Comment on Gorkov and Eliashberg's Result for the Polarizability of a Minute Metallic Particle

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The potentially important theoretical prediction of Gorkov and Eliashberg that the electronic polarizability of a minute metallic particle is enormously enhanced is shown to be invalid because of the neglect of the effect of depolarization fields. But a more serious objection is the assumption of a constant internal field.

A few years ago Gorkov and Eliashberg[1] published the remarkable theoretical prediction that the electronic polarizability of a metallic particle—sufficiently minute that its electronic energy levels are discrete—should be enormously enhanced with respect to the classical polarizability $\alpha_p = r^3$ of elementary electrostatics (r is the mean particle radius). The order of magnitude of the predicted enhancement was $(k_F r)^2$, where k_F denotes the limiting Fermi wave vector, and the effect should be observable in external fields E and at temperatures T such that the discrete electronic energy levels of the minute particle system remain unmixed. Under such conditions the minute metallic particle was considered to behave as a dielectric. Besides the intrinsic physical interest of the effect, such an anomalous enhancement of the polarizability would have important technological applications since the effect could clearly be used to synthesize dielectric materials with large controllable dielectric constants.[2] Naturally enough, several experimental investigations of the effect have subsequently been made.[3] All such attempts, however, have failed to observe the enhanced polarizability.

It is the purpose of this paper to review critically the validity of Gorkov and Eliashberg's potentially important result.

We first note that the result of Gorkov and Eliashberg (GE) can be ruled out on the grounds of classical electrostatics alone. The mathematical reasoning behind the latter statement is contained in the following familiar set of equations:

$$\alpha_p = \tfrac{4}{3}\pi r^3 P/E = (1 - E_{\text{loc}}/E) r^3 , \tag{1}$$

$$E_{\text{loc}} = E - \tfrac{4}{3}\pi P = 0 \text{ (conductor)} \geq 0 \text{ (dielectric).} \tag{2}$$

Here P denotes the induced homogeneous polarization and E_{loc} the local field inside the sphere, which differs from E on account of the depolarization field $-\tfrac{4}{3}\pi P$. Since, in general, $E_{\text{loc}} \geq 0$, we obtain the result, known in electrostatics, that the polarizability of a homogeneous dielectric sphere cannot exceed r^3, i.e., that for an isolated conducting sphere. Providing the metallic particles considered by GE are not too small, i.e., r is still large by comparison to a typical interatomic distance, the above electrostatics argument applies as well to the situation in which the electronic energy levels are discrete as to the more usual situation in which they may be regarded as continuous.

A consideration of GE's paper in the light of elementary electrostatics reveals that these authors have made a trivial, yet drastic, error in their calculation of the induced polarization P. Whereas in the presence of sufficiently weak fields P must invariably result as the linear response to the *local field* E_{loc}, GE have erroneously regarded P as the linear response to the external field E. Introducing, for the case of the minute metallic particles, the susceptibility χ_p,

$$P = \chi_p E_{\text{loc}} , \tag{3}$$

it follows from (1) and (2) that

$$E_{\text{loc}} = E/(1 + \tfrac{4}{3}\pi\chi_p) \tag{4}$$

and

$$\alpha_p = \tfrac{4}{3}\pi r^3 \chi_p/(1 + \tfrac{4}{3}\pi\chi_p) . \tag{5}$$

Now GE's calculation is essentially for the susceptibility χ_p which, for the minute-particle system, they find is very large $\sim (k_F r)^2$. Since they have written $P = \chi_p E$, they conclude that α_p is likewise very large. However, in view of (4) the very large χ_p found by GE actually implies an almost complete screening of the external field ($E_{\text{loc}} \simeq 0$) so that α_p is consequently close to the classical result $\alpha_p = r^3$, as explicitly shown by (5).

As assumed by GE, when the electronic energy levels are to be regarded as discrete, χ_p may be calculated by treating the metallic particle as a "macroscopic atom," in which case one may apply

standard linear-response theory to obtain χ_p in terms of the matrix elements of the coordinates of the electrons (i. e., oscillator strengths) and their respective energy eigenvalues. We present now a fairly general expression for χ_p. Its derivation renders transparent the underlying approximation of GE's calculation of this quantity.

Written in its most general form the linear-response expression for χ_p actually relates χ_p to the familiar static density-density response function $\chi(\vec{r}, \vec{r}')$ of the many-electron system[4]:

$$\chi_p = e^2 \int \frac{d\vec{r}}{\Omega} \int \frac{d\vec{r}'}{\Omega} r_x r_x' \chi(\vec{r}, \vec{r}'), \qquad (6)$$

where Ω denotes the volume of the system and r_x denotes the spatial coordinate in the direction of the applied field (for convenience, we have considered χ_p to be a diagonal component of the general susceptibility tensor). We recall that $\chi(\vec{r}, \vec{r}')$ is defined as

$$\chi(\vec{r}, \vec{r}') = (\Omega/i\hbar) \int_0^\infty dt \langle [\rho(\vec{r}, t), \rho(\vec{r}', 0)] \rangle,$$

where $\rho(\vec{r}, t)$ denotes the Heisenberg operator specifying the electron density at the point $\vec{r}$ and time t, and the brackets $\langle \cdots \rangle$ denote an equilibrium ensemble average. Now in the interior of the many-electron system $\chi(\vec{r}, \vec{r}')$ will be strongly peaked in the vicinity of the point $\vec{r} = \vec{r}'$, its range about this origin being of the order of the inverse of some appropriate screening wave vector q_s, i. e., of the order of an interatomic distance a. The screening wave vector may actually be defined by the relation

$$q_s^2 = (4\pi e^2/\Omega) \int d\vec{r}' \chi(\vec{r}, \vec{r}'), \qquad (7)$$

where $\vec{r}$ denotes a point in the interior of the system, in which case the integral in (7) does not depend on $\vec{r}$. For the special case of the bulk metal we would have

$$q_s^{02} = (4\pi e^2/\Omega) \int d\vec{r}' \chi(|\vec{r} - \vec{r}'|)_B$$

$$= (4\pi e^2/\Omega) \chi(\vec{q} = 0, \omega = 0)_B = 4\pi e^2 N(\epsilon_F),$$

where $\chi(\vec{q}, \omega)_B$ denotes the wave-vector- and frequency-dependent density-density response function of the bulk metal and $N(\epsilon_F)$ the corresponding density of states per unit volume at the Fermi energy ϵ_F. Clearly, q_s^0 is just the Fermi-Thomas screening wave vector. If now in (6) we neglect possible boundary effects on $\chi(\vec{r}, \vec{r}')$ in the small region of integration in the vicinity of the surface of the system ($r \gg a$) we have, to the approximation indicated,

$$\chi_p = e^2 \int \frac{d\vec{r}}{\Omega} r_x^2 \int \frac{d\vec{r}'}{\Omega} \chi(\vec{r}, \vec{r}') + O\left(\frac{1}{q_s r}\right)$$

$$= \frac{q_s^2}{4\pi} \int \frac{d\vec{r}}{\Omega} r_x^2. \qquad (8)$$

Equation (8) is our desired expression for the electronic susceptibility. For the sphere problem it reduces to

$$\chi_p = (q_s r)^2/20\pi. \qquad (9)$$

If in (9) we now replace q_s by its value for the bulk metal, and reexpress this in terms of k_F, we obtain precisely GE's result. It is therefore evident that the central approximation of GE's calculation of χ_p is the replacement of $\chi(\vec{r}, \vec{r}')$ by its value for the bulk metal.

There remains, however, a criticism of GE's original calculation of the polarizability which is much more fundamental than the neglect of the depolarization field. This is the assumption that the local internal field is constant. What we have demonstrated in the above discussion is that if one accepts this assumption the large polarizability originally found by GE is suppressed by the effect of the particle's depolarization field. However, while the assumption of a constant local field will hold in the limiting case of a metallic particle consisting of a very small number of atoms ($r q_s \gtrsim 1$), it certainly cannot be expected to hold when $r q_s$ is appreciably different from unity. The induced polarization will not be given by (3) but by

$$P = -e \int d\vec{r} \int d\vec{r}' \, r_x \phi(\vec{r}') \chi(\vec{r}, \vec{r}'), \qquad (10)$$

where $\phi(\vec{r})$ denotes the induced local electrostatic potential $[\vec{E}_{loc} = -\vec{\nabla}\phi(\vec{r})]$ obtained from the solution of the Poisson equation

$$\nabla^2 \phi(\vec{r}) = 4\pi e \int d\vec{r}' \, \phi(\vec{r}') \chi(\vec{r}, \vec{r}'). \qquad (11)$$

Thus α_p will be no longer determined by the homogeneous susceptibility defined by Eq. (6). Equations (10) and (11) are valid irrespective of whether the electronic energy levels are discrete or continuous, and they specify, of course, the extent to which the external field is screened by the many-electron system of the metallic particle. Indeed, for $q_s r$ large, the external field will always be essentially screened ($E_{loc} \simeq 0$ almost everywhere in the interior of the particle) even if r is still sufficiently small for the electronic energy levels to be discrete in the sense defined by GE.

An investigation of the electronic polarizabilities of small metallic particles and thin metallic films, based on a numerical evaluation of (10) and (11), will be published in a subsequent paper.

[1]L. P. Gorkov and G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. 48, 1407 (1965) [Sov. Phys. JETP 21, 940 (1965)].

[2]As fully realized by Gorkov and Eliashberg (Ref. 1).
[3]R. Dupree and M. A. Smithard, J. Phys. C 5, 408 (1972); F. Meier and P. Wyder, Phys. Letters 39A, 51

(1972); M. A. Smithard and R. Dupree (unpublished).

[4]For a general discussion of the application of linear-response techniques to the many-electron system see,

for example, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 6; S. Strässler, Physik Kondensierten Materie 10, 219 (1969).

Neutron Spectroscopy of Superconductors

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A complete understanding of the mechanism for superconductivity requires knowledge of the details of electrons, phonons, and their interactions, and can be summarized by the function $\alpha^2 F(\omega)$. This function is often very similar to the phonon density of states $F(\omega) = \sum \delta(\omega - \omega_Q)$, which can be derived from an analysis of neutron-scattering data. In this paper it is pointed out that the complete function $\alpha^2 F(\omega)$ is also (in principle) contained in neutron-scattering data if the intrinsic linewidth γ_Q is measured as well as the dispersion relation ω_Q. It is shown that $\alpha^2 F$ differs from F by having a weighting factor $2\gamma_Q/\pi N(0)\omega$ inside the summation, where $N(0)$ is the electronic density of states at the Fermi surface for both spin orientations. The dimensionless coupling constant λ can also be expressed in terms of $N(0)$, ω_Q, and γ_Q. In practice, for most superconductors, the average widths γ_Q are smaller than presently available resolution. However, for materials with a high density of states like $\beta - W$ superconductors, the widths γ_Q may be measurable. Also, the question of whether superconductivity arises predominantly from coupling to certain groups of phonons can be answered experimentally by searching for anomalously large widths. Estimates of average phonon widths are given for a variety of metals.

Recently, there have been several investigations of the phonon modes of high-transition-temperature superconductors by inelastic neutron scattering.[1-3] In the $A15$-structure materials[1,2] Nb_3Sn and V_3Si these studies have revealed that the soft transverse-acoustic (TA) modes (known from ultrasonic work) extend out to fairly large wave vectors. In the rocksalt-structure materials[3] like TaC, these studies have revealed anomalous regions of the LA and LO modes at large wave vector. It would be very interesting to know whether the large observed values of T_c arise in good part from electrons coupling to these anomalous phonons. This paper proposes a direct method for answering this question.

The equilibrium superconducting properties of any material can be derived from a knowledge of the spectral function $\alpha^2 F(\omega)$.[4] In the special case of strong-coupling s-p metals like lead, $\alpha^2 F$ can be deduced from tunneling data.[5] For the great majority of superconductors, however, there is no presently feasible method of determining $\alpha^2 F$. The main result of this paper is a relation between $\alpha^2 F(\omega)$ and the electron-phonon–induced width γ_Q of a phonon mode of frequency ω_Q. (The symbol Q incorporates the wave vector $\vec{Q}$ and a mode index.)

The spectral function is closely related to the density of phonon states $F(\omega)$:

$$F(\omega) = \sum_Q \delta(\omega - \omega_Q) . \tag{1}$$

However, the connection is obscured somewhat in the usual definition,

$$\alpha^2 F(\omega) \equiv \sum_{kk'} |M_{kk'}|^2 \delta(\omega - \omega_{k-k'}) \delta(\epsilon_k) \delta(\epsilon_{k'})/N(0) . \tag{2}$$

In this formula $M_{kk'}$ is the matrix element for scattering from an electron state k of energy ϵ_k to a state k' of energy $\epsilon_{k'}$, via a phonon $k - k'$. The summations are restricted by the δ functions to run over states at the Fermi energy (which is taken as the zero of energy). The symbol k incorporates the wave number $\vec{k}$, band index, and spin index. The symbol $N(0)$ is the electronic density of states at the Fermi surface of states at the Fermi surface for both spin orientations,

$$N(0) = \sum_k \delta(\epsilon_k) . \tag{3}$$

The matrix element M includes a host of many-body corrections such as screening, vertex corrections, and the measured rather than the bare-phonon frequency, as explained, for example, in Ref. 5. From a knowledge of $\alpha^2 F$ we may determine the transition temperature T_c by solving a complicated integral equation. For qualitative understanding, however, it is preferable to bypass that step and use instead the approximate equation of McMillan[6,7]