(Clarendon, Oxford, England, 1965).

[18] V. V. Goldman, J. Phys. Chem. Solids 30, 1019 (1968).

[19] G. Fritsch, Z. Angew. Math. Phys. 22, 505 (1967).

[20] G. Fritsch and E. Lüscher, J. Phys. Chem. Solids (to be published).

[21] Fa. Hewlett-Packard, Palo Alto, Calif.

[22] D. K. C. Mac Donald, W. B. Pearson, and L. T. Towle, Can. J. Phys. 34, 389 (1956).

[23] This point of view is only possible if one can define a suitable extension of the low-temperature phonon into the high-temperature region. Neutron scattering experiments give phonon peaks right up to the melting point, a result which supports the possibility of such an extension.

[24] G. Meissner, Phys. Rev. B 1, 1822 (1970).

[25] S. C. Jain, N. S. Saxena, and R. C. Bhandari, J. Chem. Phys. 52, 4629 (1970); K. S. Singwi, K. Sköld, and M. P. Tosi, Phys. Rev. A 1, 454 (1970).

[26] The assumption of the validity of the Wiedemann-Franz law is not implausible as the electrical conductivity shows no anomalous effects prior to melting.

[27] R. A. Oriani, J. Phys. Chem. Solids 30, 339 (1969).

[28] G. A. Sullivan, Phys. Rev. 154, 605 (1967).

[29] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).

[30] M. P. Greene and W. Kohn, Phys. Rev. 137, A513 (1965).

[31] Compare however the results of a computer experiment by W. G. Hoover, and F. H. Ree [J. Chem. Phys. 49, 3609 (1968)] on hard spheres. They find an instability point in their solid phase results, characterized by a diverging compressibility. The instability is above the thermodynamic transition temperature (metastability limit), but this shift could be produced by the nature of the approximations used.

[32] T. Schneider, R. Brout, H. Thomas, and Z. Feder (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Noninteracting Fermi Gas in a Square-Well Potential[*]

Carl E. Nash[†]
The Department of Physics, The University of North Carolina,
Chapel Hill, North Carolina 27514

(Received 26 April 1971)

The problem of a noninteracting Fermi gas in a finite square-well potential is solved analytically in the limit that the well becomes infinitely wide. The errors of previous authors using this model as a first approximation to the problem of a simple metal with surfaces are pointed out.

A very simple model which has been used to represent electrons in a simple metal with surfaces is a noninteracting Fermi gas in a square-well potential. Bardeen[1] was probably the first to use this model in his paper on the theory of the work function. He used the wave functions of this model to calculate the exchange potential across the surface. Huntington[2] used the same model to calculate the surface energy of a simple metal in a first approximation. More recently, Lang and Kohn[3] based their more sophisticated calculation of the surface energy and the work function of some metals at least in part on this model, and on the work of Bardeen and of Huntington. It is the purpose of this paper to calculate the exact analytic solution to this problem, since, as will be shown, incorrect assumptions about the density of states and the normalization of the wave functions of the problem have led to errors in some of the above work.

We shall define the problem somewhat differently than has been done previously in order to show the exact quantum-mechanical solution of the Schrödinger equation with the proper boundary conditions. The coordinates of the problem are such that the x axis is perpendicular to the "surfaces." The Schrödinger equation for the problem is

$$-\tfrac{1}{2}\nabla^2\Psi_{\vec{k}}(\vec{x})+V(x)\Psi_{\vec{k}}(\vec{x})=\epsilon_{\vec{k}}\Psi_{\vec{k}}(\vec{x}) , \qquad (1)$$

with the potential

$$V(x)=\begin{cases}0, & -L<x<L\\ V, & x<-L,\ x>L .\end{cases}$$

The y and z coordinates are parallel to the surfaces, and periodic boundary conditions are applied to these coordinates. The wave functions for the problem have plane-wave form in the y and z coordinates with a period L:

$$\Psi_{\vec{k}}(\vec{x})=(1/L)e^{i(k_y y+k_z z)}\psi_k(x) .$$

The x component of the wave functions can be either even or odd:

$$\psi_{k_+}(x)=\begin{cases}(N_{k_+})^{1/2}\cos k_+ x , & -L<x<L\\ (N_{k_+})^{1/2}\cos k_+ L \exp[-(2V-k_+^2)^{1/2}|x-L|], & x<-L ,\ x>L\end{cases}$$

$$\psi_{k_-}(x)=\begin{cases}(N_{k_-})^{1/2}\sin k_- x , & -L<x<L\\ (N_{k_-})^{1/2}\sin k_- L \exp[-(2V-k_-^2)^{1/2}|x-L|], & x<-L,\ x>L\end{cases}$$

where we have

$$N_{k_\pm} = [L + 1/(2V - k_\pm^2)^{1/2}]^{-1} \; . \tag{2}$$

The wave vectors are determined by the transcendental equations

$$\begin{aligned} \cos^2 k_+ L &= k_+^2/2V \; , \quad \tan k_+ L > 0 \\ \sin^2 k_- L &= k_-^2/2V \; , \quad \tan k_- L < 0 \; . \end{aligned} \tag{3}$$

The fact that the wave vector appears in the normalization will not in this case affect the results which we are deriving here and we could as well have used the approximation $N_k = 1/L$ for the limit of large L. Ignoring this small correction to the normalization led Bardeen and later Huntington to an incorrect connection between the well depth and the total number of electrons in the well. This relation [Eq. (26) in Bardeen's paper or Eq. (2) in Huntington's] is expressed in terms of the distance between the edge of the potential well and surface as determined by the charge-conservation condition.

We are interested here in calculating two results, the "surface" energy and the charge density as a function of position. The surface energy is the difference between the energy of this system and an equivalent number of Fermions in a uniform gas with the same Fermi level, per unit of surface area. These are given as follows:

$$\begin{aligned} E_s &= \frac{k_F^3 L}{3\pi^2}\left(\langle \epsilon_{\vec{k}} \rangle - \frac{3k_F^2}{10} \right) , \\ \langle \epsilon_{\vec{k}} \rangle &= \frac{k_F^2}{5} + \frac{1}{2}\left(\sum_{k<k_F} (k_F^2 - k^2)k^2 \Big/ \sum_{k<k_F} (k_F^2 - k^2) \right) , \end{aligned} \tag{4}$$

$$\rho(x) = \frac{1}{2\pi}\left(\sum_{k_-<k_F} (k_F^2 - k_-^2) |\psi_{k_-}(x)|^2 + \sum_{k_+<k_F} (k_F^2 - k_F^2) |\psi_{k_+}(x)|^2 \right) . \tag{5}$$

In the limit of large L, we may convert these sums to integrals. Some care is necessary, however, since the k's do not form an evenly spaced set. Another way of saying this is that the density of states in k space is not constant. A simple way of dealing with this difficulty is to express the k's in terms of the evenly spaced sets: $q = n\pi/L$ for the odd functions, and $p = (n - \frac{1}{2})\pi/L$ for the even functions. Here, n is a positive integer. The proper relations between k_- and q between k_+ and p are found from Eqs. (3). For the even functions, we have

$$\cos k_+ L = \pm \sin(p - k_+)L = \pm k_+/(2V)^{1/2} \; ,$$

$$(p - k_+)L = \sin^{-1} \frac{k_+}{(2V)^{1/2}} = \frac{k_+}{(2V)^{1/2}} + \frac{k_+^3}{6(2V)^{3/2}} + \cdots \; ,$$

which to first order in $1/L$ gives

$$k_+ = p[1 - 1/L(2V)^{1/2}] - p^3/6L(2V)^{3/2} \; . \tag{6}$$

The upper sign goes with odd values of n, the lower with even values. By the same process, one can find an identical relationship between k_- and q. Now in going from the sum to an integral over p or q, we need only include the constant density of states L/π.

The next important consideration in going from the sums to integrals is choosing the correct limits of integration. For the even functions the integration goes from 0 to m where $m = p_{\max} + \pi/2L$. $p_{\max}$ is the highest occupied even state. For the odd states there is no $q = 0$ term, so the limits of integration are from $\pi/2L$ to $m \pm \pi/2L$ depending on whether the highest occupied state is even or odd. The relationship between m and k_F is that $k_F = m + \delta/L$ where $[-\frac{1}{2}\pi - 1/(2V)^{1/2}] < \delta < [\frac{1}{2}\pi - 1/(2V)^{1/2}]$.

In the surface energy, it turns out that we need only go to first order in $1/L$ to obtain the correct result in the limit of large L. It also turns out that if we simply take $m = k_F$, the error in the surface energy due to this approximation goes as $1/L^2$. Thus we have for the surface energy:

$$\begin{aligned} E_s = \frac{k_F^3 L}{6\pi^2}\Bigg(&\left\{ k_F^2 \int_0^{k_F} \left[p^2 - \frac{2}{L}\left(\frac{p^2}{(2V)^{1/2}} + \frac{p^4}{6(2V)^{3/2}} \right) \right] dp \right. \\ &\left. - \int_0^{k_F} \left[p^4 - \frac{4}{L}\left(\frac{p^4}{(2V)^{1/2}} + \frac{p^6}{6(2V)^{3/2}} \right) \right] dp \right\} \Big/ \; 2\left[k_F^2 - \int_0^{k_F} p^2 - \frac{2}{L}\left(\frac{p^2}{(2V)^{1/2}} + \frac{p^4}{6(2V)^{3/2}} \right) dp \right] \\ &+ \left\{ k_F^2 \int_{\pi/2L}^{k_F + \pi/2L} \left[q^2 - \frac{2}{L}\left(\frac{q^2}{(2V)^{1/2}} + \frac{q^4}{6(2V)^{3/2}} \right) \right] dq - \int_{\pi/2L}^{k_F + \pi/2L} \left[q^4 - \frac{4}{L}\left(\frac{q^4}{(2V)^{1/2}} + \frac{q^6}{6(2V)^{3/2}} \right) \right] dq \right\} \Big/ \\ &2\left[k_F^2 - \int_{\pi/2L}^{k_F + \pi/2L} q^2 - \frac{2}{L}\left(\frac{q^2}{(2V)^{1/2}} + \frac{q^4}{6(2V)^{3/2}} \right) dq \right] - \frac{k_F^2}{10} \Bigg) , \end{aligned} \tag{7}$$

$$E_s = \frac{k_F^4}{80\pi} [1 + 32k_F^3/105(2V)^{3/2}] \; . \tag{8}$$

This expression is exact in the limit as L becomes large. It is quite different from the expression derived (incorrectly) by Huntington. For values of k_F and V characteristic of sodium ($k_F = 0.48$ a.u. and $V = 0.2$ a.u.) this expression gives $E_s = 0.000\,24$ a.u. By comparison, Huntington found the value 0.000 11 a.u. For whatever academic interest it might have, the experimental value for sodium is around 0.000 14 a.u.

To obtain the charge density near the surface, we must first make a transformation of coordinates. Let $\xi = L - x$. This coordinate has its origin at the potential discontinuity and is positive toward the inside of the system. Making this transformation in the wave functions, we have for the interior solutions

$$\begin{aligned}\psi_{k_+}(\xi) &= (N_{k_+})^{1/2}\cos[k_+(L-\xi)] \\ &= (N_{k_+})^{1/2}(\cos k_+L\,\cos k_+\xi + \sin k_+L\,\sin k_+\xi)\;.\end{aligned}$$

Squaring this and using the relations (3) we have

$$|\psi_{k_+}(\xi)|^2 = N_{k_+}\left[\left(\frac{k_+^2}{V}-1\right)\cos^2 k_+\xi + \frac{k_+}{2V}(2V-k_+^2)^{1/2} \times \sin 2k_+\xi + 1 - \frac{k_+^2}{2V}\right]. \quad (9)$$

An identical relation is obtained for the odd functions.

Since we are looking for a zero-order effect in $1/L$, we need to keep only terms which are to zeroth order in $1/L$. Thus, both sums in Eq. (5) convert to identical integrals with the same limits of integration, and the charge density is

$$\rho(\xi) = \frac{1}{\pi^2}\int_0^{k_F}(k_F^2-k^2)\left[\left(\frac{k^2}{V}-1\right)\cos^2 k\xi + 1 - \frac{k^2}{2V}\right]dk + \frac{1}{2V\pi^2}\int_0^{k_F}(k_F^2-k^2)(2V-k^2)^{1/2}\sin(2k\xi)k\,dk\;. \quad (10)$$

The first integral is straightforward and gives the result

$$\frac{k_F^3}{3\pi^2} + \frac{1}{\pi^2}\left[\frac{k_F}{4}\left(1-\frac{k_F^2}{V}\right)\frac{\cos 2k_F\xi}{\xi^2} + \left(\frac{5k_F^2}{8V}-\frac{1}{8}\right)\frac{\sin 2k_F\xi}{\xi^3} + \frac{3k_F}{4V}\frac{\cos 2k_F\xi}{\xi^4} - \frac{3}{8V}\frac{\sin 2k_F\xi}{\xi^5}\right]. \quad (11)$$

For the second integral, since k^2 is always less than $2V$, we can expand the square root as a power series in $k^2/2V$. The integral can then be done term by term, giving the result as a double sum:

$$\frac{k_F^3}{\pi^2(2V)^{1/2}}\sum_{n=0}^{\infty}\frac{\frac{1}{2}!}{n!(\frac{1}{2}-n)!}\sum_{l=0}^{n+1}\frac{k_F^{2n-2l}(-1)^l(2n+1)!}{(2V)^n(2n-2l+2)!\,2^{2l}}\left(\frac{(4n-2l+5)l\cos 2k_F\xi}{(2n-2l+3)\xi^{2l+1}} - \frac{(2l+1)(2n-l+2)\sin 2k_F\xi}{2k_F\xi^{2l+2}}\right).$$

The summations can be interchanged, and the $l = 0$ term extracted to give the result to second order in $1/\xi$:

$$-\frac{k_F^2}{2\pi^2(2V)^{1/2}}\left(1-\frac{k_F^2}{2V}\right)^{1/2}\frac{\sin 2k_F\xi}{\xi^2} + \frac{1}{4\pi^2(2V)^{1/2}}\sum_{l=1}^{\infty}\sum_{n=l-1}^{\infty}(-1)^l\frac{\frac{1}{2}!\,k_F^{2n-2l-2}(2n+1)!}{n!(\frac{1}{2}-n)!(2V)^n 2^{2l}(2n-2l+2)!} \times\left(\frac{2l(4n-2l+5)k_F\cos 2k_F\xi}{(2n-2l+3)\xi^{2l+1}} - (2l+1)(2n-2l+2)\frac{\sin 2k_F\xi}{\xi^{2l+2}}\right). \quad (12)$$

From (11) and (12) we can now give the expression to lowest order in $1/\xi$ for the charge density. This expression gives the form of the charge-density oscillations as they first appear when approaching the potential discontinuity from the inside and is valid only when $1/\xi^2 \gg 1/\xi^3$:

$$\rho(\xi) = \frac{k_F^3}{3\pi^2} + \frac{k_F\cos 2k_F\xi}{4\pi^2\xi^2} - \frac{k_F^3\cos 2k_F\xi}{4\pi^2 V\xi^2} \times\frac{k_F^2(2V-k_F^2)^{1/2}\sin 2k_F\xi}{4\pi^2 V\xi^2}\;. \quad (13)$$

If we let $\gamma_F = \sin^{-1}[k_F/(2V)^{1/2}]$, Eq. (13) can be put in the form more usually seen

$$\rho(\xi) = \frac{k_F^3}{3\pi^2} + \frac{k_F\cos 2(k_F\xi+\gamma_F)}{4\pi^2\xi}\;. \quad (14)$$

It is interesting that in the limit of large L, the corrections to the normalization and density of states shown here do not affect results for the charge-density oscillations near the surface, nor would they affect the total energy of the crystal with surfaces. The correction comes to the surface energy which requires that terms be retained to first order in $1/L$, since the zeroth-order terms cancel.

The results of this paper would be purely academic were it not for the fact that the model solved here is fairly commonly used as a first approximation to electrons in a metal or even a semiconductor at a plane discontinuity. The model is not very good, of course, since it ignores even the Hartree potential, not to mention exchange and other many-body interactions. The other difficulty with this model is that discontinuities in potential of this type simply do not exist in nature.

The author would like to thank Professor Sang-il

Choi for suggesting this problem. Thanks are also due to Professor Choi, Professor John Hernandes, Professor K. S. Dy, and Dr. N. D. Lang for reading the manuscript and making helpful comments.

---

*Research supported by the National Aeronautics and Space Administration through its University Sustaining Program.

†Present address: Public Interest Research Group, Washington, D. C. 20005.

[1] E. Wigner and J. Bardeen, Phys. Rev. 48, 84 (1935); J. Bardeen, *ibid.* 49, 653 (1936).

[2] H. B. Huntington, Phys. Rev. 81, 1035 (1951).

[3] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970): N. D. Lang, Solid State Commun. 7, 1047 (1969); N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Theory of Radiative Heat Transfer between Closely Spaced Bodies

D. Polder and M. Van Hove
Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

(Received 28 January 1971)

A general formalism is developed by means of which the radiative heat transfer between macroscopic bodies of arbitrary dispersive and absorptive dielectric properties can be evaluated. The general formalism is applied to the heat transfer across a vacuum gap between two identical semi-infinite bodies at different temperatures. The peculiarities arising when the gap width is of the order of, or smaller than, the dominant thermal radiation wavelengths are studied and quantitatively evaluated for the case of two metal bodies. The predicted strong increase with diminishing gap width is in qualitative agreement with experimental results.

I. INTRODUCTION

Consider a set of bodies of macroscopic dimensions with arbitrary dispersive and absorptive dielectric properties. These bodies emit thermal radiation depending on the local temperature. With the aid of the fluctuation-dissipation theorem and electromagnetic theory we shall derive a formula for the heat flux at an arbitrary point due to the radiating bodies. Integration of this heat flux over a closed surface gives the net power dissipated in the absorbing matter contained in the enclosed volume.

By this method we intend to determine and discuss the net heat transfer between two semi-infinite absorbing bodies with arbitrary dielectric properties at slightly different temperatures separated by vacuum of width d. The heat transfer between closely spaced bodies differs from that when the spacing is large for two reasons. Firstly, when the separation d is comparable to, or smaller than, the dominant vacuum wavelengths at the temperatures considered, interference effects must be expected in the waves multiply reflected between the two surfaces. Secondly, the evanescent fields normally present in thermal equilibrium at the outer surface of each body can reach over to the opposite body and transfer energy if the distance is sufficiently small. As will be explicitly shown for metal bodies, the latter mechanism of energy transfer is the dominant one for small distances, giving rise to a strong increase of heat transfer with decreasing d.

Rytov has developed a treatment of problems of this kind. Rytov's work and ours differ in the following respects. One difference is merely formal: Rytov starts from random thermal exciting electromagnetic fields, for which he writes down a correlation function, in which a constant factor C appears. In Ref. 1, C is determined *a posteriori* by reproducing Kirchhoff's law for radiation emitted into vacuum. In Ref. 2, C is obtained from Nyquist's formula, and a discussion of the zero correlation radius used by him (and by us) appears. In our work we take electric currents rather than fields as the random thermal sources and use the fluctuation-dissipation theorem to determine their statistical properties; this rather simplifies the formal treatment.

The second difference is that Rytov's study of the heat transfer across a gap is confined to the case of one semi-infinite absorbing body at temperature T separated by vacuum from an almost perfect mirror at zero temperature: The mirror is described by the approximate boundary conditions of Leontovich, which state that the magnetic fields are the same as if the mirror were perfect. In our work we study the heat transfer between two arbitrary identical semi-infinite bodies at different temperatures, while exact boundary con-