APPENDIX A: TEMPERATURE DEPENDENCE OF THE REFLECTION LINES

> ***. . . I came to the conclusion that the sharpness of the interference lines would not suffer but that their intensity should diminish with increasing angle of scattering, the more so the higher the temperature.***
>
> P. Debye

As the temperature of the crystal is increased, the intensity of the Bragg-reflected beams decreases, but the angular width of the reflected line does not change. Experimental intensities for aluminum are shown in Fig. 1. It is surprising that we can get a sharp x-ray reflection from atoms undergoing large amplitude random thermal motion, with instantaneous nearest-neighbor spacings differing by 10 percent at room temperature. Before the Laue experiment

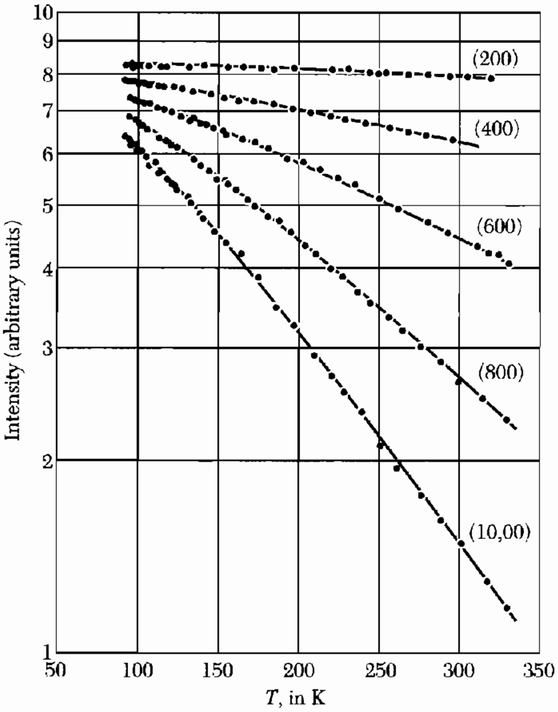

Figure 1 The dependence of intensity on temperature for the $(h00)$ x-ray reflections of aluminum. Reflections $(h00)$ with h odd are forbidden for an fcc structure. (After R. M. Nicklow and R. A. Young.)

was done, but when the proposal was discussed[1] in a coffee house in Munich, the objection was made that the instantaneous positions of the atoms in a crystal at room temperature are far from a regular periodic array, because of the large thermal fluctuation. Therefore, the argument went, one should not expect a well-defined diffracted beam.

But such a beam is found. The reason was given by Debye. Consider the radiation amplitude scattered by a crystal: let the position of the atom nominally at $\mathbf{r}_j$ contain a term $\mathbf{u}(t)$ fluctuating in time: $\mathbf{r}(t) = \mathbf{r}_j + \mathbf{u}(t)$. We suppose each atom fluctuates independently about its own equilibrium position.[2] Then the thermal average of the structure factor (2.43) contains terms

$$f_j \exp(-i\mathbf{G}\cdot\mathbf{r}_j)\langle\exp(-i\mathbf{G}\cdot\mathbf{u})\rangle \ , \tag{1}$$

where $\langle\cdots\rangle$ denotes thermal average. The series expansion of the exponential is

$$\langle\exp(-i\mathbf{G}\cdot\mathbf{u})\rangle = 1 - i\langle\mathbf{G}\cdot\mathbf{u}\rangle - \tfrac{1}{2}\langle(\mathbf{G}\cdot\mathbf{u})^2\rangle + \cdots \ . \tag{2}$$

But $\langle\mathbf{G}\cdot\mathbf{u}\rangle = 0$, because $\mathbf{u}$ is a random thermal displacement uncorrelated with the direction of $\mathbf{G}$. Further,

$$\langle(\mathbf{G}\cdot\mathbf{u})^2\rangle = G^2\langle u^2\rangle\langle\cos^2\theta\rangle = \tfrac{1}{3}\langle u^2\rangle G^2 \ .$$

The factor $\frac{1}{3}$ arises as the geometrical average of $\cos^2\theta$ over a sphere.

The function

$$\exp(-\tfrac{1}{6}\langle u^2\rangle G^2) = 1 - \tfrac{1}{6}\langle u^2\rangle G^2 + \cdots \tag{3}$$

has the same series expansion as (2) for the first two terms shown here. For a harmonic oscillator all terms in the series (2) and (3) can be shown to be identical. Then the scattered intensity, which is the square of the amplitude, is

$$I = I_0 \exp(-\tfrac{1}{3}\langle u^2\rangle G^2) \ , \tag{4}$$

where I_0 is the scattered intensity from the rigid lattice. The exponential factor is the **Debye-Waller factor**.

Here $\langle u^2\rangle$ is the mean square displacement of an atom. The thermal average potential energy $\langle U\rangle$ of a classical harmonic oscillator in three dimensions is $\frac{3}{2}k_BT$, whence

$$\langle U\rangle = \tfrac{1}{2}C\langle u^2\rangle = \tfrac{1}{2}M\omega^2\langle u^2\rangle = \tfrac{3}{2}k_BT \ , \tag{5}$$

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[1] P. P. Ewald, private communication.

[2] This is the Einstein model of a solid; it is not a very good model at low temperatures, but it works well at high temperatures.

where C is the force constant, M is the mass of an atom, and ω is the frequency of the oscillator. We have used the result $\omega^2 = C/M$. Thus the scattered intensity is

$$I(hkl) = I_0 \exp(-k_B T G^2/M\omega^2) \ , \tag{6}$$

where hkl are the indices of the reciprocal lattice vector $\mathbf{G}$. This classical result is a good approximation at high temperatures.

For quantum oscillators $\langle u^2 \rangle$ does not vanish even at $T = 0$; there is zero-point motion. On the independent harmonic oscillator model the zero-point energy is $\frac{3}{2}\hbar\omega$; this is the energy of a three-dimensional quantum harmonic oscillator in its ground state referred to the classical energy of the same oscillator at rest. Half of the oscillator energy is potential energy, so that in the ground state

$$\langle U \rangle = \tfrac{1}{2} M\omega^2 \langle u^2 \rangle = \tfrac{3}{4}\hbar\omega \ ; \qquad \langle u^2 \rangle = 3\hbar/2M\omega \ , \tag{7}$$

whence, by (4),

$$I(hkl) = I_0 \exp(-\hbar G^2/2M\omega) \tag{8}$$

at absolute zero. If $G = 10^9$ cm^{-1}, $\omega = 10^{14}$ s^{-1}, and $M = 10^{-22}$ g, the argument of the exponential is approximately 0.1, so that $I/I_0 \simeq 0.9$. At absolute zero, 90 percent of the beam is elastically scattered and 10 percent is inelastically scattered.

We see from (6) and from Fig. 1 that the intensity of the diffracted line decreases, but not catastrophically, as the temperature is increased. Reflections of low G are affected less than reflections of high G. The intensity we have calculated is that of the coherent diffraction (or the elastic scattering) in the well-defined Bragg directions. The intensity lost from these directions is the inelastic scattering and appears as a diffuse background. In inelastic scattering the x-ray photon causes the excitation or de-excitation of a lattice vibration, and the photon changes direction and energy.

At a given temperature the Debye-Waller factor of a diffraction line decreases with an increase in the magnitude of the reciprocal lattice vector $\mathbf{G}$ associated with the reflection. The larger $|\mathbf{G}|$ is, the weaker the reflection at high temperatures. The theory we have worked out here for x-ray reflection applies equally well to neutron diffraction and to the **Mössbauer effect**, the recoilless emission of gamma rays by nuclei bound in crystals.

X-rays can be absorbed in a crystal also by the inelastic processes of photoionization of electrons and Compton scattering. In the photoeffect the x-ray photon is absorbed and an electron is ejected from an atom. In the Compton effect the photon is scattered inelastically by an electron: the photon loses energy and the electron is ejected from an atom. The depth of penetration of the x-ray beam depends on the solid and on the photon energy, but 1 cm is typical. A diffracted beam in Bragg reflection may remove the energy in a much shorter distance, perhaps 10^{-3} cm in an ideal crystal.

APPENDIX B: EWALD CALCULATION OF LATTICE SUMS

The problem is to calculate the electrostatic potential experienced by one ion in the presence of all the other ions in the crystal. We consider a lattice made up of ions with positive or negative charges and shall assume that the ions are spherical.

We compute the total potential $\varphi = \varphi_1 + \varphi_2$ at an ion as the sum of two distinct but related potentials. The potential φ_1 is that of a structure with a Gaussian distribution of charge situated at each ion site, with signs the same as those of the real ions. According to the definition of the Madelung constant, the charge distribution on the reference point is not considered to contribute to the potential φ_1 or φ_2 (Fig. 1a). We therefore calculate the potential φ_1 as the difference

$$\varphi_1 = \varphi_a - \varphi_b$$

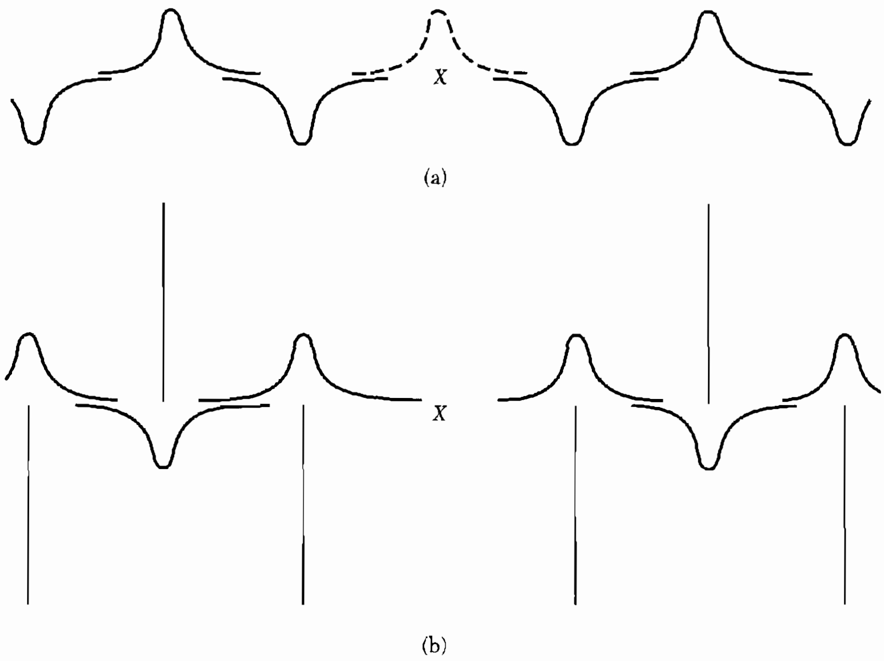

Figure 1 (a) Charge distribution used for computing potential φ_1; the potential φ_a is computed (it includes the dashed curve at the reference point), while φ_b is the potential of the dashed curve alone. (b) Charge distribution for potential φ_2. The reference point is denoted by an X.

of two potentials, φ_a being the potential of a continuous series of Gaussian distributions and φ_b being the potential of the single Gaussian distribution on the reference point.

The potential φ_2 is that of a lattice of point charges with an additional Gaussian distribution of opposite sign superposed upon the point charges (Fig. 1b).

The point of splitting the problem into the two parts φ_1 and φ_2 is that by a suitable choice of the parameter determining the width of each Gaussian peak we can get very good convergence of both parts at the same time. The Gaussian distributions drop out completely on taking the sum of the separate charge distributions giving rise to φ_1 and φ_2, so that the value of the total potential φ is independent of the width parameter, but the rapidity of convergence depends on the value chosen for that parameter.

We calculate first the potential φ_a of a continuous Gaussian distribution. We expand φ_a and the charge density ρ in Fourier series:

$$\varphi_a = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \; ; \tag{1}$$

$$\rho = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \; , \tag{2}$$

where $\mathbf{G}$ is 2π times a vector in the reciprocal lattice. The Poisson equation is

$$\nabla^2\varphi_a = -4\pi\rho \; ,$$

or

$$\Sigma\, G^2 c_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) = 4\pi\, \Sigma\, \rho_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \; ,$$

so that

$$c_{\mathbf{G}} = 4\pi\rho_{\mathbf{G}}/G^2 \; . \tag{3}$$

We suppose in finding $\rho_{\mathbf{G}}$ that there is associated with each lattice point of the Bravais lattice a basis containing ions of charge q_t at positions $\mathbf{r}_t$ relative to the lattice point. Each ion point is therefore the center of a Gaussian charge distribution of density

$$\rho(\mathbf{r}) = q_t(\eta/\pi)^{3/2}\exp(-\eta r^2) \; ,$$

where the factor in front of the exponential ensures that the total charge associated with the ion is q_t; the range parameter η is to be chosen judiciously to ensure rapid convergence of the final result (6), which is in value independent of η.

We would normally evaluate $\rho_{\mathbf{G}}$ by multiplying both sides of (2) by $\exp(-i\mathbf{G}\cdot\mathbf{r})$ and integrating over the volume Δ of one cell, so that the charge distribution to be considered is that originating on the ion points within the cell and also that of the tails of the distributions originating in all other cells. It is easy to see, however, that the integral of the total charge density times $\exp[-(i\mathbf{G}\cdot\mathbf{r})]$ over a single cell is equal to the integral of the charge density originating in a single cell times $\exp[-(i\mathbf{G}\cdot\mathbf{r})]$ over all space.

We have therefore

$$\rho_G \int_{\substack{\text{one}\\ \text{cell}}} \exp(i\mathbf{G}\cdot\mathbf{r})\exp(-i\mathbf{G}\cdot\mathbf{r})\,d\mathbf{r} = \rho_G\Delta$$

$$= \int_{\substack{\text{all}\\ \text{space}}} \sum_t q_t(\eta/\pi)^{3/2}\exp[-\eta(r-r_t)^2]\exp(-i\mathbf{G}\cdot\mathbf{r})\,d\mathbf{r} \ .$$

This expression is readily evaluated:

$$\rho_G\Delta = \sum_t q_t\exp(-i\mathbf{G}\cdot\mathbf{r}_t)\,(\eta/\pi)^{3/2} \int_{\substack{\text{all}\\ \text{space}}} \exp[-(i\mathbf{G}\cdot\boldsymbol{\xi}+\eta\xi^2)]\,d\xi$$

$$= \left(\sum_t q_t\exp(-i\mathbf{G}\cdot\mathbf{r}_t)\right)\exp(-G^2/4\eta) = S(\mathbf{G})\exp(-G^2/4\eta) \ ,$$

where $S(\mathbf{G}) = \sum_t q_t\exp(-i\mathbf{G}\cdot\mathbf{r}_t)$ is just the structure factor (Chapter 2) in appropriate units. Using (1) and (3),

$$\varphi_a = \frac{4\pi}{\Delta}\sum_{\mathbf{G}} S(\mathbf{G})G^{-2}\exp(i\mathbf{G}\cdot\mathbf{r} - G^2/4\eta) \ . \tag{4}$$

At the origin $\mathbf{r} = 0$ we have

$$\varphi_a = \frac{4\pi}{\Delta}\sum_{\mathbf{G}} S(\mathbf{G})G^{-2}\exp(-G^2/4\eta) \ .$$

The potential φ_b at the reference ion point i due to the central Gaussian distribution is

$$\varphi_b = \int_0^\infty (4\pi r^2\,dr)(\rho/r) = 2q_i(\eta/\pi)^{1/2} \ ,$$

and so

$$\varphi_1(i) = \frac{4\pi}{\Delta}\sum_{\mathbf{G}} S(\mathbf{G})G^{-2}\exp(-G^2/4\eta) - 2q_i(\eta/\pi)^{1/2} \ .$$

The potential φ_2 is to be evaluated at the reference point, and it differs from zero because other ions have the tails of their Gaussian distributions overlapping the reference point. The potential is due to three contributions from each ion point:

$$q_l\left[\frac{1}{r_l} - \frac{1}{r_l}\int_0^{r_l}\rho(\mathbf{r})\,d\mathbf{r} - \int_{r_l}^\infty \frac{\rho(\mathbf{r})}{r}\,d\mathbf{r}\right] \ ,$$

where the terms are from the point charge, from the part of the Gaussian distribution lying inside a sphere of radius r_l about the lth ion point, and from that part lying outside the sphere, respectively. On substituting for $\rho(\mathbf{r})$ and carrying out elementary manipulations, we have

$$\varphi_2 = \sum_l \frac{q_l}{r_l} F(\eta^{1/2} r_l) \ , \tag{5}$$

where

$$F(x) = (2/\pi^{1/2}) \int_x^\infty \exp(-s^2)\, ds \ .$$

Finally,

$$\varphi(i) = \frac{4\pi}{\Delta} \sum_{\mathbf{G}} S(\mathbf{G}) G^{-2} \exp(-G^2/4\eta) - 2q_i(\eta/\pi)^{1/2} + \sum_l \frac{q_l}{r_l} F(\eta^{1/2} r_l) \tag{6}$$

is the desired total potential of the reference ion i in the field of all the other ions in the crystal. In the application of the Ewald method the trick is to choose η such that both sums in (6) converge rapidly.

Ewald-Kornfeld Method for Lattice Sums for Dipole Arrays

Kornfeld extended the Ewald method to dipolar and quadrupolar arrays. We discuss here the field of a dipole array at a point which is not a lattice point. According to (4) and (5) the potential at a point $\mathbf{r}$ in a lattice of positive unit point charges is

$$\varphi = (4\pi/\Delta) \sum_{\mathbf{G}} S(\mathbf{G}) G^{-2} \exp[i\mathbf{G} \cdot \mathbf{r} - G^2/4\eta] + \sum_l F(\sqrt{\eta}\, r_l)/r_l \ , \tag{7}$$

where r_l is the distance from $\mathbf{r}$ to the lattice point l.

The first term on the right gives the potential of the charge distribution $\rho = (\eta/\pi)^{3/2} \exp(-\eta r^2)$ about each lattice point. By a well-known relation in electrostatics we obtain the potential of an array of unit dipoles pointing in the z direction by taking $-d/dz$ of the above potential. The term under discussion contributes

$$-(4\pi i/\Delta) \sum_{\mathbf{G}} S(\mathbf{G})(G_z/G^2) \exp[i\mathbf{G} \cdot \mathbf{r} - G^2/4\eta] \ ,$$

and the z component of the electric field from this term is $E_z = \partial^2\varphi/\partial z^2$, or

$$-(4\pi/\Delta) \sum_{\mathbf{G}} S(\mathbf{G})(G_z^2/G^2) \exp[i\mathbf{G} \cdot \mathbf{r} - G^2/4\eta] \ . \tag{8}$$

The second term on the right of (7) after one differentiation gives

$$-\sum_l z_l[(F(\sqrt{\eta} r_l)/r_l^3) + (2/r_l^2)(\eta/\pi)^{1/2} \exp(-\eta r_l^2)] \ ,$$

and the z component of this part of the field is

$$\begin{aligned}\sum_l \{z_l^2[(3F(\sqrt{\eta}r_l)/r_l^5) + (6/r_l^4)(\eta/\pi)^{1/2}\exp(-\eta r_l^2) \\ + (4/r_l^2)(\eta^3/\pi)^{1/2}\exp(-\eta r_l^2)] - [(F(\sqrt{\eta}r_l)/r_l^3) \\ + (2/r_l^2)(\eta/\pi)^{1/2}\exp(-\eta r_l^2)]\} \ .\end{aligned} \tag{9}$$

The total E_z is given by the sum of (8) and (9). The effects of any number of lattices may be added.

APPENDIX C: QUANTIZATION OF ELASTIC WAVES: PHONONS

Phonons were introduced in Chapter 4 as quantized elastic waves. How do we quantize an elastic wave? As a simple model of phonons in a crystal, consider the vibrations of a linear lattice of particles connected by springs. We can quantize the particle motion exactly as for a harmonic oscillator or set of coupled harmonic oscillators. To do this we make a transformation from particle coordinates to phonon coordinates, also called wave coordinates because they represent a traveling wave.

Let N particles of mass M be connected by springs of force constant C and length a. To fix the boundary conditions, let the particles form a circular ring. We consider the transverse displacements of the particles out of the plane of the ring. The displacement of particle s is q_s and its momentum is p_s. The Hamiltonian of the system is

$$H = \sum_{s=1}^{n} \left\{ \frac{1}{2M} p_s^2 + \frac{1}{2} C(q_{s+1} - q_s)^2 \right\} \ . \tag{1}$$

The Hamiltonian of a harmonic oscillator is

$$H = \frac{1}{2M} p^2 + \frac{1}{2} Cx^2 \ , \tag{2}$$

and the energy eigenvalues are, where $n = 0, 1, 2, 3, \ldots,$

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \ . \tag{3}$$

The eigenvalue problem is also exactly solvable for a chain with the different Hamiltonian (1).

To solve (1) we make a Fourier transformation from the coordinates p_s, q_s to the coordinates P_k, Q_k, which are known as phonon coordinates.

Phonon Coordinates

The transformation from the particle coordinates q_s to the phonon coordinates Q_k is used in all periodic lattice problems. We let

$$q_s = N^{-1/2} \sum_k Q_k \exp(iksa) \ , \tag{4}$$

consistent with the inverse transformation

$$Q_k = N^{-1/2} \sum_s q_s \exp(-iksa) \ . \tag{5}$$

Here the N values of the wavevector k allowed by the periodic boundary condition $q_s = q_{s+N}$ are given by:

$$k = 2\pi n/Na \ ; \ n = 0, \pm 1, \pm 2, \ldots, \pm\left(\frac{1}{2}N - 1\right), \frac{1}{2}N \ . \tag{6}$$

We need the transformation from the particle momentum p_s to the momentum P_k that is canonically conjugate to the coordinate Q_k. The transformation is

$$p_s = N^{-1/2} \sum_k P_k \exp(-iksa); \quad P_k = N^{-1/2} \sum_s p_s \exp(iksa) \ . \tag{7}$$

This is not quite what one would obtain by the naive substitution of p for q and P for Q in (4) and (5), because k and $-k$ have been interchanged between (4) and (7).

We verify that our choice of P_k and Q_k satisfies the quantum commutation relation for canonical variables. We form the commutator

$$\begin{aligned} [Q_k, P_{k'}] &= N^{-1}\left[\sum_r q_r \exp(-ikra), \sum_s p_s \exp(ik'sa)\right] \\ &= N^{-1} \sum_r \sum_s [q_r, p_s] \exp[-i(kr - k's)a] \ . \end{aligned} \tag{8}$$

Because the operators q, p are conjugate, they satisfy the commutation relation

$$[q_r, p_s] = i\hbar\delta(r, s) \ , \tag{9}$$

where $\delta(r,s)$ is the Kronecker delta symbol.

Thus (8) becomes

$$[Q_k, P_{k'}] = N^{-1}\, i\hbar \sum_r \exp[-i(k - k')ra] = i\hbar\delta(k, k') \ , \tag{10}$$

so that Q_k, P_k also are conjugate variables. Here we have evaluated the summation as

$$\begin{aligned} \sum_r \exp[-i(k - k')ra] &= \sum_r \exp[-i2\pi(n - n')r/N] \\ &= N\delta(n, n') = N\delta(k, k') \ , \end{aligned} \tag{11}$$

where we have used (6) and a standard result for the finite series in (11).

We carry out the transformations (7) and (4) on the hamiltonian (1), and make use of the summation (11):

$$\begin{aligned}\sum_s p_s^2 &= N^{-1}\sum_s\sum_k\sum_{k'} P_kP_{k'}\exp[-i(k+k')sa] \\ &= \sum_k\sum_{k'} P_kP_{k'}\delta(-k,k') = \sum_k P_kP_{-k}\ ;\end{aligned} \tag{12}$$

$$\begin{aligned}\sum_s (q_{s+1}-q_s)^2 = N^{-1}\sum_s\sum_k\sum_{k'} Q_kQ_{k'}\exp(iksa)[\exp(ika)-1] \\ \times\exp(ik'sa)[\exp(ik'a)-1] = 2\sum_k Q_kQ_{-k}(1-\cos ka)\ .\end{aligned} \tag{13}$$

Thus the hamiltonian (1) becomes, in phonon coordinates,

$$H = \sum_k\left\{\frac{1}{2M}P_kP_{-k} + CQ_kQ_{-k}(1-\cos ka)\right\}\ . \tag{14}$$

If we introduce the symbol ω_k defined by

$$\omega_k \equiv (2C/M)^{1/2}(1-\cos ka)^{1/2}\ , \tag{15}$$

we have the phonon hamiltonian in the form

$$H = \sum_k\left\{\frac{1}{2M}P_kP_{-k} + \frac{1}{2}M\omega_k^2\, Q_kQ_{-k}\right\}\ . \tag{16}$$

The equation of motion of the phonon coordinate operator Q_k is found by the standard prescription of quantum mechanics:

$$i\hbar\dot{Q}_k = [Q_k, H] = i\hbar P_{-k}/M\ , \tag{17}$$

with H given by (14). Further, using the commutator (17),

$$i\hbar\ddot{Q}_k = [\dot{Q}_k, H] = M^{-1}[P_{-k}, H] = i\hbar\omega_k^2 Q_k\ , \tag{18}$$

so that

$$\ddot{Q}_k + \omega_k^2 Q_k = 0\ . \tag{19}$$

This is the equation of motion of a harmonic oscillator with the frequency ω_k.

The energy eigenvalues of a quantum harmonic oscillator are

$$\epsilon_k = \left(n_k + \frac{1}{2}\right)\hbar\omega_k\ , \tag{20}$$

where the quantum number $n_k = 0, 1, 2, \ldots$. The energy of the entire system of all phonons is

$$U = \sum_k\left(n_k + \frac{1}{2}\right)\hbar\omega_k\ . \tag{21}$$

This result demonstrates the quantization of the energy of elastic waves on a line.

Creation and Annihilation Operators

It is helpful in advanced work to transform the phonon hamiltonian (16) into the form of a set of harmonic oscillators:

$$H = \sum_k \hbar\omega_k \left(a_k^+ a_k + \frac{1}{2} \right) \ . \tag{22}$$

Here a_k^+, a_k are harmonic oscillator operators, also called creation and destruction operators or boson operators. The transformation is derived below.

The boson creation operator a^+ which "creates a phonon" is defined by the property

$$a^+|n\rangle = (n+1)^{1/2}|n+1\rangle \ , \tag{23}$$

when acting on a harmonic oscillator state of quantum number n, and the boson annihilation operator a which "destroys a phonon" is defined by the property

$$a|n\rangle = n^{1/2}|n-1\rangle \ . \tag{24}$$

It follows that

$$a^+a|n\rangle = a^+n^{1/2}|n-1\rangle = n|n\rangle \ , \tag{25}$$

so that $|n\rangle$ is an eigenstate of the operator a^+a with the integral eigenvalue n, called the quantum number or occupancy of the oscillator. When the phonon mode k is in the eigenstate labeled by n_k, we may say that there are n_k phonons in the mode. The eigenvalues of (22) are $U = \Sigma\,(n_k + \frac{1}{2})\hbar\omega_k$, in agreement with (21).

Because

$$aa^+|n\rangle = a(n+1)^{1/2}|n+1\rangle = (n+1)|n\rangle \ , \tag{26}$$

the commutator of the boson wave operators a_k^+ and a_k satisfies the relation

$$[a, a^+] \equiv aa^+ - a^+a = 1 \ . \tag{27}$$

We still have to prove that the hamiltonian (16) can be expressed as (19) in terms of the phonon operators a_k^+, a_k. This can be done by the transformation

$$a_k^+ = (2\hbar)^{-1/2}[(M\omega_k)^{1/2}Q_{-k} - i(M\omega_k)^{-1/2}P_k] \ ; \tag{28}$$

$$a_k = (2\hbar)^{-1/2}[(M\omega_k)^{1/2}Q_k + i(M\omega_k)^{-1/2}P_{-k}] \ . \tag{29}$$

The inverse relations are

$$Q_k = (\hbar/2M\omega_k)^{1/2}(a_k + a_{-k}^+) \ ; \tag{30}$$

$$P_k = i(\hbar M\omega_k/2)^{1/2}(a_k^+ - a_{-k}) \ . \tag{31}$$

By (4), (5), and (29) the particle position operator becomes

$$q_s = \sum_k (\hbar/2NM\omega_k)^{1/2}[a_k \exp(iks) + a_k^+ \exp(-iks)] \ . \tag{32}$$

This equation relates the particle displacement operator to the phonon creation and annihilation operators.

To obtain (29) from (28), we use the properties

$$Q^+_{-k} = Q_k \; ; \qquad P^+_k = P_{-k} \tag{33}$$

which follow from (5) and (7) by use of the quantum mechanical requirement that q_s and p_s be hermitian operators:

$$q_s = q_s^+ \; ; \qquad p_s = p_s^+ \; . \tag{34}$$

Then (28) follows from the transformations (4), (5), and (7). We verify that the commutation relation (33) is satisfied by the operators defined by (28) and (29):

$$\begin{aligned}[] [a_k, a_k^+] = (2\hbar)^{-1}(M\omega_k[Q_k, Q_{-k}] - i[Q_k,P_k] + i[P_{-k},Q_{-k}] \\ + [P_{-k},P_k]/M\omega_k) \; . \end{aligned} \tag{35}$$

By use of $[Q_k,P_{k'}] = i\hbar\delta(k,k')$ from (10) we have

$$[a_k, a_{k'}^+] = \delta(k,k') \; . \tag{36}$$

It remains to show that the versions of (16) and (22) of the phonon hamiltonian are identical. We note that $\omega_k = \omega_{-k}$ from (15), and we form

$$\hbar\omega_k(a_k^+a_k + a_{-k}^+a_{-k}) = \frac{1}{2M}(P_kP_{-k} + P_{-k}P_k) + \frac{1}{2}M\omega_k^2(Q_kQ_{-k} + Q_{-k}Q_k) \; .$$

This exhibits the equivalence of the two expressions (14) and (22) for H. We identify $\omega_k = (2C/M)^{1/2}(1 - \cos ka)^{1/2}$ in (15) with the classical frequency of the oscillator mode of wavevector k.

APPENDIX D: FERMI-DIRAC DISTRIBUTION FUNCTION[1]

The Fermi-Dirac distribution function[1] may be derived in several steps by use of a modern approach to statistical mechanics. We outline the argument here. The notation is such that conventional entropy S is related to the fundamental entropy σ by $S = k_B\sigma$, and the Kelvin temperature T is related to the fundamental temperature τ by $\tau = k_BT$, where k_B is the Boltzmann constant with the value 1.38066×10^{-23} J K.

The leading quantities are the entropy, the temperature, the Boltzmann factor, the chemical potential, the Gibbs factor, and the distribution functions. The

[1] This appendix follows closely the introduction to C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed., Freeman, 1980.

entropy measures the number of quantum states accessible to a system. A closed system might be in any of these quantum states and (we assume) with equal probability. The fundamental assumption is that quantum states are either accessible or inaccessible to the system, and the system is equally likely to be in any one accessible state as in any other accessible state. Given g accessible states, the entropy is defined as $\sigma = \log g$. The entropy thus defined will be a function of the energy U, the number of particles N, and the volume V of the system.

When two systems, each of specified energy, are brought into thermal contact, they may transfer energy; their total energy remains constant, but the constraints on their individual energies are lifted. A transfer of energy in one direction, or perhaps in the other, may increase the product g_1g_2 that measures the number of accessible states of the combined systems. What we call the fundamental assumption biases the outcome in favor of that allocation of the total energy that maximizes the number of accessible states: more is better, and more likely. This statement is the kernel of the law of increase of entropy, which is the general expression of the second law of thermodynamics.

We have brought two systems into thermal contact so that they may transfer energy. What is the most probable outcome of the encounter? One system will gain energy at the expense of the other, and meanwhile *the total entropy* of the two systems will increase. Eventually the entropy will reach a maximum for the given total energy. It is not difficult to show that the maximum is attained when *the value of* $(\partial\sigma/\partial U)_{N,V}$ *for one system is equal to the value of the* same quantity for the second system. This equality property for two systems in thermal contact is the property we expect of the temperature. Accordingly, the *fundamental temperature* τ is defined by the relation

$$\frac{1}{\tau} \equiv \left(\frac{\partial\sigma}{\partial U}\right)_{N,V} . \tag{1}$$

The use of $1/\tau$ assures that energy will flow from high τ to low τ; no more complicated relation is needed.

Now consider a very simple example of the Boltzmann factor. Let a small system with only two states, one at energy 0 and one at energy ϵ, be placed in thermal contact with a large system that we call the reservoir. The total energy of the combined systems is U_0; when the small system is in the state of energy 0, the reservoir has energy U_0 and will have $g(U_0)$ states accessible to it. When the small system is in the state of energy ϵ, the reservoir will have energy $U_0 - \epsilon$ and will have $g(U_0 - \epsilon)$ states accessible to it. By the fundamental assumption, the ratio of the probability of finding the small system with energy ϵ to the probability of finding it with energy 0 is

$$\frac{P(\epsilon)}{P(0)} = \frac{g(U_0 - \epsilon)}{g(U_0)} = \frac{\exp[\sigma(U_0 - \epsilon)]}{\exp[\sigma(U_0)]} . \tag{2}$$

The reservoir entropy σ may be expanded in a Taylor series:

$$\sigma(U_0 - \epsilon) \simeq \sigma(U_0) - \epsilon(\partial\sigma/\partial U_0) = \sigma(U_0) - \epsilon/\tau \ , \tag{3}$$

by the definition (1) of the temperature. Higher order terms in the expansion may be dropped. Cancellation of the term $\exp[\sigma(U_0)]$, which occurs in the numerator and denominator of (2) after the substitution of (3), leaves us with

$$P(\epsilon)/P(0) = \exp(-\epsilon/\tau) \ . \tag{4}$$

This is Boltzmann's result. To show its use, we calculate the thermal average energy $\langle\epsilon\rangle$ of the two-state system in thermal contact with a reservoir at temperature τ:

$$\langle\epsilon\rangle = \sum_i \epsilon_i P(\epsilon_i) = 0 \cdot P(0) + \epsilon P(\epsilon) = \frac{\epsilon \exp(-\epsilon/\tau)}{1 + \exp(-\epsilon/\tau)} \ , \tag{5}$$

where we have imposed the normalization condition on the sum of the probabilities:

$$P(0) + P(\epsilon) = 1 \ . \tag{6}$$

The argument can be generalized immediately to find the average energy of a harmonic oscillator at temperature τ, as in the Planck law.

The most important extension of the theory is to systems that can transfer particles as well as energy with the reservoir. For two systems in diffusive and thermal contact, the entropy will be a maximum with respect to the transfer of particles as well as to the transfer of energy. Not only must $(\partial\sigma/\partial U)_{N,V}$ be equal for the two systems, but $(\partial\sigma/\partial N)_{U,V}$ must also be equal, where N refers to the number of particles of a given species. The new equality condition is the occasion for the introduction[2] of the chemical potential μ:

$$-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} \ . \tag{7}$$

For two systems in thermal and diffusive contact, $\tau_1 = \tau_2$ and $\mu_1 = \mu_2$. The sign in (7) is chosen to ensure that the direction of particle flow is from high chemical potential to low chemical potential as equilibrium is approached.

The Gibbs factor is an extension of the Boltzmann factor (4) and allows us to treat systems that can transfer particles. The simplest example is a system with two states, one with 0 particles and 0 energy, and one with 1 particle and energy ϵ. The system is in contact with a reservoir at temperature τ and chemical potential μ. We extend (3) for the reservoir entropy:

$$\begin{aligned} \sigma(U_0 - \epsilon; N_0 - 1) &= \sigma(U_0; N_0) - \epsilon(\partial\sigma/\partial U_0) - 1 \cdot (\partial\sigma/\partial N_0) \\ &= \sigma(U_0; N_0) - \epsilon/\tau + \mu/\tau \ . \end{aligned} \tag{8}$$

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[2] *TP* Chapter 5 has a careful treatment of the chemical potential.

By analogy with (4), we have the Gibbs factor

$$P(1,\epsilon)/P(0,0) = \exp[(\mu - \epsilon)/\tau] \ , \tag{9}$$

for the ratio of the probability that the system is occupied by 1 particle at energy ϵ to the probability that the system is unoccupied, with energy 0. The result (9) after normalization is readily expressed as

$$P(1,\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/\tau] + 1} \ . \tag{10}$$

This is the Fermi-Dirac distribution function.

APPENDIX E: DERIVATION OF THE *dk/dt* EQUATION

The simple and rigorous derivation that follows is due to Kroemer. In quantum mechanics, for any operator A we have

$$d\langle A\rangle/dt = (i/\hbar)\langle [H, A]\rangle \ , \tag{1}$$

where H is the hamiltonian. See also C. L. Cook, American J. Phys. **55**, 953 (1987).

We let A be the lattice translation operator T defined by

$$Tf(x) = f(x + a) \ , \tag{2}$$

where a is a basis vector, here in one dimension. For a Bloch function

$$T\psi_k(x) = \exp(ika)\psi_k(x) \ . \tag{3}$$

This result is usually written for one band, but it holds even if ψ_k is a linear combination of Bloch states from any number of bands, but having the identical wavevector k in the reduced zone scheme.

The crystal hamiltonian H_0 commutes with the lattice translation operator T, so that $[H_0,T] = 0$. If we add a uniform external force F, then

$$H = H_0 - Fx \ , \tag{4}$$

and

$$[H, T] = FaT \ . \tag{5}$$

From (1) and (5),

$$d\langle T\rangle/dt = (i/\hbar)(Fa)\langle T\rangle \ . \tag{6}$$

From (6) we form

$$\langle T\rangle^* d\langle T\rangle/dt = (iFa/\hbar)|\langle T\rangle|^2 \ ;$$

$$\langle T\rangle d\langle T^*\rangle/dt = -(iFa/\hbar)|\langle T\rangle|^2 \ .$$

On addition,

$$d|\langle T\rangle|^2/dt = 0 \ . \tag{7}$$

This is the equation of a circle in the complex plane. The coordinate axes in the plane are the real and imaginary parts of the eigenvalue $\exp(ika)$. If $\langle T\rangle$ is initially on the unit circle, it will remain on the unit circle.

For ψ's that satisfy periodic boundary conditions, $\langle T\rangle$ can lie on the unit circle only if ψ_k is a single Bloch function or a superposition of Bloch functions from different bands, but with the same reduced k.

As $\langle T\rangle$ moves around the unit circle, the wavevector k changes exactly at the same rate for the components of ψ_k in all bands. With $\langle T\rangle = \exp(ika)$, we have from (6) that

$$ia\, dk/dt = iFa/\hbar \ , \tag{8}$$

or

$$dk/dt = F/\hbar \ , \tag{9}$$

an exact result.

This does not mean that interband mixing (such as Zener tunneling) does not occur under the influence of applied electric fields. It just means that k evolves at a constant rate for every component of a wave packet. The result is easily extended to three dimensions.

APPENDIX F: BOLTZMANN TRANSPORT EQUATION

The classical theory of transport processes is based on the Boltzmann transport equation. We work in the six-dimensional space of Cartesian coordinates $\mathbf{r}$ and velocity $\mathbf{v}$. The classical distribution function $f(\mathbf{r},\mathbf{v})$ is defined by the relation

$$f(\mathbf{r},\mathbf{v})d\mathbf{r}d\mathbf{v} = \text{number of particles in } d\mathbf{r}d\mathbf{v} \ . \tag{1}$$

The Boltzmann equation is derived by the following argument. We consider the effect of a time displacement dt on the distribution function. The Liouville theorem of classical mechanics tells us that if we follow a volume element along a flowline the distribution is conserved:

$$f(t + dt,\mathbf{r} + d\mathbf{r},\mathbf{v} + d\mathbf{v}) = f(t,\mathbf{r},\mathbf{v}) \ , \tag{2}$$

in the absence of collisions. With collisions

$$f(t + dt,\mathbf{r} + d\mathbf{r},\mathbf{v} + d\mathbf{v}) - f(t,\mathbf{r},\mathbf{v}) = dt(\partial f/\partial t)_{\mathrm{coll}}\ . \tag{3}$$

Thus

$$dt(\partial f/\partial t) + d\mathbf{r}\cdot \mathrm{grad}_{\mathbf{r}}\, f + d\mathbf{v}\cdot \mathrm{grad}_{\mathbf{v}}\, f = dt(\partial f/\partial t)_{\mathrm{coll}}\ . \tag{4}$$

Let α denote the acceleration $d\mathbf{v}/dt$; then

$$\boxed{\partial f/\partial t + \mathbf{v}\cdot \mathrm{grad}_{\mathbf{r}}\, f + \alpha \cdot \mathrm{grad}_{\mathbf{v}}\, f = (\partial f/\partial t)_{\mathrm{coll}}} \tag{5}$$

This is the **Boltzmann transport equation**.

In many problems the collision term $(\partial f/\partial t)_{\mathrm{coll}}$ may be treated by the introduction of a relaxation time $\tau_c(\mathbf{r},\mathbf{v})$, defined by the equation

$$(\partial f/\partial t)_{\mathrm{coll}} = -(f - f_0)/\tau_c\ . \tag{6}$$

Here f_0 is the distribution function in thermal equilibrium. Do not confuse τ_c for relaxation time with τ for temperature. Suppose that a nonequilibrium distribution of velocities is set up by external forces which are suddenly removed. The decay of the distribution towards equilibrium is then obtained from (6) as

$$\frac{\partial(f - f_0)}{\partial t} = -\frac{f - f_0}{\tau_c}\ , \tag{7}$$

if we note that $\partial f_0/\partial t = 0$ by definition of the equilibrium distribution. This equation has the solution

$$(f - f_0)_t = (f - f_0)_{t=0}\exp(-t/\tau_c)\ . \tag{8}$$

It is not excluded that τ_c may be a function of $\mathbf{r}$ and $\mathbf{v}$.

We combine (1), (5), and (6) to obtain the Boltzmann transport equation in the relaxation time approximation:

$$\boxed{\frac{\partial f}{\partial t} + \alpha \cdot \mathrm{grad}_{\mathbf{v}} f + \mathbf{v}\cdot \mathrm{grad}_{\mathbf{r}} f = -\frac{f - f_0}{\tau_c}\ .} \tag{9}$$

In the steady state $\partial f/\partial t = 0$ by definition.

Particle Diffusion

Consider an isothermal system with a gradient of the particle concentration. The steady-state Boltzmann transport equation in the relaxation time approximation becomes

$$v_x df/dx = -(f - f_0)/\tau_c\ , \tag{10}$$

where the nonequilibrium distribution function f varies along the x direction. We may write (10) to first order as

$$f_1 = f_0 - v_x \tau_c df_0/dx \ , \tag{11}$$

where we have replaced $\partial f/\partial x$ by df_0/dx. We can iterate to obtain higher order solutions when desired. Thus the second order solution is

$$f_2 = f_0 - v_x \tau_c df_1/dx = f_0 - v_x \tau_c df_0/dx + v_x^2 \tau_c^2 d^2 f_0/dx^2 \ . \tag{12}$$

The iteration may be used in the treatment of nonlinear effects.

Classical Distribution

Let f_0 be the distribution function in the classical limit:

$$f_0 = \exp[(\mu - \epsilon)/\tau] \ . \tag{13}$$

We are at liberty to take whatever normalization for the distribution function is most convenient because the transport equation is linear in f and f_0. We can take the normalization as in (13) rather than as in (1). Then

$$df_0/dx = (df_0/d\mu)(d\mu/dx) = (f_0/\tau)(d\mu/dx) \ , \tag{14}$$

and the first order solution (11) for the nonequilibrium distribution becomes

$$f = f_0 - (v_x \tau_c f_0/\tau)(d\mu/dx) \ . \tag{15}$$

The particle flux density in the x direction is

$$J_n^x = \int v_x f D(\epsilon) d\epsilon \ , \tag{16}$$

where $D(\epsilon)$ is the density of electron states per unit volume per unit energy range:

$$D(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2} \epsilon^{1/2} \ . \tag{17}$$

Thus

$$J_n^x = \int v_x f_0 D(\epsilon) d\epsilon - (d\mu/dx) \int (v_x^2 \tau_c f_0/\tau) D(\epsilon) d\epsilon \ . \tag{18}$$

The first integral vanishes because v_x is an odd function and f_0 is an even function of v_x. This confirms that the net particle flux vanishes for the equilibrium distribution f_0. The second integral will not vanish.

Before evaluating the second integral, we have an opportunity to make use of what we may know about the velocity dependence of the relaxation time τ_c. Only for the sake of example we assume that τ_c is constant, independent of velocity; τ_c may then be taken out of the integral:

$$J_n^x = -(d\mu/dx)(\tau_c/\tau) \int v_x^2 f_0 D(\epsilon) d\epsilon \ . \tag{19}$$

The integral may be written as

$$\tfrac{1}{3}\int v^2 f_0 D(\epsilon)d\epsilon = \frac{2}{3M}\int (\tfrac{1}{2}Mv^2)f_0 D(\epsilon)d\epsilon = n\tau/M \ , \tag{20}$$

because the integral is just the kinetic energy density $\frac{3}{2}n\tau$ of the particles. Here $\int f_0 D(\epsilon)d\epsilon = n$ is the concentration. The particle flux density is

$$J_n^x = -(n\tau_c/M)(d\mu/dx) = -(\tau_c\tau/M)(dn/dx) \ , \tag{21}$$

because

$$\mu = \tau \log n + \text{constant} \ . \tag{22}$$

The result (21) is of the form of the diffusion equation with the diffusivity

$$D_n = \tau_c\tau/M = \tfrac{1}{3}\langle v^2\rangle\tau_c \ . \tag{23}$$

Another possible assumption about the relaxation time is that it is inversely proportional to the velocity, as in $\tau_c = l/v$, where the mean free path l is constant. Instead of (19) we have

$$J_n^x = -(d\mu/dx)(l/\tau)\int (v_x^2/v)f_0 D(\epsilon)d\epsilon \ , \tag{24}$$

and now the integral may be written as

$$\tfrac{1}{3}\int v f_0 D(\epsilon)d\epsilon = \tfrac{1}{3}n\bar{c} \ , \tag{25}$$

where $\bar{c}$ is the average speed. Thus

$$J_n^x = -\tfrac{1}{3}(l\bar{c}n/\tau)(d\mu/dx) = -\tfrac{1}{3}l\bar{c}(dn/dx) \ , \tag{26}$$

and the diffusivity is

$$D_n = \tfrac{1}{3}l\bar{c} \ . \tag{27}$$

Fermi-Dirac Distribution

The distribution function is

$$f_0 = \frac{1}{\exp[(\epsilon - \mu)/\tau] + 1} \ . \tag{28}$$

To form df_0/dx as in (14) we need the derivative $df_0/d\mu$. We argue below that

$$df_0/d\mu = \delta(\epsilon - \mu) \ , \tag{29}$$

at low temperatures $\tau \ll \mu$. Here δ is the Dirac delta function, which has the property for a general function $F(\epsilon)$ that

$$\int_{-\infty}^{\infty} F(\epsilon)\delta(\epsilon - \mu)d\epsilon = F(\mu) \ . \tag{30}$$

Now consider the integral $\int_0^\infty F(\epsilon)(df_0/d\mu)d\epsilon$. At low temperatures $df_0/d\mu$ is very large for $\epsilon \simeq \mu$ and is small elsewhere. Unless the function $F(\epsilon)$ is very rapidly varying near μ, we may take $F(\epsilon)$ outside the integral, with the value $F(\mu)$:

$$\begin{aligned} \int_0^\infty F(\epsilon)(df_0/d\mu)d\epsilon &\simeq F(\mu)\int_0^\infty (df_0/d\mu)d\epsilon = -F(\mu)\int_0^\infty (df_0/d\epsilon)d\epsilon \\ &= -F(\mu)[f_0(\epsilon)]_0^\infty = F(\mu)f_0(0) \ , \end{aligned} \tag{31}$$

where we have used $df_0/d\mu = -df_0/d\epsilon$. We have also used $f_0 = 0$ for $\epsilon = \infty$. At low temperatures $f(0) \simeq 1$; thus the right-hand side of (31) is just $F(\mu)$, consistent with the delta function approximation. Thus

$$df_0/dx = \delta(\epsilon - \mu)d\mu/dx \ . \tag{32}$$

The particle flux density is, from (16),

$$J_n^x = -(d\mu/dx)\tau_c \int v_x^2 \delta(\epsilon - \mu)D(\epsilon)d\epsilon \ , \tag{33}$$

where τ_c is the relaxation time at the surface $\epsilon = \mu$ of the Fermi sphere. The integral has the value

$$\tfrac{1}{3}v_F^2(3n/2\epsilon_F) = n/m \ , \tag{34}$$

by use of $D(\mu) = 3n/2\epsilon_F$ at absolute zero, where $\epsilon_F \equiv \frac{1}{2}mv_F^2$ defines the velocity v_F on the Fermi surface. Thus

$$J_n^x = -(n\tau_c/m)d\mu/dx \ . \tag{35}$$

At absolute zero $\mu(0) = (\hbar^2/2m)(3\pi^2 n)^{2/3}$, whence

$$\begin{aligned} d\mu/dx &= [\tfrac{2}{3}(\hbar^2/2m)(3\pi^2)^{2/3}/n^{1/3}]dn/dx \\ &= \tfrac{2}{3}(\epsilon_F/n)dn/dx \ , \end{aligned} \tag{36}$$

so that (33) becomes

$$J_n^x = -(2\tau_c/3m)\epsilon_F\, dn/dx = -\tfrac{1}{3}v_F{}^2\,\tau_c\, dn/dx \ . \tag{37}$$

The diffusivity is the coefficient of dn/dx:

$$D_n = \tfrac{1}{3}v_F^2\tau_c \ , \tag{38}$$

closely similar in form to the result (23) for the classical distribution of velocities. In (38) the relaxation time is to be taken at the Fermi energy.

We see we can solve transport problems where the Fermi-Dirac distribution applies, as in metals, as easily as where the classical approximation applies.

Electrical Conductivity

The isothermal electrical conductivity σ follows from the result for the particle diffusivity when we multiply the particle flux density by the particle charge q and replace the gradient $d\mu/dx$ of the chemical potential by the gradient $qd\varphi/dx = -qE_x$ of the external potential, where E_x is the x component of the electric field intensity. The electric current density follows from (21):

$$\mathbf{J}_q = (nq^2\tau_c/m)\mathbf{E} \ ; \qquad \sigma = nq^2\tau_c/m \ , \tag{39}$$

for a classical gas with relaxation time τ_c. For the Fermi-Dirac distribution, from (35),

$$\mathbf{J}_q = (nq^2\tau_c/m)\mathbf{E} \ ; \qquad \sigma = nq^2\tau_c/m \ . \tag{40}$$

APPENDIX G: VECTOR POTENTIAL, FIELD MOMENTUM, AND GAUGE TRANSFORMATIONS

This section is included because it is hard to find the magnetic vector potential **A** discussed thoroughly in one place, and we need the vector potential in superconductivity. It may seem mysterious that the hamiltonian of a particle in a magnetic field has the form derived in (18) below:

$$H = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 + Q\varphi \ , \tag{1}$$

where Q is the charge; M is the mass; **A** is the vector potential; and φ is the electrostatic potential. This expression is valid in classical mechanics and in quantum mechanics. Because the kinetic energy of a particle is not changed by a static magnetic field, it is perhaps unexpected that the vector potential of the magnetic field enters the hamiltonian. As we shall see, the key is the observation that the momentum **p** is the sum of two parts, the kinetic momentum

$$\mathbf{p}_{\text{kin}} = M\mathbf{v} \tag{2}$$

which is familiar to us, and the potential momentum or field momentum

$$\mathbf{p}_{\text{field}} = \frac{Q}{c}\mathbf{A} \ . \tag{3}$$

The total momentum is

$$\boxed{\mathbf{p} = \mathbf{p}_{\mathrm{kin}} + \mathbf{p}_{\mathrm{field}} = M\mathbf{v} + \frac{Q}{c}\mathbf{A}\ ,} \tag{4}$$

and the kinetic energy is

$$\frac{1}{2}Mv^2 = \frac{1}{2M}(Mv)^2 = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 \ . \tag{5}$$

The vector potential[1] is related to the magnetic field by

$$\mathbf{B} = \mathrm{curl}\,\mathbf{A}\ . \tag{6}$$

We assume that we work in nonmagnetic material so that **H** and **B** are treated as identical.

Lagrangian Equations of Motion

To find the Hamiltonian, the prescription of classical mechanics is clear: we must first find the Lagrangian. The Lagrangian in generalized coordinates is

$$L = \frac{1}{2}M\dot{q}^2 - Q\varphi(\mathbf{q}) + \frac{Q}{c}\dot{\mathbf{q}}\cdot\mathbf{A}(\mathbf{q})\ . \tag{7}$$

This is correct because it leads to the correct equation of motion of a charge in combined electric and magnetic fields, as we now show.

In Cartesian coordinates the Lagrange equation of motion is

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0\ , \tag{8}$$

and similarly for y and z. From (7) we form

$$\frac{\partial L}{\partial x} = -Q\frac{\partial \varphi}{\partial x} + \frac{Q}{c}\left(\dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_y}{\partial x} + \dot{z}\frac{\partial A_z}{\partial x}\right)\ ; \tag{9}$$

$$\frac{\partial L}{\partial \dot{x}} = M\dot{x} + \frac{Q}{c}A_x\ ; \tag{10}$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = M\ddot{x} + \frac{Q}{c}\frac{dA_x}{dt} = M\ddot{x} + \frac{Q}{c}\left(\frac{\partial A_x}{\partial t} + \dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_x}{\partial y} + \dot{z}\frac{\partial A_x}{\partial z}\right)\ . \tag{11}$$

Thus (8) becomes

$$M\ddot{x} + Q\frac{\partial \varphi}{\partial x} + \frac{Q}{c}\left[\frac{\partial A_x}{\partial t} + \dot{y}\left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x}\right) + \dot{z}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right] = 0\ , \tag{12}$$

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[1] For an elementary treatment of the vector potential see E. M. Purcell, *Electricity and magnetism*, 2nd ed., McGraw-Hill, 1984.

or

$$M\frac{d^2x}{dt^2} = QE_x + \frac{Q}{c}[\mathbf{v}\times\mathbf{B}]_x \ , \tag{13}$$

with

$$E_x = -\frac{\partial\varphi}{\partial x} - \frac{1}{c}\frac{\partial A_x}{\partial t} \ ; \tag{14}$$

$$\mathbf{B} = \mathrm{curl}\,\mathbf{A} \ . \tag{15}$$

Equation (13) is the Lorentz force equation. This confirms that (7) is correct. We note in (14) that **E** has one contribution from the electrostatic potential φ and another from the time derivative of the magnetic vector potential **A**.

Derivation of the Hamiltonian

The momentum **p** is defined in terms of the Lagrangian as

$$\mathbf{p} \equiv \frac{\partial L}{\partial \dot{\mathbf{q}}} = M\dot{\mathbf{q}} + \frac{Q}{c}\mathbf{A} \ , \tag{16}$$

in agreement with (4). The hamiltonian $H(\mathbf{p},\mathbf{q})$ is defined by

$$H(\mathbf{p},\mathbf{q}) \equiv \mathbf{p}\cdot\dot{\mathbf{q}} - L \ , \tag{17}$$

or

$$H = M\dot{q}^2 + \frac{Q}{c}\dot{\mathbf{q}}\cdot\mathbf{A} - \frac{1}{2}M\dot{q}^2 + Q\varphi - \frac{Q}{c}\dot{\mathbf{q}}\cdot\mathbf{A} = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 + Q\varphi \ , \tag{18}$$

as in (1).

Field Momentum

The momentum in the electromagnetic field that accompanies a particle moving in a magnetic field is given by the volume integral of the Poynting vector, so that

$$\mathbf{p}_{\mathrm{field}} = \frac{1}{4\pi c}\int dV\,\mathbf{E}\times\mathbf{B} \ . \tag{19}$$

We work in the nonrelativistic approximation with $v \ll c$, where v is the velocity of the particle. At low values of v/c we consider **B** to arise from an external source alone, but **E** arises from the charge on the particle. For a charge Q at $\mathbf{r}'$,

$$\mathbf{E} = -\nabla\varphi \ ; \qquad \nabla^2\varphi = -4\pi Q\,\delta(\mathbf{r}-\mathbf{r}') \ . \tag{20}$$

Thus

$$\mathbf{p}_f = -\frac{1}{4\pi c}\int dV\,\nabla\varphi\times\mathrm{curl}\,\mathbf{A} \ . \tag{21}$$

By a vector relation we have

$$\int dV\, \nabla\varphi \times \text{curl}\,\mathbf{A} = -\int dV\,[\mathbf{A} \times \text{curl}\,(\nabla\varphi) - \mathbf{A}\,\text{div}\,\nabla\varphi - (\nabla\varphi)\,\text{div}\,\mathbf{A}] \ . \quad (22)$$

But curl $(\Delta\varphi) = 0$, and we can always choose the gauge such that div $\mathbf{A} = 0$. This is the transverse gauge.

Thus, we have

$$\mathbf{p}_f = -\frac{1}{4\pi c}\int dV\,\mathbf{A}\,\nabla^2\varphi = \frac{1}{c}\int dV\,\mathbf{A}Q\,\delta(\mathbf{r}-\mathbf{r}') = \frac{Q}{c}\mathbf{A} \ . \qquad (23)$$

This is the interpretation of the field contribution to the total momentum $\mathbf{p} = M\mathbf{v} + Q\mathbf{A}/c$.

GAUGE TRANSFORMATION

Suppose $H\psi = \epsilon\psi$, where

$$H = \frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 \ . \qquad (24)$$

Let us make a gauge transformation to $\mathbf{A}'$, where

$$\mathbf{A}' = \mathbf{A} + \nabla\chi \ , \qquad (25)$$

where χ is a scalar. Now $\mathbf{B}$ = curl $\mathbf{A}$ = curl $\mathbf{A}'$, because curl $(\nabla\chi) \equiv 0$. The Schrödinger equation becomes

$$\frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}' + \frac{Q}{c}\nabla\chi\right)^2 \psi = \epsilon\psi \ . \qquad (26)$$

What ψ' satisfies

$$\frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}'\right)^2 \psi' = \epsilon\psi' \ , \qquad (27)$$

with the same ϵ as for ψ? Equation (27) is equivalent to

$$\frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A} - \frac{Q}{c}\nabla\chi\right)^2 \psi' = \epsilon\psi' \ . \qquad (28)$$

We try

$$\psi' = \exp(iQ\chi/\hbar c)\psi \ . \qquad (29)$$

Now

$$p\psi' = \exp(iQ\chi/\hbar c)\mathbf{p}\psi + \frac{Q}{c}(\nabla\chi)\exp(iQ\chi/\hbar c)\psi \ ,$$

so that

$$\left(\mathbf{p} - \frac{Q}{c}\nabla\chi\right)\psi' = \exp(iQ\chi/\hbar c)\mathbf{p}\psi$$

and

$$\frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A} - \frac{Q}{c}\nabla\chi\right)^2 \psi' = \exp(iQ\chi/\hbar c)\frac{1}{2M}\left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right)^2 \psi$$
$$= \exp(iQ\chi/\hbar c)\epsilon\psi \ . \tag{30}$$

Thus $\psi' = \exp(iQ\chi/\hbar c)\psi$ satisfies the Schrödinger equation after the gauge transformation (25). The energy ϵ is invariant under the transformation.

The gauge transformation on **A** merely changes the local phase of the wavefunction. We see that

$$\psi'^*\psi' = \psi^*\psi \ , \tag{31}$$

so that the charge density is invariant under a gauge transformation.

Gauge in the London Equation

Because of the equation of continuity in the flow of electric charge we require that in a superconductor

$$\operatorname{div}\mathbf{j} = 0 \ ,$$

so that the vector potential in the London equation $\mathbf{j} = -c\mathbf{A}/4\pi\lambda_L^2$ must satisfy

$$\operatorname{div}\mathbf{A} = 0 \ . \tag{32}$$

Further, there is no current flow through a vacuum/superconductor interface. The normal component of the current across the interface must vanish: $j_n = 0$, so that the vector potential in the London equation must satisfy

$$A_n = 0 \ . \tag{33}$$

The gauge of the vector potential in the London equation of superconductivity is to be chosen so that (32) and (33) are satisfied.

APPENDIX H: COOPER PAIRS

For a complete set of states of a two-electron system that satisfy periodic boundary conditions in a cube of unit volume, we take plane wave product functions

$$\varphi(\mathbf{k}_1,\mathbf{k}_2;\mathbf{r}_1,\mathbf{r}_2) = \exp[i(\mathbf{k}_1\cdot\mathbf{r}_1 + \mathbf{k}_2\cdot\mathbf{r}_2)] \ . \tag{1}$$

We assume that the electrons are of opposite spin.

We introduce center-of-mass and relative coordinates:

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \ ; \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \ ; \tag{2}$$

$$\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2 \ ; \qquad \mathbf{k} = \tfrac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2) \ , \tag{3}$$

so that

$$\mathbf{k}_1 \cdot \mathbf{r}_1 + \mathbf{k}_2 \cdot \mathbf{r}_2 = \mathbf{K} \cdot \mathbf{R} + \mathbf{k} \cdot \mathbf{r} \ . \tag{4}$$

Thus (1) becomes

$$\varphi(\mathbf{K},\mathbf{k};\mathbf{R},\mathbf{r}) = \exp(i\mathbf{K} \cdot \mathbf{R}) \exp(i\mathbf{k} \cdot \mathbf{r}) \ , \tag{5}$$

and the kinetic energy of the two-electron system is

$$\epsilon_{\mathbf{K}} + E_{\mathbf{k}} = (\hbar^2/m)(\tfrac{1}{4}K^2 + k^2) \ . \tag{6}$$

We give special attention to the product functions for which the center-of-mass wavevector $\mathbf{K} = 0$, so that $\mathbf{k}_1 = -\mathbf{k}_2$. With an interaction H_1 between the two electrons, we set up the eigenvalue problem in terms of the expansion

$$\chi(\mathbf{r}) = \Sigma g_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \ . \tag{7}$$

The Schrödinger equation is

$$(H_0 + H_1 - \epsilon)\chi(\mathbf{r}) = 0 = \Sigma_{\mathbf{k}'} [(E_{\mathbf{k}'} - \epsilon)g_{\mathbf{k}'} + H_1 g_{\mathbf{k}'}]\exp(i\mathbf{k}' \cdot \mathbf{r}) \ , \tag{8}$$

where H_1 is the interaction energy of the two electrons. Here ϵ is the eigenvalue.

We take the scalar product with $\exp(i\mathbf{k} \cdot \mathbf{r})$ to obtain

$$(E_{\mathbf{k}} - \epsilon)g_{\mathbf{k}} + \Sigma_{\mathbf{k}} g_{\mathbf{k}'} (\mathbf{k}|H_1|\mathbf{k}') = 0 \ , \tag{9}$$

the secular equation of the problem.

Now transform the sum to an integral:

$$(E - \epsilon)g(E) + \int dE' \, g(E')H_1(E,E')N(E') = 0 \ , \tag{10}$$

where $N(E')$ is the number of two electron states with total momentum $\mathbf{K} = 0$ and with kinetic energy in dE' at E'.

Now consider the matrix elements $H_1(E,E') = (\mathbf{k}|H_1|\mathbf{k}')$. Studies of these by Bardeen suggest that they are important when the two electrons are confined to a thin energy shell near the Fermi surface—within a shell of thickness $\hbar\omega_D$ above E_F, where ω_D is the Debye phonon cutoff frequency. We assume that

$$H_1(E,E') = -V \tag{11}$$

for E,E' within the shell and zero otherwise. Here V is assumed to be positive.

Thus (10) becomes

$$(E - \epsilon)g(E) = V \int_{2\epsilon_F}^{2\epsilon_m} dE' \, g(E')N(E') = C \ , \tag{12}$$

with $\epsilon_m = \epsilon_F + \hbar\omega_D$. Here C is a constant, independent of E.

From (12) we have

$$g(E) = \frac{C}{E - \epsilon} \tag{13}$$

and

$$1 = V \int_{2\epsilon_F}^{2\epsilon_m} dE' \, \frac{N(E')}{E' - \epsilon} \; . \tag{14}$$

With $N(E')$ approximately constant and equal to N_F over the small energy range between $2\epsilon_m$ and $2\epsilon_F$, we take it out of the integral to obtain

$$1 = N_F V \int_{2\epsilon_F}^{2\epsilon_m} dE' \, \frac{1}{E' - \epsilon} = N_F V \log \frac{2\epsilon_m - \epsilon}{2\epsilon_F - \epsilon} \; . \tag{15}$$

Let the eigenvalue ϵ of (15) be written as

$$\epsilon = 2\epsilon_F - \Delta \; , \tag{16}$$

which defines the binding energy Δ of the electron pair, relative to two free electrons at the Fermi surface. Then (15) becomes

$$1 = N_F V \log \frac{2\epsilon_m - 2\epsilon_F + \Delta}{\Delta} = N_F V \log \frac{2\hbar\omega_D + \Delta}{\Delta} \; , \tag{17}$$

or

$$1/N_F V = \log(1 + 2\hbar\omega_D/\Delta) \; . \tag{18}$$

This result for the binding energy of a Cooper pair may be written as

$$\Delta = \frac{2\hbar\omega_D}{\exp(1/N_F V) - 1} \; . \tag{19}$$

For V positive (attractive interaction) the energy of the system is lowered by excitation of a pair of electrons above the Fermi level. Therefore the Fermi gas is unstable in an important way. The binding energy (19) is closely related to the superconducting energy gap E_g. The BCS calculations show that a high density of Cooper pairs may form in a metal.

APPENDIX I: GINZBURG-LANDAU EQUATION

We owe to Ginzburg and Landau an elegant theory of the phenomenology of the superconducting state and of the spatial variation of the order parameter in that state. An extension of the theory by Abrikosov describes the structure of the vortex state which is exploited technologically in superconducting magnets. The attractions of the GL theory are the natural introduction of the coherence length and of the wavefunction used in the theory of the Josephson effects in Chapter 12.

We introduce the **order parameter** $\psi(\mathbf{r})$ with the property that

$$\psi^*(\mathbf{r})\psi(\mathbf{r}) = n_S(\mathbf{r}) \ , \tag{1}$$

the local concentration of superconducting electrons. The mathematical formulation of the definition of the function $\psi(\mathbf{r})$ will come out of the BCS theory. We first set up a form for the free energy density $F_S(\mathbf{r})$ in a superconductor as a function of the order parameter. We assume that in the general vicinity of the transition temperature

$$F_S(\mathbf{r}) = F_N - \alpha|\psi|^2 + \tfrac{1}{2}\beta|\psi|^4 + (1/2m)|(-i\hbar\nabla - qA/c)\psi|^2 - \int_0^{B_a} \mathbf{M}\cdot d\mathbf{B}_a \ , \tag{2}$$

with the phenomenological positive constants α, β, and m, of which more will be said. Here:

1. F_N is the free energy density of the normal state.

2. $-\alpha|\psi|^2 + \frac{1}{2}\beta|\psi|^4$ is a typical Landau form for the expansion of the free energy in terms of an order parameter that vanishes at a second-order phase transition. This term may be viewed as $-\alpha n_S + \frac{1}{2}\beta n_S^2$ and by itself is a minimum with respect to n_S when $n_S(T) = \alpha/\beta$.

3. The term in $|\text{grad}\ \psi|^2$ represents an increase in energy caused by a spatial variation of the order parameter. It has the form of the kinetic energy in quantum mechanics.[1] The kinetic momentum $-i\hbar\nabla$ is accompanied by the field momentum $-q\mathbf{A}/c$ to ensure the gauge invariance of the free energy, as in Appendix G. Here $q = -2e$ for an electron pair.

4. The term $-\int\mathbf{M}\cdot d\mathbf{B}_a$, with the fictitious magnetization $\mathbf{M} = (\mathbf{B} - \mathbf{B}_a)/4\pi$, represents the increase in the superconducting free energy caused by the expulsion of magnetic flux from the superconductor.

The separate terms in (2) will be illustrated by examples as we progress further. First let us derive the GL equation (6). We minimize the total free energy $\int dV\, F_S(\mathbf{r})$ with respect to variations in the function $\psi(\mathbf{r})$. We have

$$\delta F_S(\mathbf{r}) = [-\alpha\psi + \beta|\psi|^2\psi + (1/2m)(-i\hbar\nabla - q\mathbf{A}/c)\psi\cdot(i\hbar\nabla - q\mathbf{A}/c)\delta\psi^* + \text{c.c.}] \tag{3}$$

We integrate by parts to obtain

$$\int dV\,(\nabla\psi)(\nabla\delta\psi^*) = -\int dV\,(\nabla^2\psi)\delta\psi^* \ , \tag{4}$$

if $\delta\psi^*$ vanishes on the boundaries. It follows that

$$\delta\int dV\, F_S = \int dV\, \delta\psi^*[-\alpha\psi + \beta|\psi|^2\psi + (1/2m)(-i\hbar\nabla - q\mathbf{A}/c)^2\psi] + \text{c.c.} \tag{5}$$

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[1] A contribution of the form $|\nabla\mathbf{M}|^2$, where **M** is the magnetization, was introduced by Landau and Lifshitz to represent the exchange energy density in a ferromagnet; see *QTS*, p. 65.

This integral is zero if the term in brackets is zero:

$$\boxed{[(1/2m)(-i\hbar\nabla - q\mathbf{A}/c)^2 - \alpha + \beta|\psi|^2]\psi = 0 \ .} \tag{6}$$

This is the Ginzburg-Landau equation; it resembles a Schrödinger equation for ψ.

By minimizing (2) with respect to $\delta\mathbf{A}$ we obtain a gauge-invariant expression for the supercurrent flux:

$$\mathbf{j}_S(\mathbf{r}) = -(iq\hbar/2m)(\psi^*\nabla\psi - \psi\nabla\psi^*) - (q^2/mc)\psi^*\psi\mathbf{A} \ . \tag{7}$$

At a free surface of the specimen we must choose the gauge to satisfy the boundary condition that no current flows out of the superconductor into the vacuum: $\hat{\mathbf{n}} \cdot \mathbf{j}_S = 0$, where $\hat{\mathbf{n}}$ is the surface normal.

Coherence Length. The intrinsic coherence length ξ may be defined from (6). Let $\mathbf{A} = 0$ and suppose that $\beta|\psi|^2$ may be neglected in comparison with α. In one dimension the GL equation (6) reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \alpha\psi \ . \tag{8}$$

This has a wavelike solution of the form $\exp(ix/\xi)$, where ξ is defined by

$$\xi \equiv (\hbar^2/2m\alpha)^{1/2} \ . \tag{9}$$

A more interesting special solution is obtained if we retain the nonlinear term $\beta|\psi|^2$ in (6). Let us look for a solution with $\psi = 0$ at $x = 0$ and with $\psi \rightarrow \psi_0$ as $x \rightarrow \infty$. This situation represents a boundary between normal and superconducting states. Such states can coexist if there is a magnetic field H_c in the normal region. For the moment we neglect the penetration of the field into the superconducting region: we take the field penetration depth $\lambda \ll \xi$, which defines an extreme type I superconductor.

The solution of

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\psi + \beta|\psi|^2\psi = 0 \ , \tag{10}$$

subject to our boundary conditions, is

$$\psi(x) = (\alpha/\beta)^{1/2}\tanh(x/\sqrt{2}\xi) \ . \tag{11}$$

This may be verified by direct substitution. Deep inside the superconductor we have $\psi_0 = (\alpha/\beta)^{1/2}$, as follows from the minimization of the terms $-\alpha|\psi|^2 + \frac{1}{2}\beta|\psi|^4$ in the free energy. We see from (11) that ξ marks the extent of the coherence of the superconducting wavefunction into the normal region.

We have seen that deep inside the superconductor the free energy is a minimum when $|\psi_0|^2 = \alpha/\beta$, so that

$$F_S = F_N - \alpha^2/2\beta = F_N - H_c^2/8\pi \ , \tag{12}$$

by definition of the thermodynamic critical field H_c as the stabilization free energy density of the superconducting state. It follows that the critical field is related to α and β by

$$H_c = (4\pi\alpha^2/\beta)^{1/2} \ . \tag{13}$$

Consider the penetration depth of a weak magnetic field ($B \ll H_c$) into a superconductor. We assume that $|\psi|^2$ in the superconductor is equal to $|\psi_0|^2$, the value in the absence of a field. Then the equation for the supercurrent flux reduces to

$$\mathbf{j}_S(\mathbf{r}) = -(q^2/mc)|\psi_0|^2\mathbf{A} \ , \tag{14}$$

which is just the London equation $\mathbf{j}_S(\mathbf{r}) = -(c/4\pi\lambda^2)\mathbf{A}$, with the penetration depth

$$\lambda = \left(\frac{mc^2}{4\pi q^2|\psi_0|^2}\right)^{1/2} = \left(\frac{mc^2\beta}{4\pi q^2\alpha}\right)^{1/2} \ . \tag{15}$$

The dimensionless ratio $\kappa \equiv \lambda/\xi$ of the two characteristic lengths is an important parameter in the theory of superconductivity. From (9) and (15) we find

$$\kappa = \frac{mc}{q\hbar}\left(\frac{\beta}{2\pi}\right)^{1/2} \ . \tag{16}$$

We now show that the value $\kappa = 1/\sqrt{2}$ divides type I superconductors ($\kappa < 1/\sqrt{2}$) from type II superconductors ($\kappa > 1/\sqrt{2}$).

Calculation of the Upper Critical Field. Superconducting regions nucleate spontaneously within a normal conductor when the applied magnetic field is decreased below a value denoted by H_{c2}. At the onset of superconductivity $|\psi|$ is small and we linearize the GL equation (6) to obtain

$$\frac{1}{2m}(-i\hbar\nabla - q\mathbf{A}/c)^2\psi = \alpha \ . \tag{17}$$

The magnetic field in a superconducting region at the onset of superconductivity is just the applied field, so that $\mathbf{A} = B(0,x,0)$ and (17) becomes

$$-\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{1}{2m}\left(i\hbar\frac{\partial}{\partial y} + \frac{qB}{c}x\right)^2\psi = \alpha\psi \ . \tag{18}$$

This is of the same form as the Schrödinger equation of a free particle in a magnetic field.

We look for a solution in the form $\exp[i(k_y y + k_z z)]\varphi(x)$ and find

$$(1/2m)[-\hbar^2 d^2/dx^2 + \hbar^2 k_z^2 + (\hbar k_y - qBx/c)^2]\varphi = \alpha\varphi \ , \tag{19}$$

this is the equation for an harmonic oscillator, if we set $E = \alpha - (\hbar^2/2m)(k_y^2 + k_z^2)$ as the eigenvalue of

$$(1/2m)[-\hbar^2 d^2/dx^2 + (q^2B^2/c^2)x^2 - (2\hbar k_y qB/c)x]\varphi = E\varphi \ . \tag{20}$$

The term linear in x can be transformed away by a shift of the origin from 0 to $x_0 = \hbar k_y qB/2mc$, so that (20) becomes, with $X = x - x_0$,

$$-\left[\frac{\hbar^2}{2m}\frac{d^2}{dX^2} + \tfrac{1}{2}m(qB/mc)^2X^2\right]\varphi = (E + \hbar^2k_y^2/2m)\varphi \ . \tag{21}$$

The largest value of the magnetic field B for which solutions of (21) exist is given by the lowest eigenvalue, which is

$$\tfrac{1}{2}\hbar\omega = \hbar qB_{\max}/2mc = \alpha - \hbar^2k_z^2/2m \ , \tag{22}$$

where ω is the oscillator frequency qB/mc. With k_z set equal to zero,

$$B_{\max} \equiv H_{c2} = 2\alpha mc/q\hbar \ . \tag{23}$$

This result may be expressed by (13) and (16) in terms of the thermodynamic critical field H_c and the GL parameter $\kappa = \lambda/\xi$:

$$H_{c2} = \frac{2\alpha mc}{q\hbar}\cdot\frac{H_c}{(4\pi\alpha^2/\beta)^{1/2}} = \sqrt{2}\,\frac{mc}{\hbar q}\sqrt{\frac{\beta}{2\pi}}\,H_c = \sqrt{2}\kappa H_c \ . \tag{24}$$

When $\lambda/\xi > 1/\sqrt{2}$, a superconductor has $H_{c2} > H_c$ and is said to be of type II.

It is helpful to write H_{c2} in terms of the flux quantum $\Phi_0 = 2\pi\hbar c/q$ and $\xi^2 = \hbar^2/2m\alpha$:

$$H_{c2} = \frac{2mc\alpha}{q\hbar}\cdot\frac{q\Phi_0}{2\pi\hbar c}\cdot\frac{\hbar^2}{2m\alpha\xi^2} = \frac{\Phi_0}{2\pi\xi^2} \ . \tag{25}$$

This tells us that at the upper critical field the flux density H_{c2} in the material is equal to one flux quantum per area $2\pi\xi^2$, consistent with a fluxoid lattice spacing of the order of ξ.

APPENDIX J: ELECTRON-PHONON COLLISIONS

Phonons distort the local crystal structure and hence distort the local band structure. This distortion is sensed by the conduction electrons. The important effects of the coupling of electrons with phonons are

- Electrons are scattered from one state $\mathbf{k}$ to another state $\mathbf{k}'$, leading to electrical resistivity.

- Phonons can be absorbed in the scattering event, leading to the attenuation of ultrasonic waves.
- An electron will carry with it a crystal distortion, and the effective mass of the electron is thereby increased.
- A crystal distortion associated with one electron can be sensed by a second electron, thereby causing the electron-electron interaction that enters the theory of superconductivity.

The deformation potential approximation is that the electron energy $\epsilon(\mathbf{k})$ is coupled to the crystal dilation $\Delta(\mathbf{r})$ or fractional volume change by

$$\epsilon(\mathbf{k},\mathbf{r}) = \epsilon_0(\mathbf{k}) + C\Delta(\mathbf{r}) \ , \tag{1}$$

where C is a constant. The approximation is useful for spherical band edges $\epsilon_0(\mathbf{k})$ at long phonon wavelengths and low electron concentrations. The dilation may be expressed in terms of the phonon operators $a_{\mathbf{q}}$, $a^+_{\mathbf{q}}$ of Appendix C by

$$\Delta(\mathbf{r}) = i\sum_{q} (\hbar/2M\omega_{\mathbf{q}})^{1/2}|\mathbf{q}|[a_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}) - a^+_{\mathbf{q}}\exp(-i\mathbf{q}\cdot\mathbf{r})] \ . \tag{2}$$

as in *QTS*, p. 23. Here M is the mass of the crystal. The result (2) also follows from (C.32) on forming $q_s - q_{s-1}$ in the limit $k \ll 1$.

In the Born approximation for the scattering we are concerned with the matrix elements of $C\Delta(\mathbf{r})$ between the one-electron Bloch states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$, with $|\mathbf{k}\rangle = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$. In the wave field representation the matrix element is

$$\begin{aligned} H' &= \int d^3x\, \psi^+(\mathbf{r})C\Delta(\mathbf{r})\psi(\mathbf{r}) = \sum_{\mathbf{k}'\mathbf{k}} c^+_{\mathbf{k}'}c_{\mathbf{k}}\langle\mathbf{k}'|C\Delta|\mathbf{k}\rangle \\ &= iC\sum_{\mathbf{k}'\mathbf{k}} c^+_{\mathbf{k}'}c_{\mathbf{k}}\sum_{\mathbf{q}} (\hbar/2M\omega_{\mathbf{q}})^{1/2}|\mathbf{q}|(a_{\mathbf{q}}\int d^3x\, u^*_{\mathbf{k}'}u_{\mathbf{k}}e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{r}} \\ &\quad - a^+_{\mathbf{q}}\int d^3x\, u^*_{\mathbf{k}}u_{\mathbf{k}}e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{q})\cdot\mathbf{r}}) \ , \end{aligned} \tag{3}$$

where

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}}\varphi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \ , \tag{4}$$

where $c^+_{\mathbf{k}}$, $c_{\mathbf{k}}$ are the fermion creation and annihilation operators. The product $u^*_{\mathbf{k}'}(\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$ involves the periodic parts of the Bloch functions and is itself periodic in the lattice; thus the integral in (3) vanishes unless

$$\mathbf{k} - \mathbf{k}' \pm \mathbf{q} = \begin{cases} 0 \\ \text{vector in the reciprocal lattice.} \end{cases}$$

In semiconductors at low temperatures only the possibility zero (N processes) may be allowed energetically.

Let us limit ourselves to N processes, and for convenience we approximate $\int d^3x\, u_{\mathbf{k}'} u_{\mathbf{k}}$ by unity. Then the deformation potential perturbation is

$$H' = iC \sum_{\mathbf{kq}} (\hbar/2M\omega_{\mathbf{q}})^{1/2} |\mathbf{q}| (a_{\mathbf{q}} c^+_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} - a^+_{\mathbf{q}} c^+_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}}) \ . \tag{5}$$

Relaxation Time. In the presence of the electron-phonon interaction the wavevector **k** is not a constant of the motion for the electron alone, but the sum of the wavevectors of the electron and virtual phonon is conserved. Suppose an electron is initially in the state $|\mathbf{k}\rangle$; how long will it stay in that state?

We calculate first the probability ω per unit time that the electron in **k** will emit a phonon **q**. If $n_{\mathbf{q}}$ is the initial population of the phonon state,

$$w(\mathbf{k} - \mathbf{q}; n_{\mathbf{q}} + 1 | \mathbf{k}; n_{\mathbf{q}}) = (2\pi/\hbar) |\langle \mathbf{k} - \mathbf{q}; n_{\mathbf{q}} + 1 | H' | \mathbf{k}; n_{\mathbf{q}} \rangle|^2 \, \delta(\epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}} - \epsilon_{\mathbf{k}-\mathbf{q}}) \tag{6}$$

by time-dependent perturbation theory. Here

$$|\langle \mathbf{k} - \mathbf{q}; n_{\mathbf{q}} + 1 | H' | \mathbf{k}; n_{\mathbf{q}} \rangle|^2 = [C^2 \hbar q / 2Mc_S (n_{\mathbf{q}} + 1)] \ . \tag{7}$$

The total collision rate W of an electron in the state $|\mathbf{k}\rangle$ with a phonon system at absolute zero is, with $n_{\mathbf{q}} = 0$,

$$W = \frac{C^2}{4\pi\rho c_s} \int_{-1}^{1} d(\cos\theta_{\mathbf{q}}) \int_0^{q_m} dq\, q^3 \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \hbar\omega_{\mathbf{q}}) \ , \tag{8}$$

where ρ is the mass density.

The argument of the delta function is

$$\frac{\hbar^2}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2) - \hbar c_s q = \frac{\hbar^2}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2 - qq_c) \ , \tag{9}$$

where $q_c = 2\hbar m^* c_s$, with c_s the velocity of sound. The minimum value of k for which the argument can be zero is $k_{\text{min}} = \frac{1}{2}(q + q_c)$, which for $q = 0$ reduces to $k_{\text{min}} = \frac{1}{2}q_c = m^* c_s/\hbar$. For this value of k the electron group velocity $v_{\text{g}} = k_{\text{min}}/m^*$ is equal to the velocity of sound. Thus the threshold for the emission of phonons by electrons in a crystal is that the electron group velocity should exceed the acoustic velocity. This requirement resembles the Cerenkov threshold for the emission of photons in crystals by fast electrons. The electron energy at the threshold is $\frac{1}{2}m^* c_s^2 \sim 10^{-27} \cdot 10^{11} \sim 10^{-16}$ erg ~ 1 K. An electron of energy below this threshold will not be slowed down in a perfect crystal at absolute zero, even by higher order electron-phonon interactions, at least in the harmonic approximation for the phonons.

For $k \gg q_c$ we may neglect the qq_c term in (9). The integrals in (8) become

$$\int_{-1}^{1} d\mu \int dq\, q^3 (2m^*/\hbar^2 q) \delta(2k\mu - q) = (8m^*/\hbar^2) \int_0^1 d\mu\, k^2 \mu^2 = 8m^* k^2/3\hbar^2 \ , \tag{10}$$

and the phonon emission rate is

$$W(\text{emission}) = \frac{2C^2 m^* k^2}{3\pi\rho c_s \hbar^2} , \tag{11}$$

directly proportional to the electron energy $\epsilon_{\mathbf{k}}$. The loss of the component of wavevector parallel to the original direction of the electron when a phonon is emitted at an angle θ to $\mathbf{k}$ is given by $q \cos\theta$. The fractional rate of loss of k_z is given by the transition rate integral with the extra factor $(q/k)\cos\theta$ in the integrand. Instead of (10), we have

$$(2m^*/\hbar^2 k) \int_0^1 d\mu\, 8k^3\mu^4 = 16m^* k^2/5\hbar^2 , \tag{12}$$

so that the fractional rate of decrease of k_z is

$$W(k_z) = 4C^2 m^* k^2/5\pi\rho c_s \hbar^2 . \tag{13}$$

This quantity enters into the electrical resistivity.

The above results apply to absolute zero. At a temperature $k_B T \gg \hbar c_s k$ the integrated phonon emission rate is

$$W(\text{emission}) = \frac{C^2 m^* k k_B T}{\pi c_s^2 \rho \hbar^3} . \tag{14}$$

For electrons in thermal equilibrium at not too low temperatures the required inequality is easily satisfied for the rms value of k. If we take $C = 10^{-12}$ erg; $m^* = 10^{-27}$ g; $k = 10^7\ \text{cm}^{-1}$; $c_s = 3 \times 10^5\ \text{cm s}^{-1}$; $\rho = 5\ \text{g cm}^{-3}$; then $W \simeq 10^{12}\ \text{s}^{-1}$. At absolute zero (13) gives $W \simeq 5 \times 10^{10}\ \text{s}^{-1}$ with these same parameters.