\nu$ and the integral becomes

$$0=\frac{1}{F}\int_0^1 d\nu\,\nu^2\int_0^\infty e^{-s}\left[\exp\left[-\frac{\nu s^2}{2F^2}\frac{\partial F}{\partial z}+\cdots\right]\frac{\partial G(z+\nu s/F)}{\partial z}+\exp\left[\frac{\nu s^2}{2F^2}\frac{\partial F}{\partial z}+\cdots\right]\frac{\partial G(z-\nu s/F)}{\partial z}\right], \tag{60}$$

$$0=\frac{2}{3F}\frac{\partial G}{\partial z}\left[1-\frac{3}{5F^3}\frac{\partial^2 F}{\partial z^2}+\cdots\right]+\frac{2}{5F^3}\frac{\partial^3 G}{\partial z^3}-\frac{6}{5F^4}\frac{\partial F}{\partial z}\frac{\partial^2 G}{\partial z^2}+\cdots . \tag{61}$$

What kind of functions $G(z)$ satisfy this equation. The trivial solution is $G=\text{const}$, so that every term in the series is identically zero. The Benedicks effect is given by a function $G=C_1 z$. However, this solution is not allowed. The first term is nonzero, and proportional to C_1. However, all other terms are zero since they contain high derivatives of $G(z)$. This is true even for all terms besides those few shown. That is, if one disallows solutions such as $G\propto z^n$ for $n>1$, then $n=1$ is also not allowed. We assume that the function $G(z)$ has no periodic terms: the ac terms in T^2 are cancelled by equal and opposite ac terms in μ^2. Otherwise one cannot satisfy $0=\partial G/\partial z$ for all values of z. Then the only remaining question is whether $G(z)$ has a linear term. The above series does not permit a nonzero value of C_1.

There is a Benedicks effect. Real metals have a MFP which does depend upon temperature and upon the Fermi wave vector. Below we will show how to obtain a nonzero value of C_1 in this case. Previous derivations[6,9] have obtained a Benedicks effect while assuming that the MFP is a constant—independent of either position or Fermi wave vector. We regard those derivations as incorrect. Generally their mistake was in not treating the two currents $J^{(E)}$ and $J^{(T)}$ on an equal footing. An expansion was made in the nonlinear, or nonlocal, properties of one current, but not the other. However, they must be treated together, since the two terms almost completely cancel their contributions at each order of perturbation theory.

Now we derive the Benedicks effect. We must allow the MFP to depend upon position, and we must retain the derivative factor of L. We rewrite the argument of the integral as

$$\left[\frac{\partial G}{\partial z'}+b\frac{\partial T^2}{\partial z'}(L-1)\right]e^{-f}=e^{-f}\left[\frac{\partial G}{\partial z'}-b\frac{\partial T^2}{\partial z'}\frac{\partial f}{\partial \ln\mu_0}\right], \tag{62}$$

where μ_0 is the equilibrium chemical potential. This formula is used in the integrand in (52). One evaluates the integral again. There are new terms arising from the last term in the above equation. The series (61) has new terms which are

$$b\frac{\partial \ln F}{\partial \ln\mu_0}\left[-\frac{2}{3F}\frac{\partial T^2}{\partial z}+\frac{4!}{5F^4}\frac{\partial^2 T^2}{\partial z^2}\frac{\partial F}{\partial z}+\frac{4!}{15F^4}\frac{\partial T^2}{\partial z}\frac{\partial^2 F}{\partial z^2}+\cdots\right]. \tag{63}$$

The first term is oscillatory. It has the same form as the first term in (61). These two terms are combined into a new term $H=G-bT^2\Lambda$, where $\Lambda=\partial\ln F/\partial\ln\mu_0$. Now the oscillatory terms in $H(z)$ cancel, leaving only the linear term which is the Benedicks effect. The next two terms can produce constant terms, and hence contribute to C_1. The functions T^2 and F are both oscillatory. The product of two oscillatory functions can produce a constant term which does not oscillate: e.g., $2\cos^2\theta=1+\cos(2\theta)$. There are other terms depending upon $\partial^{n+1}F/\partial z^n\partial\ln\mu_0$. They usually vanish, since F is usually a product of a factor which depends upon z and a factor which depends upon k_F, in which case the double derivative of $\ln F$ will vanish. Recalling that $C_1=2\mu_0\partial\mu_0/\partial z$ is the dc component of μ^2, we finally derive an expression for the dc component of the chemical potential, which is the Benedicks effect:

$$\left[\frac{\partial\mu}{\partial z}\right]_{\rm dc}=-\frac{3\pi^2 k_B^2}{10a\mu_0}\int_0^a dz\frac{1}{[F(z)]^3}\left[\frac{\partial\ln F}{\partial\ln\mu_0}\right]\times\left[3\frac{\partial^2 T^2}{\partial z^2}\frac{\partial F}{\partial z}+\frac{\partial T^2}{\partial z}\frac{\partial^2 F}{\partial z^2}\right]. \tag{64}$$

Here we have retained only the largest term. We also averaged over a period, in order to eliminate the oscillatory components. Generally the factor with the logarithmic derivative does not oscillate. For example, in (24) we show the usual case for metals at high temperature where $F=\nu\gamma_k T$. For this case the above result simplifies to

$$\left[\frac{\partial\mu}{\partial z}\right]_{\rm dc}=-\frac{3\hbar^2(1-\xi)}{10ma\lambda_t^2}\times\int_0^a dz\frac{1}{[T(z)]^3}\left[3\left[\frac{\partial T}{\partial z}\right]^3+4T\frac{\partial T}{\partial z}\frac{\partial^2 T}{\partial z^2}\right], \tag{65}$$

$$\xi=\frac{\partial\ln\sigma(\mu)}{\partial\ln\mu} . \tag{66}$$

The second term in brackets can be integrated by parts, which shows that it has the same form as the first term. Combining them gives

$$\left[\frac{\partial\mu}{\partial z}\right]_{\rm dc}=-\frac{21\hbar^2(1-\xi)}{10ma\lambda_t^2}\int_0^a dz\frac{1}{[T(z)]^3}\left[\frac{\partial T}{\partial z}\right]^3 . \tag{67}$$

Since λ_t is dimensionless, the voltage scale over one period is given by $\Delta V\sim(\hbar^2/ma^2)(\Delta T/T)^3$, where a is the length scale of the temperature variation.

The dimensionless factor of ξ is of order unity. For example, for alkali metals at their melting temperature,[17,18] they range in value from $\xi = -6$ for lithium to $\xi = +4$ for potassium. This quantity can be inferred from the measurement of the thermopower.

This expression is evaluated for the numerical example discussed in Ref. 9. The variation over a single period has a sawtooth shape $T(z) = T_0 + (T_1 - T_0)(3z/2a)$ for $0 < z < 2a/3$ and $T(z) = T_0 + 3(T_1 - T_0)(1 - z/a)$ for $2a/3 < z < a$. Their values were $T_1 = 600$ K, $T_0 = 300$ K, $a = 10\ \mu$m. In this case, the two terms in the integrand of (65) contribute a similar amount, and the result is

$$\Delta V = a \left[\frac{\partial \mu}{\partial z} \right] = -\frac{4\times 10^{-9}\ \mathrm{V}}{\lambda_t^2}(1-\xi) \ . \tag{68}$$

If one uses a metal such as silver with $\lambda_t \sim 0.13$ the value of $\Delta V \sim 0.2\ \mu$V. This is smaller than the estimate in Ref. 9. As we said above, our expression is different because we systematically expanded together the two terms in the current, and only obtained a nonzero result because the mean free path depends upon the position and wave vector.

VI. DISCUSSION

We have derived the nonlocal response for electron transport in metals. We have used the nonlocal expressions for the electrical current to derive a formula for the Benedicks effect, which is the voltage between two points in the solid which are at the same temperature. We show that the Benedicks effect exists if three conditions are satisfied: (i) the temperature varies in an asymmetrical way between the two points, (ii) the electron mean free path depends upon position, and (iii) the electron mean free path depends upon the wave vector of the electron. Granted that these conditions are met, the size of the voltage is given approximately by the expression

$$\Delta V \sim \frac{\hbar^2 a}{m \lambda_t^2} \left\langle \left[\frac{\partial \ln T}{\partial z} \right]^3 \right\rangle \ . \tag{69}$$

The voltage is generally quite small.

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