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Strong coupling superconductivity in small particles *

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Electrons and phonons in a small solid particle (i.e. a big cluster of atoms) behave differently than in the solid in bulk. Due to the finite number of atoms in the small particle, the electron band is discrete and soft phonon modes are enhanced. Furthermore, any defect in the small particle surface will induce fluctuations in the discrete electronic spectrum, giving rise to a statistical effect which may manifest itself in many instances. For example, the transition temperature from the superconducting to the normal state in a small particle might differ from that of the bulk superconductor.

In this note we consider Eliashberg's equations [1] for strong-coupling superconductors and take explicitly into account both the discreteness of the electron energy levels and the spectrum fluctuations. We then obtain an equation for the transition temperature T_c which turns out to be a function of the size of the particle and of the spectrum fluctuations. The resulting equation for T_c is not exact, however, since the treatment has been done using the grand-canonical ensemble, so the constancy of the number of electrons within each small particle is not taken care of. Nevertheless, since this number is of the order of several thousands, the error in T_c thereby introduced should not be large [2]. Furthermore, we should also mention that our treatment is not complete, since we have not allowed for changes in the phonon spectrum due to the finite size of the particle.

We start from Eliashberg's coupled equations for the renormalization function $Z(\omega)$ and the gap parameter $\Delta(\omega)$ and perform an angular average over the electron states as done by Scalapino *et al.* [3]; we write them as

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$$2\hbar\omega[1 - Z(\omega)] = \sum_{\mathbf{p}} J_+(\omega, \omega_p) \tag{1}$$

$$\Delta(\omega) = -\frac{1}{2Z(\omega)} \sum_{\mathbf{p}} \frac{\Delta(\omega_p)}{\hbar\omega_p} [J_-(\omega, \omega_p) + J_c(\omega, \omega_p)] , \tag{2}$$

where the summation over the electron states must be performed taking into account the discrete nature of the electronic spectrum.

In Eqs. (1) and (2), $J_\pm$ are the electron-phonon interaction kernels, given by

$$J_\pm(\omega, \omega_p) = \int \frac{d\Omega_{\mathbf{q}}}{4\pi} \sum_i \int_0^\infty d\nu |g_{\mathbf{q}i}|^2 B_i(\mathbf{q}, \nu)$$

$$\times \left\{ \left[\frac{f(-\omega_p)}{\omega - \omega_p - \nu} + \frac{f(\omega_p)}{\omega - \omega_p + \nu} \right] \right.$$

$$\left. \pm \left[\frac{f(\omega_p)}{\omega + \omega_p - \nu} + \frac{f(-\omega_p)}{\omega + \omega_p + \nu} \right] \right\} , \tag{3}$$

where $f(\omega_p)$ is the Fermi distribution function and $\hbar\omega_p$ are the quasi-particle energies, related to the bare electron energies ϵ_p which are measured from the Fermi level $\epsilon_F = p_F^2/2m$, in the form

$$\hbar\omega_p = \sqrt{\epsilon_p{}^2 + [\Delta(\omega_p)Z(\omega_p)]^2} . \tag{4}$$

To obtain (3) an angular average over the momentum transfer $\mathbf{q}$, due to the electron-phonon interaction, which is proportional to the coupling constant $g_{\mathbf{q}i}$, has been performed. It is reasonable to assume that this angular average can be carried out for the small particle as much as it can for the metal in bulk, since the interactions are of short range.

In these equations the phonon spectrum is described by the spectral weight function $B_i(\mathbf{q}, \nu)$, where i indicates the bare phonon modes. This function will certainly be altered by the existence of the particle surface but, as we have already mentioned, we shall not take this effect into account. In case we did, the integration over the phonon frequencies ν in Eq. (3) should also be converted into a discrete sum.

The kernel J_c appearing in Eliashberg equations is due to the screened Coulomb potential $V(|\mathbf{q}|)$ and is given by

$$J_c(\omega, \omega_p) = \frac{1}{4\pi}\int d\Omega_{\mathbf{q}}\, V(\mathbf{q}) \tanh(\beta\hbar\omega_p/2) \ , \tag{5}$$

where $\beta = (kT)^{-1}$, k being Boltzmann's constant and T the temperature. In all these expressions the contribution from thermal phonons has been neglected, an approximation which is as good at low temperatures for small particles as it is for the solid in bulk.

We now perform the discrete sum over $\mathbf{p}$ in two steps. The sum over the angular part of $\mathbf{p}$ is done in much the same way as in the bulk [3], but the sum over the absolute value of $\mathbf{p}$, or over the single electron energies ϵ_p, is affected by the discreteness of the spectrum, so we explicitly retain it. The appropriate coupled equations for a small particle then become

$$2[1 - Z(\omega)]\hbar\omega =$$

$$\sum_{\epsilon_p}\int_0^{\infty} \frac{d\nu\Lambda(\nu)}{N(0)} \left\{ f(-\omega_p)\left[\frac{1}{\omega - \omega_p - \nu} + \frac{1}{\omega + \omega_p + \nu}\right] \right.$$

$$\left. + f(\omega_p)\ \frac{1}{\omega - \omega_p + \nu} + \frac{1}{\omega + \omega_p - \nu} \right. \tag{6}$$

and

$$2Z(\omega)\cdot\Delta(\omega) = -\sum_{\epsilon_p} \frac{\Delta(\omega_p)}{\hbar\omega_p}\int_0^{\infty} \frac{d\nu\Lambda(\nu)}{N(0)} \times \left\{ f(-\omega_p) \right.$$

$$\times\left[\frac{1}{\omega - \omega_p - \nu} - \frac{1}{\omega + \omega_p + \nu}\right]$$

$$\left. + f(\omega_p)\ \left[\frac{1}{\omega - \omega_p + \nu} - \frac{1}{\omega + \omega_p - \nu}\right]\right\}$$

$$- V_c \sum_{\epsilon_p} \frac{\Delta(\omega_p)}{\hbar\omega_p} \tanh(\beta\hbar\omega_p/2) \ , \tag{7}$$

where

$$\Lambda(\nu) = N(0) \sum_i \int \frac{d\Omega_q}{4\pi} \int_0^{2p_F} \frac{qdq}{2p_F^2} |g_{qi}|^2 B_i(q, \nu) \ . \tag{8}$$

Here V_c is the Coulomb pseudo-potential [3] and $N(0)$ is the single-electron density of states evaluated at the Fermi energy. For a small particle of volume v and a spectrum with mean-level spacing D, we have

$$D = 1/N(0)v \ . \tag{9}$$

We shall now, following McMillan [4], obtain an approximate solution to Eqs. (6) and (7). This will allow us to show where the main differences between the solutions for a small particle and those for the metal in bulk come from. A trial function $\Delta(\omega)$ is introduced, such that for a phonon cutoff frecuency ω_0

$$\tilde{\Delta}(\omega) = \begin{cases} \Delta_0 & 0 \leqslant \omega \leqslant \omega_0 \\ \\ \Delta_\infty & \omega \geqslant \omega_0 \end{cases} \ . \tag{10}$$

Taking into account that $f(-\omega_p) \simeq 1$ and $f(\omega_p) \simeq 0$ when $\omega \geqslant \omega_0$, the gap equation (7) becomes

$$Z(0)\Delta_0 = \Delta_0 S_1 \left[\frac{\lambda}{N(0)} - V_c\right] + \Delta_\infty \left[\frac{\lambda\langle\omega\rangle S_2}{N(0)} - V_c S_3\right] \tag{11a}$$

$$Z(\infty)\Delta_\infty = -V_c[\Delta_0 S_1 + \Delta_\infty S_3] \ , \tag{11b}$$

where the strong-coupling constant λ is as usual

$$\lambda = 2\int_0^\infty \frac{d\nu}{\nu} \Lambda(\nu) \tag{12}$$

and $\langle\omega\rangle$ is an average phonon frequency [4].

The influence of the discreteness and of the fluctuations of the electron spectrum is contained in the renormalization function $Z(\omega)$ and in the summations

$$S_1(T) = \frac{1}{2} \sum_{|\omega_p| \leq \omega_0} (\hbar\omega_p)^{-1} \tanh(\beta\hbar\omega_p/2) , \tag{13a}$$

$$S_2(T) = \frac{1}{2} \sum_{|\omega_p| > \omega_0} (\hbar\omega_p)^{-2} , \tag{13b}$$

and

$$S_3(T) = \frac{1}{2} \sum_{|\omega_p| > \omega_0} (\hbar\omega_p)^{-1} \tanh(\beta\hbar\omega_p/2) . \tag{13c}$$

Regarding $Z(\omega)$, McMillan obtains for the bulk limit the values $Z_b(0) = 1 + \lambda$ and $Z_b(\infty) = 1$. For a small particle, on the other hand, we can write from Eq. (6)

$$Z(0) = 1 + [N(0)]^{-1} \sum_{|\omega_p| < \omega_0} \int_0^\infty \frac{d\nu}{\nu} \Lambda(\nu) \frac{f(\omega_p)}{(\omega_p - \nu)^2} \tag{14}$$

and the second term does not reduce to λ. Nevertheless we can obtain a good approximation for this term in the form $\lambda \langle A \rangle$, where the phonon average of A over n phonon frecuencies is

$$\langle A \rangle = \frac{1}{2\omega_0 N(0)} \left(\frac{1}{n}\right) \sum_{j=1}^{n} \sum_{\omega_p' = -1}^{1} \frac{\nu_j'}{(\omega_p' - \nu_j')^2} , \tag{15}$$

where the primes indicate that the variables are given in units of ω_0. We also find that $Z(\infty) = 1$ just as in the bulk limit.

We can obtain numerical values for $Z(\omega)$ and S_i in the simplest possible case: when $T = T_c$, the transition temperature from the normal to the superconducting state. Then $\hbar\omega_p = \epsilon_p$ and Eqs. (11a) and (11b) reduce to a system of two linear homogeneous equations in Δ_0 and Δ_∞. A non-trivial solution is obtained only if the following condition on T_c is satisfied:

$$1 = \frac{DS_1}{1 + \lambda\langle A \rangle} [\lambda - \mu - \lambda\mu\langle\omega\rangle DS_2] , \tag{16}$$

where

$$\mu = V_c/(1 + V_c S_3) \ . \tag{17}$$

We consider two discrete spectra with constant mean-level spacing D and different fluctuation properties: an equally spaced spectrum (ES) and a completely random spectrum (P), for which the spacing distribution is a Poisson distribution [2]. For convenience we measure D in units of $\hbar\omega_0$.

For an ES spectrum we find numerically that

$$\langle A\rangle^{\mathrm{ES}} = 1 + D \tag{18}$$

and that S_2 and S_3 equal their bulk limits $DS_2 = DS_3 = 1$. On the other hand, DS_1^{ES} varies with D in the form

$$DS_1^{\mathrm{ES}} = \ln\left[\frac{1.134(1 + D/2)\hbar\omega_0}{kT_c}\right]. \tag{19}$$

This leads to a generalization of the well-known formula of McMillan for the transition temperature,

$$\frac{T_c^{\mathrm{ES}}(D)}{T_c^{\mathrm{BULK}}} = (1 + D/2)\exp\left[-\lambda D/(\lambda - \mu - \lambda\mu\langle\omega\rangle)\right] \tag{20}$$

Things are a bit more complicated for a completely random spectrum. Now

$$\langle A\rangle^{\mathrm{P}} = 1 + 3D/2 \tag{21}$$

and S_1 changes with D as indicated in Fig. 1. As in the equally-spaced spectrum, S_2 and S_3 take their bulk values.

For the Poisson case it is not possible to obtain a closed expression for T_c such as (20), but Eq. (16) must be solved using a numerical simulation. We have recently done this [2] and compared the resulting values with experimental points for different materials, i.e. different values of the strong-coupling constant λ. The comparison between theory and experiment indicates that a Poisson spectrum seems to be more realistic for a small particle, contrary to what is sometimes stated in the literature [5].

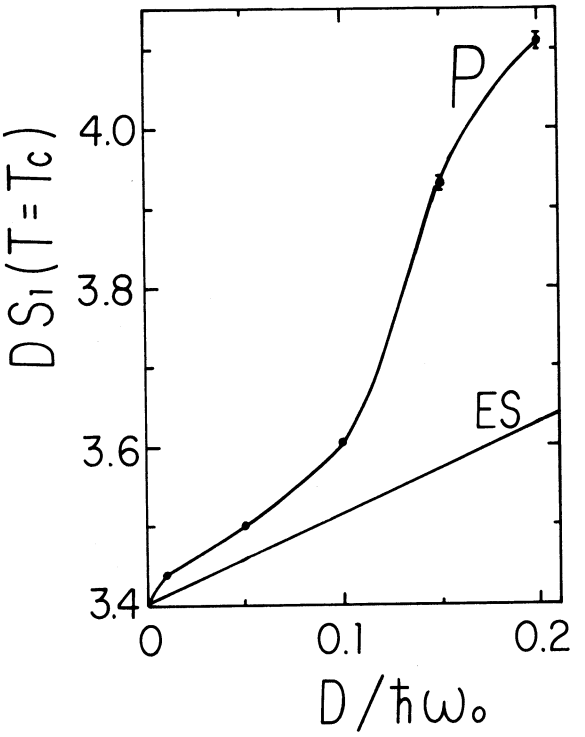

Figure 1 Values of $DS_1(T_C)$ as a function of $D/\hbar\omega_0$ for an equally spaced spectrum (ES) and for an ensemble of 100 completely random spectra (P).

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REFERENCES

1. GM Eliashberg, *Sov Phys-JETP* **11**, 696 (1960).
2. J Barojas, E Blaisten-Barojas, J Flores, and E Cota, *Kinam* **1**, 361 (1979).
3. DJ Scalapino, JR Schrieffer, and JW Wilkins, *Phys Rev* **148**, 263 (1966).
4. WL McMillan, *Phys Rev* **167**, 331 (1968).
5. See, for instance, the proceedings of the "International Meeting on Small Particles and Inorganic Clusters", *J Phys (Paris)* **38**, C2 (1977).