Nonlocal theory of thermal conductivity

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We have derived a nonlocal theory of thermal conductivity for the case in which the heat is carried by phonons. There is a nonlocal relation between the heat current $J(r)$ and the temperature gradient $\nabla T(r')$. The nonlocal theory is needed whenever the phonon mean free path is long compared to the distance scale of the variation in ∇T. The theory is used to explain some previous experiments in silicon.

I. INTRODUCTION

Energy is transported by many different kinds of particles or excitations. The process in inherently nonlocal, since the particles or excitations arrive at a point in space having brought the energy from other points. Generally, a nonlocal theory of transport is required whenever the mean free path of the particles or excitations is long compared to the distance scale of variations in the driving force. A local theory is adequate when the mean free paths are relatively short. Nonlocal theories are used routinely for photon[1] and neutron[2] transport. In solids, a nonlocal theory is used for electron transport in the anomalous skin effect.[3]

Thermal conductivity has always been described using a local theory. We have been unable to find a single reference of a nonlocal theory. Undoubtedly the local theory has worked well in many applications. However, the local theory was unable to explain some recent experiments in silicon and germanium.[4] We have derived a nonlocal theory of heat flow by phonon transport. Our calculations indicate that the experiments in silicon and germanium can be explained by the nonlocal theory.

Laser-annealing experiments on surface layers of silicon generate large thermal gradients and heat fluxes in the underlying substrate.[4,5] Earlier modeling of these experiments gave a poor fit when using the well-known thermal conductivity of silicon.[6] It was suggested that the coefficient of thermal conductivity $\kappa(T)$ needed to be reduced by about one-third in order to fit the data at high temperatures and at high-temperature gradients.[4] Here we show that the data can be explained by a model which utilizes the nonlocal nature of the heat transport. The heat current is reduced in regions of high flux because the nonlocality averages these regions with others of lower thermal flux. Thus the heat flow is reduced, but not the coefficient of thermal conductivity. These two quantities are proportional for steady, constant, heat flow. We show that transient heat flow requires a nonlocal analysis.

II. DIMENSIONAL ANALYSIS OF NONLINEAR EFFECTS

Measurements in silicon and germanium show that the heat flow is reduced 30% when the temperature and temperature gradient are quite large.[4] We do some elementary dimensional analysis in order to ascertain whether the effect is due to changes in the electronic or phonon parts of the thermal conductivity.

The purpose of dimensional analysis is to see whether certain effects are large or small. All of the combinations of parameters we investigate here have been derived in a Green's-function analysis of nonlinear and nonlocal heat flow. However, each combination is rather obvious, and stands alone. Numerical data are used from Ref. 4 in order to provide concrete examples. They show a temperature profile $T(z,t)$ at a time of $t=16$ ns after the laser pulse. From these data one can deduce the following parameters at the point where the temperature is $T=1000$ K:

$$\frac{\partial T}{\partial z}\sim 2.0\times 10^{7}\ \mathrm{K/cm}\ ,$$

$$\frac{\partial^2 T}{\partial z^2}\sim 0.8\times 10^{12}\ \mathrm{K/cm}^2\ ,$$

$$\xi\sim 3.3\times 10^{-16}\ \mathrm{s}\ .$$

These typical values will be the basis of our analysis. The quantity ξ is defined below.

A. Electronic thermal conductivity

In both silicon and germanium the thermal conductivity is entirely provided by phonons, except at temperatures near melting. At these high temperatures one can thermally excite electron-hole pairs, which contribute a bipolar part to the thermal conductivity. This electronic contribution is about 30% of the total at melting.[6] It has been observed that the experiments can be explained by the elimination of the electronic portion of the thermal conductivity.[4] However, the following dimensional analysis suggests that this does not happen.

We examine how quantities such as the particle lifetime depend on the temperature gradients. Parity arguments prevent scalar quantities, such as the lifetime τ or mean free path l, from depending on the vector quantity ∇T. Instead, the leading dependence must be on the scalars $(\nabla T)^2$ or $\nabla^2 T$. Dimensionless quantities can be constructed from these using the mean free path (MFP) l and a characteristic energy E_c,

$$\delta_1 = kl^2\nabla^2 T/E_c \ ,$$

$$\delta_2 = k^2 l^2 (\nabla T)^2/E_c^2 \ ,$$

where k is Boltzmann's constant. How does one choose the characteristic energy E_c? It is taken to be the smallest of all of the energy variables associated with electrons or holes. Among the energy gap E_g, the thermal energy kT, and the lifetime uncertainty $\Gamma = h/2\pi\tau$, one has the clear progression in size of $E_g \gg kT > \Gamma$. Thus we take $E_c = \Gamma$. The MFP is evaluated using $l = v\tau$ and $v^2 \sim kT/m^*$ to get

$$l^2 = 3kT\hbar^2/m^*\Gamma^2 \ ,$$

$$\delta_1 = 3k^2\hbar^2 T\nabla^2 T/m^*\Gamma^3 \ ,$$

$$\delta_2 = 3k^3\hbar^2 T(\nabla T)^2/m^*\Gamma^4 \ .$$

The lifetime τ is estimated from the electron mobility. Sze[7] lists this at $T = 1000$ K as $\mu = 100\ \mathrm{cm^2/V\,s} = 3\times 10^4$ esu s/g. Setting this equal to $e\tau/m^*$ and taking $m^* = 0.5m$ gives

$$\tau = 2.8\times 10^{-14}\ \mathrm{s} \ ,$$

$$\Gamma = 3.8\times 10^{-14}\ \mathrm{ergs} \ ,$$

$$kT = 1.4\times 10^{-13}\ \mathrm{ergs} \ ,$$

$$\delta_1 = 0.002 \ ,$$

$$\delta_2 = 0.003 \ .$$

Both δ_1 and δ_2 are negligible. Neither provide the 30% correction which is required to explain the reduction in the thermal conductivity.

Whenever we use Green's functions or similar theories to calculate how the temperature gradients affect the particle lifetime or similar quantities, we always find that $\delta\tau/\tau \sim \delta_1$ or δ_2. Our conclusion is that the thermal gradients have little effect upon the electronic contribution to the thermal conductivity in silicon or germanium.

B. Phonon heat conduction

The same type of analysis is much more promising when applied to phonons. We take the same definitions of $\delta_{1,2}$ as before. Now for the velocity v we use the average speed of sound $v = 6.5\times 10^5$ cm/s in silicon. For the lifetime we use the formula of Ref. 6 for a phonon of frequency ω,

$$1/\tau = \omega^2\xi \ ,$$

$$\xi = B_U T + B_H T^2 \ ,$$

$$B_U = 1.5\times 10^{-19}\ \mathrm{s/K} \ ,$$

$$B_H = 1.6\times 10^{-22}\ \mathrm{s/K^2} \ .$$

One can write, for δ_1 and δ_2,

$$\delta_1 = v^2 k\nabla^2 T/\omega^6\xi^3 h \equiv (\omega_1/\omega)^6 \ , \tag{1}$$

$$\delta_2 = v^2 k^2 (\nabla T)^2/\omega^8\xi^4 h^2 \equiv (\omega_2/\omega)^8 \ , \tag{2}$$

where ω_1 and ω_2 are characteristic frequencies. We find in silicon at 1000 K the values

$$\hbar\omega_1 = 21\ \mathrm{meV} \ ,$$

$$\hbar\omega_2 = 41\ \mathrm{meV} \ .$$

Both of these numbers are large. The δ's are large for all phonon frequencies smaller than their characteristic energy. This seems to include a large fraction of the phonons. We conclude that the temperature gradients have a large effect on the thermal transport by the phonons. Thus we tentatively propose that the reduction in thermal transport comes from the phonon contribution rather than the electronic contribution.

In our Green's-function analysis, the quantity which occurs most often is

$$\delta_3 = l^2\nabla^2\Gamma/\Gamma \ ,$$

$$\nabla^2\Gamma = \hbar\omega^2\{B_U\nabla^2 T + 2B_H[T\nabla^2 T + (\nabla T)^2]\} \ .$$

The frequency dependence of this quantity is

$$\delta_3 = (\omega_3/\omega)^4 \ ,$$

$$\omega_3^4 = v^2\nabla^2\xi/\xi^3 \ , \tag{3}$$

$$\hbar\omega_3 = 5\ \mathrm{meV} \ ,$$

where ω_3 is smaller than ω_1 or ω_2. Nevertheless, the phonon system appears to be the one influenced by thermal gradients.

III. NONLOCAL HEAT FLOW

Dimensional analysis was used above to evaluate the importance of various mechanisms contributing to the thermal conductivity of silicon and germanium. It was concluded that the phonon contribution to the thermal conductivity was most affected. The main contribution was from low-frequency phonons scattered by the anharmonic three- and four-phonon processes. There are two kinds of terms. One is of the form $\nabla^n T$ for $n > 1$. These types of terms are included in a nonlocal analysis, as described below. Other kinds of terms are nonlinear of the form $(\nabla T)^n$. Some of these terms are included in our nonlocal solution, while others are not. In order to clarify the last remark, consider the standard theory for temperature diffusion,

$$\frac{\partial}{\partial t}T = \frac{1}{C(T)}\frac{\partial}{\partial z}\left[\kappa(T)\frac{\partial}{\partial z}T\right] \ , \tag{4}$$

where $C(T)$ is the specific heat. This equation is nonlinear since the right-hand side contains $(\partial T/\partial z)^2$. Our nonlocal equation reduces to (4) in the limit of short mean free path. Thus our nonlocal solutions also contain nonlinear terms. However, here the main emphasis is on including the terms $\nabla^n T$, which requires a nonlocal theory. We solve the Boltzmann equation[8–11] for low-frequency phonons, and use the result to calculate the energy current.

Since the nonlinearity occurs at high temperature, all phonon occupation factors $n_B(\omega)$ can be accurately approximated by K/ω, where the symbol $K=k_BT$; T is temperature and k_B is Boltzmann's constant. We also assume that the phonons are on the mass shell so their frequency $\omega=\omega_q$. Then the evaluation of the heat current involves finding the phonon energy distribution $K_s(\mathbf{q},\mathbf{r})$ and using it to evaluate the energy current J,

$$\mathbf{J}=\int \frac{d^3q}{(2\pi)^3}\nabla\omega_q K_s(\mathbf{q},\mathbf{r}) , \tag{5}$$

$$\left[\omega\frac{\partial}{\partial t}+\tfrac{1}{2}(\nabla_q\omega_q^2)\cdot\nabla\right]K_s(q)=\Gamma(K-K_s) . \tag{6}$$

The quantity Γ is ω divided by the phonon lifetime, and at low frequency it has the dependence $\Gamma=\omega^3\xi$, where $\xi=B_UT+B_HT^2$ is a function of temperature. The Boltzmann equation has been written in the relaxation-time approximation. The time dependence will be ignored in this section, and will be included in a later section.

Since we are primarily interested in long-wavelength phonons, we can use the Debye approximation $\omega=vq$, where v is the speed of sound. Let the temperature variation be in one direction, say z, and let $\nu=\cos\theta$, where θ is the angle that the vector $\mathbf{q}$ makes with the direction z. Then these expressions have the form

$$J=\frac{v}{4\pi^2}\int_0^{q_D}q^2dq\int_{-1}^{1}d\nu\,\nu K_s(q,z,\nu) , \tag{7}$$

$$\left[1+\frac{\nu}{q^2\xi v}\frac{\partial}{\partial z}\right]K_s(q,z,\nu)=K . \tag{8}$$

Since ξ depends on $T(z)$, it is useful to define the variable x according to

$$x=v\int_0^z dz'\xi(z') . \tag{9}$$

x has the dimensions of length squared. Using the variable x allows us to include some nonlinear effects in a simple fashion. The notation $\partial_x\equiv\partial/\partial x$ permits Eq. (8) to be rewritten as

$$[1+(\nu/q^2)\partial_x]K_s=K , \tag{10}$$

which has the obvious solution

$$K_s=\frac{1}{1+(\nu/q^2)\partial_x}K ,$$

$$K_s=[1-(\nu/q^2)\partial_x+(\nu/q^2)^2\partial_x^2-(\nu/q^2)^3\partial_x^3+\cdots]K .$$

After inserting the series solution into the integral (7) for J, only the odd terms contribute because of the integral over $d\nu$. The first term makes sense and is

$$J^{(1)}=-\frac{vq_D}{6\pi^2}\frac{\partial}{\partial x}K=-\frac{q_D}{6\pi^2\xi}\frac{\partial}{\partial z}K . \tag{11}$$

This is the usual term in the thermal current which is proportional to the first derivative of the temperature. The coefficient of thermal conductivity is $\kappa=q_D/6\pi^2\xi$.

The next term in the series expansion contains second derivatives. It vanishes due to the angular integrals. The third term survives the angular integrals, but has an infrared divergence. Its wave-vector integral has the form

$$\int_0 dq/q^4$$

which diverges. Only the first term in the series makes sense, while the subsequent terms all diverge. The series method can not be used to evaluate higher-derivative terms such as ∇^nT for $n>1$.

Another method has been found to evaluate Eq. (10). Since it is a first-order linear-differential equation, the exact solution is obtained easily. The geometry is to have an interface at $z=0$ which has a fixed temperature $K(0)$. Heat flows away from this boundary to the right. The general solution is

$$K_s(q,x,\nu)=K(x)+e^{-q^2x/\nu}[K_s(q,0,\nu)-K(0)] - \int_0^x dx'\frac{\partial K(x')}{\partial x'}\exp[-q^2(x-x')/\nu] .$$

The quantity $K_s(q,0,\nu)$ is a boundary condition which needs to be determined. It must be found for the two cases of $\nu<0$ and $\nu>0$. The former is found easily, so it is done first. For heat flow to the right, the answer should converge to some asymptotic result which is finite. The above solutions have a factor which grows exponentially according to $\exp(-q^2x/\nu)$ when $\nu<0$. The parameter $K_s(q,0,\nu)$ is selected to make this term vanish at infinity

$$K_s(q,0,\nu)=K(0)+\int_0^\infty dx'\frac{\partial K(x')}{\partial x'}\exp(q^2x'/\nu) \quad (\nu<0) . \tag{12}$$

This boundary conditions provide the following result for the distribution function when $\nu<0$:

$$K_s(q,x,\nu)=K(x)+\int_x^\infty dx'\frac{\partial K(x')}{\partial x'}e^{q^2(x'-x)/\nu} \quad (\nu<0) . \tag{13}$$

The boundary condition for $\nu<0$ is easy because we are assuming a semi-infinite solid. The phonons going left come from the right. We know their history since the solid extends to infinity in this direction.

The phonons going to the right ($\nu>0$) at the surface have a less obvious history. Some of them emanate from the liquid on the left, while others come from the right and are reflected at the surface. The interface can scatter phonons specularly, diffusively, and perhaps nonlinearly. A microscopic theory is complicated. Instead, we have developed a phenomenological model which is quite simple and seems to contain the correct physics.

At this point we stop and evaluate the current (7) using (13) for $\nu<0$ and leaving unspecified the boundary condition for $\nu>0$. The q variable is changed to $s=q/q_D$,

$$J=-\frac{vq_D^3}{24\pi^2}\left[\int_0^\infty dx'\frac{\partial K(x')}{\partial x'}I(q_D^2\,|x-x'|)+G(q_D^2x)\right],$$
$$I(u)=6\int_0^1 s^2ds\int_0^1 v\,dv\exp(-s^2u/v)\,, \tag{14}$$
$$G(u)=-6\int_0^1 s^2ds\int_0^1 v\,dv\exp(-s^2u/v)\times[K_s(q_Ds,0,v)-K(0)]\,.$$

The first term contains I and is the volume contribution. The surface term G comes from the boundary conditions for $v>0$. This formula demonstrates the nonlocal nature of the volume part of the heat current. The thermal current at a point x depends upon the temperature gradients at other points in the solid. This spatial averaging is due to the finite MFP of the phonons.

Our theory includes terms such as (1) and (3) which depend on higher derivatives of the temperature. The integrand in the volume term can be written as $K'(|x-x'|)I(x')$ and then K' expanded in a Taylor series. In that way one can express the answer as a power series in higher derivatives of the temperature. However, as noted above, this series does not converge.

The integral I is normalized so $I(0)=1$. It is most easily evaluated by changing variables to $t=s^2/v$ and interchanging the order of integration,

$$I(u)=\frac{6}{7}\left[\int_0^1\sqrt{t}\;dt\,e^{-ut}+\int_1^\infty\frac{dt}{t^3}e^{-ut}\right]. \tag{15}$$

A plot of $I(u)$ is provided in Fig. 1. At large u it decreases as $u^{-3/2}$.

IV. BOUNDARY CONDITIONS

This section is devoted to a discussion of the surface term G in Eq. (14). This function depends on the boundary condition at the surface $z=0$ for the phonons with $v>0$. This information is contained in the function $K_s(q,0,v)$.

As a preamble, we first discuss the solution for the case of constant current flow. There the temperature profile must be linear in x. For this case let $K(x)=K_0+xK_1$, where K_0 and K_1 are constants. Inserting this $K(x)$ into the solution (13) for $v<0$ gives

$$K_s(q,x,v)=K(x)-(v/q^2)K_1\,. \tag{16}$$

This steady-state solution is assumed to be valid for all values of v. Inserting it into (7) for the heat current gives

$$J=-\frac{vq_D}{6\pi^2}K_1\,,$$

which is the correct result (11) for the constant heat flow. Constant heat flow requires a linear temperature variation in the x variable. In the laboratory variable z this becomes the following profile for constant heat flow:

$$T(z)=\frac{T(0)}{[1+rT(0)]\exp(az)-rT(0)}\,,$$

$$r=B_H/B_U\,,$$

$$a=6\pi^2JB_U/k_Bq_D\,.$$

For small values of az this formula can be expanded to obtain the usual linear relation between T and z. For constant heat flow the boundary condition when $v>0$ is the same as (16) when $x=0$. Presumably, the boundary condition is different when the flow is transient.

We consider next a standard model in transient heat flow. The solid is initially at a constant temperature, which we take to be 292 K. At some initial time ($t=0$) the surface temperature is raised to $T(0)=1680$ K. This temperature is fixed, so that the surface is a source of heat, which flows into the solid ($z>0$) and gradually raises its temperature. The transient problem is derived from the equation for energy continuity

$$C\frac{\partial T}{\partial t}+\frac{\partial J}{\partial z}=0\,, \tag{17}$$

where $C(T)$ is the specific heat. This equation is derived from (6) by taking a moment. Local models of thermal conduction have $J=-\kappa\,\partial T/\partial z$, which produces a diffusion equation for temperature

$$\frac{\partial}{\partial t}T=D\frac{\partial^2}{\partial z^2}T\,, \tag{18}$$

where $D=\kappa/C$. The above equation is valid when the coefficient of thermal conductivity κ is temperature independent. Our theory is more complicated since κ depends on temperature, and the current J is a nonlocal function of the temperature gradient.

Equation (17) has a feature which is important for the present problem. The quantity $\partial J/\partial z=0$ at the interface. This follows from the fact that $T(0)$ is a constant in

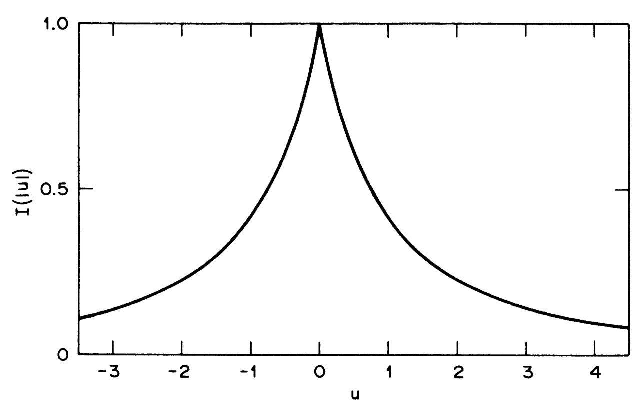

FIG. 1. Plot of the kernel $I(u)$. It is defined in Eq. (15) and used in (14) and (19) in expressions for the heat current. It has a value of 1 at the origin, and a total area of 4. At large u it behaves asymptotically according to $u^{-3/2}$.

time, so $\partial T/\partial t=0$ at $z=0$. The requirement that $\partial J/\partial z=0$ at the surface imposes a constraint upon $G'(z=0)$. In the experiments of Ref. 4 the interface moves with time, so there is a time dependence to the boundary conditions. That feature we are not considering in the present analysis. So, in (14) we define

$$H(x)=\int_0^\infty dx'\frac{\partial^2 K(x')}{\partial x'^2}I(q_D^2\,|x-x'|)\ .$$

Then the boundary condition from (16) is $q_D^2G'(0)=-H(0)+\partial K/\partial x$. One choice for the function $G(x)$ which satisfies the boundary condition is

$$J(x)=-\frac{vq_D^3}{24\pi^2}\left[\int_0^\infty dx'\frac{\partial K(x')}{\partial x'}[I(q_D^2\,|x-x'|)+I(q_D^2(x+x'))]\right],$$
$$\frac{\partial J(x)}{\partial x}=-\frac{vq_D^3}{24\pi^2}\left[\int_0^\infty dx'\frac{\partial^2 K(x')}{\partial x'^2}[I(q_D^2\,|x-x'|)-I(q_D^2(x+x'))]\right]. \tag{19}$$

There is no particular reason to use this boundary condition, except that it is simple. Below we describe some calculations using it. However, many other choices of boundary condition are also valid. If $f(x)$ is any function of x, then the boundary conditions are satisfied if $q_D^2G'(x)=-f(x)H(0)/f(0)$. Generally, one wants to choose a function $f(x)$ which decays to zero away from the surface.

V. NUMERICAL EXAMPLES

First, we present an example where the temperature profile is assumed to be exponential, $K(z)=[292+T_1\exp(-\alpha z)]$. This simple example is chosen because the experimental profile from Ref. 4 at $t=16$ ns is very close to an exponential with $\alpha=2\ \mu\text{m}^{-1}$. We show that the heat current close to the boundary is reduced because of the nonlocal nature of the heat flow. For this example, we employ the form of the boundary conditions of (19).

For this case we simplify the algebra by assuming that ξ is a constant independent of temperature. Then $x=v\xi z$ is proportional to z and it is convenient to solve the problem using the z variable. Furthermore, it is useful to introduce the dimensionless parameter $B=\xi v q_D^2/\alpha$. By using the representation (15) for I, the z integral in (19) can be done analytically. This brings us to the final expression for the heat current for an exponential temperature profile,

$$J=\frac{-q_D}{6\pi^2\xi}\frac{\partial K(z)}{\partial z}j(\alpha z,B)\ ,$$

where

$$j(u,B)=\tfrac{3}{7}\int_0^\infty\frac{D(t)dt}{t^2-1/B^2}\{t-\exp[-u(tB-1)]/B\}\ ,$$

$$D(t)=\begin{cases}\sqrt{t}\,, & t<1\\ 1/t^3, & t>1\ .\end{cases}$$

This integral has several interesting limits. At $B=\infty$, then $j(u,\infty)=1$. The parameter B controls the degree of nonlocality. Another limit is at $u=0$, where the integral can be evaluated analytically,

$$j(0,B)=\frac{3}{7}\left[2-\frac{\pi}{\sqrt{B}}+\frac{2}{\sqrt{B}}\arctan(1/\sqrt{B}\,)+B[0.5-B+B^2\ln(1+1/B)]\right].$$

This example is plotted in Fig. 2, where we show $\exp(-u)$ and also this quantity multiplied by $j(u,B)$ for several values of B. There is about a 30% reduction in the heat flow at the interface when $B=10$. We estimate B using $q_D=\pi/a$, where $a=5.43$ Å for silicon. Then with $\alpha=2\ \mu\text{m}^{-1}$ we find $B=30$. However, smaller values of B are found if q_D is taken as the wave vector where the Debye model ceases to be valid, rather than as the zone boundary. This example shows the reduction in the heat current at one instant of time.

The second example is a calculation of the transient heat flow. Again, we simplify the problem by taking ξ=const, which makes κ=const. Then it is convenient to solve for the z variable. Equations (17) and (19) can be combined into

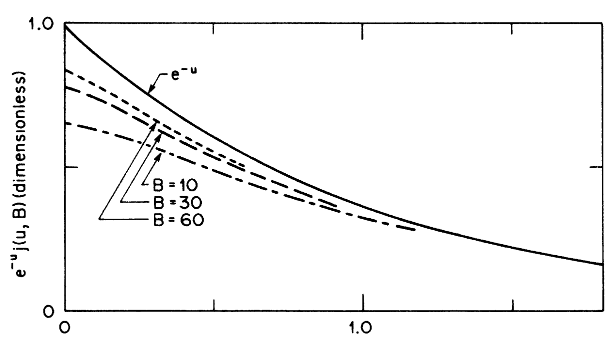

FIG. 2. Plot of the dimensionless thermal current as a function of position for an exponential temperature profile. A local theory would give $\exp(-u)$ shown as the solid line. The nonlocal theory gives a smaller heat current according to the value of the parameter $B=q_D^2\xi v/\alpha$.

$$\frac{\partial T}{\partial t}=\frac{DQ}{4}\int dz'\frac{\partial^2 T(z')}{\partial z'^2}[I(Q\,|z-z'|)-I(Q(z+z'))] ,$$

where $Q=q_D^2 v\xi=2\times 10^6$ cm^{-1}. The equation can be cast into dimensionless form by defining $y=Qz$ and $\tau=DtQ^2$,

$$\frac{\partial T}{\partial \tau}=\tfrac{1}{4}\int_0^\infty dy'\frac{\partial^2 T(y')}{\partial y'^2}[I(|y-y'|)-I(y+y')] . \quad (20)$$

The local version of this equation from (18) is

$$\frac{\partial T}{\partial \tau}=\frac{\partial^2 T}{\partial y^2} . \quad (21)$$

These two equations were solved for the same problem. A semi-infinite bar has the initial temperature of 292 K. At $\tau=0$ the end is placed in contact with a heat reservoir of $T(0)=1750$ K. For $\tau>0$ heat flows into the bar and raises its temperature. Equation (21) is solved using an error function. Equation (20) was solved digitally. The solutions at $\tau=5$ are shown in Fig. 3. The nonlocal theory of Eq. (20) has a much lower temperature profile than the local theory of Eq. (21). This difference persists to all values of τ. There is much less heat flow in the nonlocal theory. This behavior of the nonlocal theory is exactly what is needed to explain the transient experiments of Ref. 4.

VI. RETARDATION

In solving (5) we have heretofore neglected the time derivative. Now, Boltzmann's equation is solved including this term. It introduces the phenomena of retardation. The phonons take a finite time to travel, so that the heat current at a point depends on $\partial K(x,t)/\partial x$ at a previous time. In order to treat this case, we simplify (6) to the case where τ is a constant,

$$\left[1+\tau\frac{\partial}{\partial t}+\tau v \nu\frac{\partial}{\partial z}\right]K_s(z,t,\nu)=K(z,t) . \quad (22)$$

The time variable is solved by use of a Laplace transform where t becomes p. This equation is solved for $\nu<0$ following the steps of Sec. III,

$$K_s(z,p,\nu)=\frac{-1}{v\nu\tau}\int_z^\infty dz'\exp[(z'-z)(1+p\tau)/v\nu\tau][K(z',p)+\tau K_s(z',0,\nu)] .$$

Taking the inverse Laplace transform gives, for $\nu<0$,

$$K_s(z,t,\nu)=-K_s(z-tv\nu,0,\nu)e^{-t/\tau}-\frac{1}{v\tau\nu}\int_z^\infty dz'\exp[(z'-z)/v\nu\tau]K(z',t+(z'-z)/v\nu) .$$

The first term is a transient which dies away quickly. The second term is similar to (13), after an integration by parts. The time dependence in the integrand has been altered by the retardation factor $(z'-z)/v\nu$, which is the time required for the phonon to get from z' to z. Thus the major effect of the time dependence of K_s is in the retardation of the phonons. This effect seems to be small for silicon since v is large.

The above solution for K_s is the inhomogeneous solution of (22), which depends on $K(z,t)$. There are also solutions of the homogeneous equation which are independent of $K(z,t)$. Such solutions have the form

$$K_s(z,t,\nu)=A(t-\tau z/a,\nu)e^{-z/a}+B(t-\tau z/a,\nu)e^{-t/\tau} ,$$

where $a=\tau v\nu$, and A and B are arbitrary functions. These terms can also contribute to the boundary conditions.

When retardation is small, its effects can be included approximately by expanding the argument of the integrand in a Taylor series,

$$K(z',t+\delta)\approx K(z',t)+\delta\frac{\partial K(z',t)}{\partial t} .$$

One advantage of this approach is that it can be done in the original Eq. (22),

$$\left[1+v\tau\nu\frac{\partial}{\partial z}\right]K_s(z,t,\nu)=K(z,t)-\tau\frac{\partial}{\partial t}K_s(z,t,\nu)$$
$$\approx\left[1-\tau\frac{\partial}{\partial t}\right]K(z,t) .$$

This approach works even when τ depends on temperature and phonon frequency. It can be used for the original Eq. (5), which has these additional complications. We have not done any numerical examples using retardation.

VII. DISCUSSION

We have derived a nonlocal theory of thermal conductivity by phonons, and have applied it to interpret experiments in silicon and germanium. As illustrated in Fig. 3, the nonlocal theory predicts a much lower temperature profile near the interface between the liquid and solid silicon than does the local theory. Exactly this behavior is required to explain the experiments in Ref. 4.

Note that in the present theory the coefficient of thermal conductivity κ is not reduced. Also notice that if $\partial T/\partial x$ is a constant, then our theory reduces exactly to the local theory. The need for the nonlocal theory does not depend on whether $\partial T/\partial x$ is large or small. Instead, it depends on whether $\partial^2 T/\partial x^2$ varies rapidly on the distance scale of a phonon mean free path. If it does, then

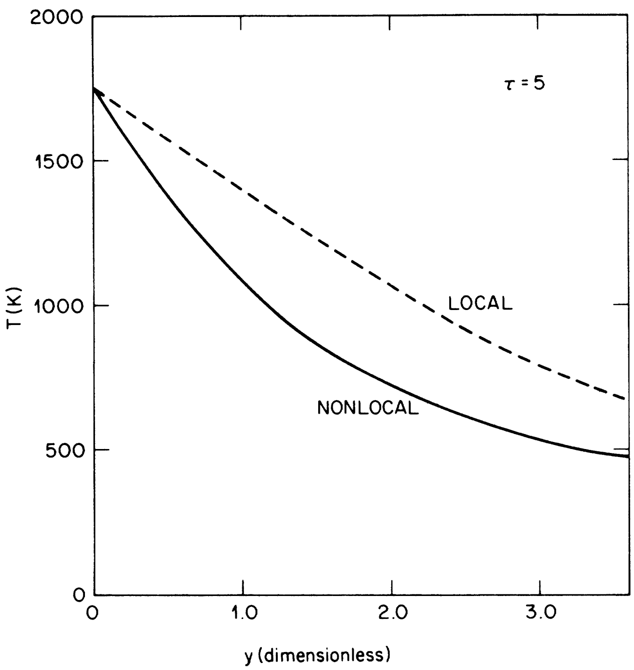

FIG. 3. Comparison of the local and nonlocal theories for transient heat flow. Shown here is the temperature profile after a time of $\tau = 5$. The local theory is calculated using Eq. (21), while the nonlocal theory uses (20). Both assume an initial constant $T = 292$ K at $\tau = 0$ with a boundary condition at the surface of a fixed $T(y = 0) = 1750$ K.

the nonlocal theory is required. However, the phonon MPF $l \sim \omega^{-2}$. No matter what distance scale one has for $\partial^2 T/\partial z^2$, there are phonons of small ω with a longer MPF. Thus the nonlocal theory is needed for all transient calculations.

The present theory includes some contributions such as $(\partial T/\partial z)^2$ which arise from the temperature dependence of the thermal conductivity. However, other terms of the same form are ignored. They were omitted because the starting Boltzmann equation (6) has linearized the dependence on T, except in the dependence of the lifetime $\tau(T)$. This approximation is being presently investigated, in order to see if a solution can be obtained with a more accurate version of (6) which permits terms with higher powers of T.

The main result we report is a new theory of the thermal conductivity which emphasizes its nonlocal nature. Our nonlocal theory should be used whenever the temperature is changing rapidly with distance. It is particularly important when $T(z)$ is not a linear function of temperature.

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[1]V. Sobolev, *A Treatise on Radiation Transfer* (Consultants Bureau, New York, 1963).

[2]B. Davison, *Neutron Transport Theory* (Clarendon, Oxford, 1957).

[3]See, for example, J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960), Eq. (11.7.10).

[4]B. C. Larsen, J. Z. Tischler, and D. M. Mills, J. Mater. Res. **1**, 144 (1986); the germanium results are unpublished.

[5]A. M. Malvezzi, C. Y. Huang, H. Kurz, and N. Bloembergen, in *Beam-Solid Interactions and Phase Transformations,* edited by H. Kurz, G. L. Olsen, and J. M. Poate (MRS, Pittsburgh, 1986), Vol. 51.

[6]C. J. Glassbrenner and G. A. Slack, Phys. Rev. **134**, A1058 (1964).

[7]S. M. Sze, *The Physics of Semiconductor Devices* (Wiley, New York, 1981).

[8]H. Beck, P. F. Meier, and A. Thellung, Phys. Status Solidi A **24**, 11 (1974).

[9]C. Horie and J. A. Krumhansl, Phys. Rev. **136**, A1397 (1964).

[10]H. Beck, in *Dynamical Properties of Solids,* edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1979), Vol. 2, Chap. 4.

[11]F. Kaiser and M. Wagner, Z. Naturforsch. **32a**, 375 (1977).