Phys. Rev. Lett. 16, 347 (1966). For an excellent review of the theoretical and experimental situation see S. A. Akhmanov, A. P. Sukhorukov, and R. V. Khokhlov, Usp. Fiz. Nauk 93, 19 (1967) [Sov. Phys. Usp. 10, 609 (1968)], and Zh. Eksp. Teor. Fiz. 50, 1537 (1966) [Sov. Phys. JETP 23, 1025 (1966)].

[4]M. Maier, G. Wendl, and W. Kaiser, Phys. Rev. Lett. 24, 352 (1970); M. M. T. Loy and Y. R. Shen, Phys. Rev. Lett. 14, 380 (1969); D. Grischkowsky, Phys. Rev. Lett. 24, 866 (1970).

[5]For these parameters the plasma frequency is ω_p =1.54×10^{13} rad/sec, and the ratio of the speed of light in the medium to c^* is 67. The critical power for the incident beam is 551.8 W. The dielectric constant ϵ_2 is 1.26×10^{-7} esu. The incident intensity here is 2.8 $\times 10^7$ W/cm^2 which lies below the surface ionization intensity for InSb of 3×10^7 W/cm^2.

[6]N. Tzoar and J. I. Gersten, to be published.

[7]The initial beam profile is assumed to be of the form $E^2 = E_0^2 \exp(-2r^2/a^2)$.

Thermal Boundary Resistance

H. Budd and J. Vannimenus

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Faculté des Sciences,
Paris V, France
(Received 22 February 1971)

A simple model of heat flow across a metal-insulator interface is used to calculate the spatial variation of the temperature. The characteristic distance for the temperature gradient to reach its bulk value is shown to be of the order of the phonon mean free path in both the metal and the insulator. Explicit expressions are presented for the electron and phonon contributions to the interfacial thermal resistivity.

In this Letter we present a semiclassical description of heat transport across a metal-insulator interface. We shall be particularly interested in the temperature profile near the interface, where the usual local relation between the heat flux and the temperature gradient is no longer satisfied.

A knowledge of the temperature distribution is important in determining the thermal boundary resistance between two solids, or a solid and a liquid, since the temperature at the interface is usually obtained by a linear extrapolation[1] of the temperature measured relatively far from the boundary. Most theoretical studies[2] of these phenomena seek to determine the temperature difference across the interface, and do not consider the details of its spatial variation.

In addition, the electron contribution to the heat flux across the interface has received relatively little attention since it is commonly assumed that they are almost uncoupled to the phonons in the insulator. Little,[3] and subsequently Andreev,[4] presented the first models of just how such a coupling might arise.

In the present work we use a simple Boltzmann-equation approach to provide a phenomenological description of thermal transport across a metal-insulator interface. This allows an explicit calculation of the temperature profile and a qualitative assessment of the effects of different surface conditions as well as the *nonlocality* of the transport near the interface. The latter leads to some rather interesting results concerning the role of electrons, even in the limiting case of zero electronic heat flux exactly at the surface.

We take the metal to occupy the right half-space $x > 0$, and the insulator the left half-space. A steady heat flux J is imposed, and we seek the steady-state temperature distribution.

The electronic contribution to the heat flux J_e is obtained by solving the usual Boltzmann equation[5] for the electron distribution function $f = f_0(T(x)) + \varphi$:

$$V_x \frac{\partial \varphi}{\partial x} + \frac{\varphi}{\tau} = V_x \frac{\partial f_0}{\partial \epsilon} \left(\frac{\epsilon - u}{T} \frac{\partial T}{\partial x} \right), \tag{1}$$

where f_0 is the Fermi-Dirac distribution at the local temperature $T(x)$ and Fermi energy $u(x)$, and τ is the relaxation time. The thermoelectric force, which is necessary to assure that the electrical current is zero, will be neglected here since it leads to a correction to ∇T of the order of $(kT/u)^2$.

The relaxation-time approximation is a crude representation of the effect of collisions and is subject to the usual criticism in that it does not accurately describe inelastic scattering. It furthermore fails to take account of the different relaxation rates of the various anisotropies in the spherical harmonic

expansion of φ. It is nonetheless the simplest representation of the scattering processes and will be employed here.

In the same spirit the interface will be represented by a boundary condition

$$\bar{\varphi}(V_x, V_y, V_z) = p\bar{\varphi}(-V_x, V_y, V_z) \text{ at } x = 0,$$ (2)

where $\bar{\varphi}$ ($\bar{\varphi}$) represents the incident (reflected) electrons.

The $p = 0$ case represents the limiting condition of thermalization on contact, while $p = 1$ represents specular reflection and therefore zero heat flux across the interface. Equations (1) and (2) are readily solved and the corresponding heat flux, calculated to lowest order in kT/u, is given by

$$J = -\frac{CV}{2} \int_0^\infty dx' \, \nabla T(x') \left[E_3 \left(\frac{|x + x'|}{l} \right) - p E_3 \left(\frac{x + x'}{l} \right) \right],$$ (3)

where C, V, and $l = V\tau$ represent the electronic specific heat, Fermi velocity, and mean free path, respectively. The kernel is given by the exponential integral

$$E_n(x) = \int_1^\infty \frac{dt}{t^3} e^{-xt}, \quad \frac{dE_n}{dx} = -E_{n-1}.$$ (4)

A similar analysis for the phonon heat flux yields, in the Debye model, a result identical to Eq. (3) with C, l, and V replaced by the appropriate quantities for the phonons. Strictly speaking one obtains a sum of three terms, corresponding to the different values of these parameters for the three acoustic branches. For simplicity we retain the single term, Eq. (3), with an average sound velocity, etc. The general case is also readily soluble by the methods to be presented below.

When only one type of excitation is considered on each side of the interface, we must solve Eq. (3) for ∇T in each half-space. For $p = 0$ the latter is readily soluble by the Wiener-Hopf method,[6] and is in fact closely related to the well-known Milne problem.[7] Anticipating the result we decompose $\nabla T = T_M(0)\delta(x) + \nabla T_M(x)$ into a singular (δ function) part and smooth part T_M which, as we now show, satisfies the Milne equation. Inserting this decomposition in Eq. (3) with $p = 0$, and integrating by parts, we obtain from Eq. (4)

$$J = \frac{CVl}{2} \left[\int_0^x dx' \, T_M(x') E_2 \left(\frac{x - x'}{l} \right) - \int_x^\infty dx' \, T_M(x') E_2 \left(\frac{x' - x}{l} \right) \right].$$ (5)

Differentiating with respect to x yields Milne's equation:

$$T_M(x) = \tfrac{1}{2} \int_0^\infty dx' \, T_M(x') E_1(|x - x'|/l).$$ (6)

This equation has been studied in considerable detail and approximate expressions for the temperature near to and far from the interface, with κ the bulk thermal conductivity, are given by[8]

$$T(x) - T(0) \cong -\frac{Jl}{\kappa\sqrt{3}} (1 - \tfrac{1}{2}z \ln z), \quad 0 < z = \frac{x}{l} \ll 1$$

$$\cong -\frac{Jl}{\kappa} (z + 0.71), \quad z \gg 1.$$ (7)

The temperature distribution is therefore given exactly by the solution of the Milne equation, and an identical solution obviously applies in the left half-space, with a κ and l appropriate to the relevant excitations. The ideal contact, $p = 0$, is therefore characterized by a surface resistance

$$R_S = \frac{\delta T}{J} = \sqrt{3} \left[\frac{1}{C_l V_l} + \frac{1}{C_R V_R} \right],$$

the subscripts referring to the thermal carriers on the left and right.

If the surface temperature difference is obtained by an extrapolation from far from the interface, the "measured" surface resistance will be $1.23 R_S$ as is seen from Eq. (7).

The Wiener-Hopf method can equally well be applied to situations where several different types of excitations contribute to the heat flow in parallel, as long as $p = 0$. In such cases the kernel of integral equation for ∇T is a difference kernel which decreases exponentially at large distances. For $p \neq 0$ one no longer has a difference kernel and the solution is far more complicated.

We shall therefore concentrate on the one-dimensional case since the kernels then become simple exponential integrals, Eq. (4). We see in fact from Eqs. (3) and (4) that the three-dimensional case can be regarded as a superposition of a continuum of thermal excitations in one dimension, with mean free paths l/t ($1 < t < \infty$) and relative weights dt/t^3. This corresponds to the continuous angular distribution in three dimensions, where $t^{-1} = |Vx|/V$.

If there are N types of excitations in a given medium, the one-dimensional analog of Eq. (3) is

$$J = \sum_{i=1}^{N} J_i; \quad J_i = -\frac{C_i V_i}{2} \int_0^\infty dx' \, \nabla T(x') \left\{ \exp\left(-\frac{|x-x'|}{l_i}\right) - p_i \exp\left[\frac{-(x+x')}{l_i}\right] \right\} \tag{8}$$

Considering first only a single excitation, we obtain for $x > 0$

$$T(x) - T_0 = -\frac{J}{\kappa}\left[x + \frac{l}{\alpha(p)}\right], \quad \alpha(p) = \frac{1-p}{1+p}. \tag{9}$$

We note that the temperature jump at the interface persists for all p except $p = -1$, in which case T is equal to its bulk value just as if there were no surface. This is also true in three dimensions as can be seen from Eq. (3). The $p = 1$ case leads to an infinite temperature jump which is expected since this boundary condition requires that the heat flux vanish at $x = 0$.

With two types of excitations the solution of Eq. (8) yields

$$\frac{\nabla T(x)}{\nabla T(\infty)} - 1 = \left[(B_2 - B_1)\delta(x) + \left(\frac{\alpha_2}{l_2} - \frac{\alpha_1}{l_1}\right) \exp\left(\frac{-x}{L}\right)\right]\left[B_2 \frac{\alpha_1}{l_1} - B_1 \frac{\alpha_2}{l_2}\right]^{-1} \tag{10}$$

$$B_i = (L^2 + Ll_i\alpha_i)/(L^2 - l_i^2), \quad \nabla T(\infty) = -J/(\kappa_1 + \kappa_2),$$

where α is defined in Eq. (9). The characteristic length L is given by

$$\sum_i \kappa_i/(L^2 - l_i^2) = 0 \tag{11}$$

and is obviously intermediate between l_1 and l_2. If there are N excitations instead of 2, there are $N-1$ characteristic lengths L located between adjacent values of l_i as can be seen from Eq. (11). The three-dimensional case, considered from this point of view, leads to the conclusion that Eq. (10) is then modified to contain a continuum of exponentials with characteristic lengths between 0 and l. In the Milne problem this is indeed the form of the exact solution.[7] It is further interesting to note that with an appropriate choice of the parameters, Eq. (10) fits this exact solution to within 2%.[8] This means that in the present context, a simple model using two different mean free paths provides a surprisingly accurate approximation to the exact solution for a continuum of mean free paths.

We now apply Eq. (10) to simultaneous heat conduction by electrons and phonons in a metal. We take $l_e \gg l_p$, $V_e \gg V_p$, and $\alpha_p \gtrsim \alpha_e$; and we obtain for $x > 0$

$$T(x) - T(0) \simeq -\frac{Jx}{\kappa} - \frac{J}{C_p V_p \alpha_p} \frac{1 + \alpha_p(1+R)^{-1/2}\{1 + R[1 - \exp(-x/l_p(1+R)^{1/2})]\}}{1 + \alpha_e[\alpha_p^{-1} + (1+R)^{1/2}]C_e V_e/C_p V_p},$$

where $R = C_p \tau_e/C_e \tau_p$.

The first term multiplying the bracket represents the phonon contribution to the interfacial resistance, while the remaining terms describe the modifications due to the electrons. We note that the electron coupling at the interface α_e is multiplied by $C_e V_e/C_p V_p \sim T^{-2}$, and can therefore become quite important at low temperatures even for relatively small values of α_e. This will clearly have the effect of reducing the interfacial resistance.

Secondly even if $\alpha_e \equiv 0$, i.e., no electron coupling at the interface, the electrons still contribute to the surface resistance by virtue of the nonlocal relation between the heat flux and the temperature gradient. A quantitative estimate of their contribution would require a knowledge of R, which contains the ratio of the electron and phonon relaxation times.

We shall not attempt this here since in addition to the considerable uncertainties with regard to the phonon contribution to the thermal conductivity in metals, one is faced with the problem of choosing an appropriate relaxation time. The latter can be quite different near the surface and in the bulk since the distribution functions are highly anisotropic near $x = 0$. Further progress in this direction would require a rather detailed study of the coupled electron-phonon system, without invoking the relaxation

time approximation.

Finally we note that the characteristic length in Eq. (11) is of the order of the phonon mean free path. It is within this distance that the electron heat current rises from its surface to bulk value. This is independent of the α's and is much shorter than the electron mean free path. We expect this conclusion to be approximately valid in three dimensions as well, so that the large temperature gradients are within a distance of order l_p from the surface. Further on the temperature gradient is approximately constant and therefore one essentially observes bulk behavior for distances greater than l_p. This is perhaps an explanation of why measurements of ∇T in metals have failed to show any mean-free-path effects since the relevant distance l_p is much shorter than l_e.

[1]G. L. Pollack, Rev. Mod. Phys. **41**, 48 (1969).

[2]J. D. N. Cheeke, J. Phys. (Paris) **31**, Suppl. 10, 129 (1970).

[3]W. A. Little, Phys. Rev. **123**, 435 (1961), and **130**, 596 (1963).

[4]A. F. Andreev, Zh. Eksp. Teor. Fiz. **43**, 1535 (1962) [Sov. Phys. JETP **16**, 1084 (1963)].

[5]J. M. Ziman, *Principles of the Theory of Solids*, (Cambridge U. Press, Cambridge, England, 1965), p. 181.

[6]P. Morse and H. Feshbach, in *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 978.

[7]D. Davison, *Neutron Transport Theory* (Clarendon, Oxford, England, 1957), p. 67.

[8]C. Mark, Phys. Rev. **72**, 558 (1947).

Pseudopotential Calculation of the Latent Heats of Melting of Simple Metals[*]

W. M. Hartmann

Michigan State University, East Lansing, Michigan 48823

(Received 19 April 1971)

The latent heats of melting for simple metals at normal pressure are calculated by the pseudopotential method. The Percus-Yevick hard-sphere model is used for the liquid-structure factor, and an uncorrelated harmonic oscillator model is used for the solid-structure factor. Numerical results agree well enough with experiment and are sufficiently stable against changes in the parameters to make further calculations of the latent heat seem worthwhile.

In this Letter we propose that the latent heat of melting may be calculated for simple metals by the pseudopotential method. Along the melting curve the Gibbs functions for liquid and solid phases must be equal. Therefore, the latent heat of melting L is

$$L = T_m \Delta S = \Delta U + p\Delta V,$$

where Δ denotes the difference between liquid and solid quantities. At atmospheric pressure $p\Delta V$ is entirely negligible, and the latent heat is given by the difference in internal energies ΔU.

The internal energy of a simple metal, in rydbergs per ion, includes the kinetic, exchange, and correlation energies of the electron gas[1]:

$$U_g = 2.21Z/r_s^2 - 0.916Z/r_s - (0.115 - 0.031\ln r_s)Z,$$

where r_s is the Wigner-Seitz radius in atomic units and we have used the Nozières-Pines interpolation formula for the correlation energy.[2]

The energies of the conduction electrons are changed by interaction with the ions, and the treatment of this interaction by the pseudopotential method makes the calculation tractable. Because of macroscopic charge neutrality the homogeneous parts of the bare electron-ion interaction, electron-electron direct interaction, and interionic direct interaction sum to a finite result, the Hartree energy:

$$U_H = \lim_{q \to 0} [w_b(q) + 8\pi Z/q^2]Z\Omega_0^{-1},$$

where Ω_0 is the volume per ion and $w_b(q)$ is the bare ion pseudopotential. The contribution to the latent heat from the above terms depends only upon the volume change on melting and is independent of structure. Since the kinetic energies of the ion cores at melting are $U_K = \frac{3}{2}k_B T_m$ for both liquid and solid, only two important contributions to the system energy remain.

The difference between the direct ion interaction $V_D(q) = 8\pi Z^2/q^2$ for the structure of the system and that of the homogeneous jellium is, for