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Electronic spectrum fluctuations in small particles*

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In this paper, finite size and electronic spectrum fluctuations effects in small particles are analyzed. We give qualitative arguments concerning the nature of these fluctuations. Theoretical calculations as well as their comparison with available experimental results for several properties of small systems are described. Finally, we comment on some open problems in this field.

I. CHARACTERISTICS OF SMALL PARTICLES

The simplest model used to describe the behaviour of electrons in metals is of course the free-electron model. The electrons are assumed to move without interacting with one another and in a jellium of positive charge, so as to insure overall charge neutrality. The electrons occupy their energy eigenstates ϵ according to the Fermi distribution $n(\epsilon)$. As the temperature T tends to zero, $n(\epsilon)$ becomes a step function, which is equal to one for $\epsilon < \epsilon_F$, the Fermi energy, and zero otherwise. For $T \neq 0$ there is a band of states, whose width is of the order of $k_B T$, around the Fermi energy, for which $n(\epsilon)$ is neither zero nor one; here k_B is Boltzmann's constant.

With this simple model at hand one can obtain a host of electron properties in metals at low temperatures. For example, when the free electron gas is in contact with a heat reservoir at temperature T only those

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electrons in an energy band of width $k_B T$ arround ϵ_F can be excited, since all other excitations are quenched by the Pauli principle. The internal energy is then proportional to T^2 and consequently the specific heat at constant volume C_v is linear in T. In a similar fashion, one can see that the magnetic suceptibility χ will be independent of T for this case. The argument goes as follows: non-interacting particles with a permanent magnetic moment μ will show a Curie type law in which $\chi \sim T^{-1}$. Since only $k_B T$ electrons can be excited when the system is at a low temperature T, we have that χ is a constant, which is known as the Pauli spin susceptibility.

What happens when the size of the metal is very small, becoming a particle of a typical length L which is of the order of 100 Å, say? For such a small size, the electron eigenstates do not any longer form a continuum but rather a discrete spectrum. The mean spacing D between these levels, which varies as L^{-3}, represents then a characteristic energy for the small system.[1] Whenever the relevant energies in a given phenomenon are of the order of D, differences between the small particle and the bulk material might show up [1]. If, for example, the absorption of light with frequency ω by a small particle is analyzed, anomalous behaviour might be observed whenever

$$\hbar\omega \lesssim D \quad . \tag{1.1}$$

For $L \sim 100$ Å, this implies that absorption of light in the far infrared regime by small particles might differ from that of the bulk material [2, 3]. Similarly, superconductive properties of small systems will change when

$$k_B T_c \sim D \quad , \tag{1.2}$$

where T_c is the transition temperature from the normal to the superconducting state. More generally, at low enough temperatures such that

$$k_B T \lesssim D \quad , \tag{1.3}$$

the thermodynamic properties of small particles and those of the metal in bulk differ.

But the thermodynamics of small particles will differ from the bulk metal for other reasons as well. If $L \sim 100$ Å, the energy required to extract an electron from the particle will be of the order of 0.1 eV, since this

1. When $L = 100$ Å, for example, $D \sim 10^{-4}$ eV or 1 K.

ionization requires an energy proportional to e^2/L due to Coulomb attraction. If condition (1.3) holds, there will be no ionization and the number of electrons within one particle remains constant. This means that the most appropriate thermodynamic ensemble to be used might be the canonical ensemble [1]. Furthermore, frequently appearing quantities such as $n(\epsilon)$ will also show corrections with respect to their bulk values, which will be dependent on the number of electrons in each particle [3]. Let us see, for instance, how this affects the behaviour of C_ν and χ with T at low temperatures for a single small particle.

Consider the specific heat first. At very low T, the number of excited electrons on the level inmediately above the Fermi energy ϵ_F will be one or two, depending if the total number of electrons is odd or even. For both even and odd small particles C_ν behaves as

$$\exp\left[-(\epsilon_{F+1} - \epsilon_F)/k_B T\right] \tag{1.4}$$

at low T, which is radically different from the linear behaviour observed for the metal in bulk. The same argument shows that χ is proportional to

$$T^{-1} \exp\left[-(\epsilon_{F+1} - \epsilon_F)/k_B T\right] \tag{1.5}$$

for a particle with an even number of electrons, and proportional to T^{-1} when this number is odd. Both differ from the Pauli spin susceptibility.

The fact that the small system behaviour deviates from that of infinite systems, due to the discreteness of its electronic spectrum, is known as the *quantum size effect.* Once this effect is recognized, other characteristics of discrete spectra must be included as well. In particular, spectrum fluctuations of the type encountered in the highly-excited regions of nuclear spectra, might prove of importance. Since experiments are performed on many ($\sim 10^{14}$) particles and not on a single one, the anomalous behaviour of an assembly of small particles might depend not only on D but also on such statistical properties of the spectrum as level spacing distributions.

Both aspects, the quantum size effect and the electronic spectrum fluctuations, are the subject matter of this review. In section II we show the dependence on D of different observable quantities, such as C_ν and χ for normal small particles and the transition temperature T_c for small superconducting particles. In other terms, we shall compare the predicted behaviour of those quantities in terms of D, in two extreme situations: in the bulk when $D = 0$, and for an equally spaced spectrum (ES) for which there are no level fluctuations, the energies being $\epsilon_k = kD$, with k an

integer. In section III we give qualitative arguments and numerical evidence concerning the nature of spectrum fluctuations [4, 5]. In section IV we calculate C_ν and T_c when two kinds of fluctuations are considered, one corresponding to a completely random spectrum and another to the Gaussian Orthogonal Ensemble (GOE) of the random matrix theory [6]. We then compare the theoretical results with available experimental data. Finally, in section V we discuss some open problems in the field. Among these, the influence of a fixed number of electrons in each particle and possible differences between a canonical and grand canonical description stand out. These will be particularly important to understand the electronic magnetic susceptibility of normal small particles, in which case particles with odd and even number of electrons behave so differently [7, 8].

II. THE QUANTUM SIZE EFFECT

When one is dealing with a problem which has already been tackled in the bulk limit and for which a theoretical formulation exists, there comes a point at which one has to perform integrations, which are obtained as limits of summations over energy eigenstates (or the like). These energies are assumed to form a continuum described by a given level density $\rho(\epsilon)$. It is precisely at this point that the quantum size effect comes into the theoretical description: one should *not* proceed to the limit $D \to 0$, but rather conserve the discrete sums and perform them directly. This implies, unfortunately, that almost no analytical results can be obtained, since the sums have to be evaluated numerically. Futhermore, in some cases the formulation for the bulk material has only been done in the framework of the grand canonical ensemble. This could lead to corrections for very small particles. Let us see how this technique works out in some particular examples, first for a normal metal and then for a superconductor.

II.1 Specific heat and magnetic susceptibility

Since the spectrum is discrete for finite systems, the number of possible excited states is smaller than for the bulk. Therefore, as the system gets smaller and D grows, the corresponding value of C_ν at a given T will be smaller than that of the bulk, for which $C_\nu \sim T$ at low temperatures. This is shown in Fig. 1 for particles of different sizes with equally-spaced electronic spectra [6, 8]; the values of C_ν for particles of even and odd number of electrons have been averaged. Here the canonical ensemble has been used.

The magnetic susceptibility χ behaves differently with temperature if the number of electrons is even or odd. In the latter case, due to the

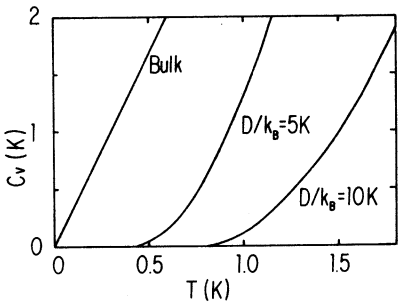

Figure 1 The quantity $C_V = C_V D/2k_B\rho(\epsilon_F)$, where C_V is the specific heat at constant volume in units of k_B, is shown for the metal in bulk (D=0) and for two different finite values of D.

presence of an unpaired electron, a Curie type law $\chi \sim T^{-1}$ is obtained if the spectrum is discrete. The T^{-1} dependence of χ was found experimentally when no effort to distinguish particles with odd or even number of electrons was made. This has then been interpreted as conclusive evidence that the quantum size effect exists [9].

For particles with an even number of electrons the discreteness of the spectrum affects considerably the resulting χ at very low values of T, as the calculations of Denton *et al.* have shown [8]. The resulting values of χ as a function of $k_B T$ are given in Fig. 2 for two values of D.

The curves in Fig. 1 were obtained using the free-electron picture, which according to Shiba [7] lacks an essential ingredient: a spin-orbit term, which can flip the electron spins. He obtains $\chi(T)$ for an ES spectrum, with the Hamiltonian

$$H_{Sh} = \sum_{k} \epsilon_k \, c^{+}_{ks} \, c_{ks} + \sum_{\substack{kk' \\ ss'}} (V_{so})_{kk'} \cdot \sigma_{ss'} \, c^{+}_{ks} \, c_{k's'} \quad , \tag{2.1}$$

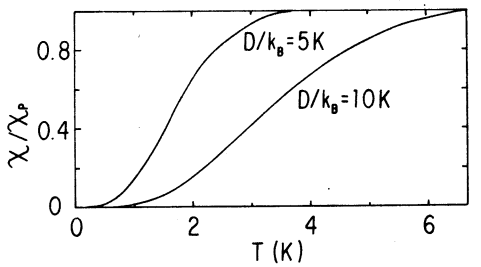

Figure 2 Paramagnetic susceptibility measured in units of the Pauli spin susceptibility $\chi_P = 3\mu^2(\epsilon_F)/2$ as a function of T for two values of D.

where c_{ks}^{+} and c_{ks} are electron creation and annihilation operators and σ are the Pauli matrices. Shiba's results are shown in Fig. 3, where one can now observe that χ is different from zero as $T \to 0$, when $V_{so} \neq 0$. We should remark here that the grand canonical ensemble has been used by Shiba in his calculation and therefore the constancy of the number of electrons in each particle has not been taken into account.

II.2 Critical temperature for small superconducting particles

We now discuss the transition temperature from superconducting to normal state for a small particle as a function of D for both weak and strong-coupling superconductors. The dynamical description is essentially the same as for the bulk material, except that the discreteness of the electron spectrum has been explicitly taken into account. Furthermore, thermal averages have been performed using the grand canonical ensemble, just as in the calculation by Shiba mentioned above. This allows us to make use of Eliashberg's scheme [10] for dealing with the electron-phonon interaction.

Assume you are given a weak-coupling superconductor, for which a BCS description is reasonable. Under the usual BCS assumptions [11], the energy gap Δ (which is taken as independent of k) is obtained from the following equation:

$$1 = g \sum_{|\epsilon_k| \leq \hbar\omega} (1/E_k) \tanh (E_k/2k_B T) \quad , \tag{2.2}$$

where E_k, the quasi-particle energy, is given by

$$E_k = (\epsilon_k^2 + \Delta^2)^{1/2} \tag{2.3}$$

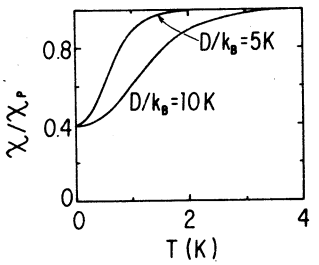

Figure 3 Electronic susceptibility measured in units of χ_P for the Hamiltonian (2.1) as a function of T. The parameter ρ of reference 7 equals 1.

Here g is the strength of the pairing interaction and $\hbar\omega$ is a characteristic phonon frequency. We can obtain some interesting results solving Eq. (2.2). First, take $T = 0$ and solve for the gap parameter at zero temperature $\Delta(0)$. Or second, assume that $T = T_c$ for which $\Delta = 0$ and obtain the transition temperature as a function of D. Dependence on the size of the particle will emerge from differences between the summation over energy states in (2.2) and the corresponding integral

$$1 = g/2 \int_0^{\hbar\omega} \rho(\epsilon) \frac{\tanh (E/2k_B T)\, d\epsilon}{E} \quad , \tag{2.4}$$

where $\rho(\epsilon)$ is the density of states.

For the transition temperature, for example, we obtain numerically that in the range $D < 0.1$

$$k_B T_c \simeq k_B T_c^{\text{bulk}} \, (1 + D/2\hbar\omega) \quad . \tag{2.5}$$

where

$$k_B T_c^{\text{bulk}} = 1.13\, \hbar\omega \, \exp[-1/g\rho(\epsilon_F)] \quad , \tag{2.6}$$

which is the well known BCS result. A similar result is obtained for $\Delta(0)$, which also grows with D, as shown in Fig. 8, section IV. On the other hand, $\Delta(T)/\Delta(0)$ is a universal function of T/T_c independent of D and of other parameters.

A somewhat similar conclusion is reached if one modifies Eliashberg's equations [10] for strong-coupling superconductors to take into account the quantum size effect [12]. Following McMillan [13], the next condition for T_c can be obtained

$$1 = \frac{D\nu}{1 + \lambda(1 + D)} \left\{ S_1 [(\lambda - \mu^*) - \lambda\mu^* \langle\omega\rangle D\nu S_2] \right\} , \tag{2.7}$$

where S_1 and S_2 are discrete summations depending implicity on D, measured in units of $\hbar\omega_0$ (the cut-off phonon frequency):

$$S_1 = \sum_{|\epsilon_k| < \hbar\omega_0} [(1/\epsilon_k) \tanh(\epsilon_k/2k_B T_c)] \tag{2.8a}$$

$$S_2 = \sum_{|\epsilon_k| \geq \hbar\omega_0} [1/\epsilon_k^2] \quad . \tag{2.8b}$$

These summations contain most of the deviations from the continuum case. Here $\nu \sim D^{-1}$ is the particle volume, λ is a constant proportional to an average electron-phonon coupling, μ^* is due to the electron-electron Coulomb potential and $\langle\omega\rangle$ is an average phonon frequency, where possible changes in the phonon spectrum with respect to the bulk limit have not been taken into account.

Two limiting cases are of interest here. When we deal with a weak-coupling superconductor, $\lambda - \mu^*$ is small and then Eq. (2.7) reduces to the BCS condition for T_c extracted from Eq. (2.2). On the other hand, when $D \to 0$ Eq. (2.7) reduces to that obtained by McMillan [13] for the bulk material.

For an ES spectrum one obtains readily from (2.7) that

$$T_c = T_c^{\text{bulk}} (1 + D/2) \exp -[\lambda D/\nu(\lambda - \mu^* - \lambda\mu^*\langle\omega\rangle)] \tag{2.9}$$

which shows that T_c can be smaller as D grows when λ corresponds to a strong-coupling superconductor.

As we have already mentioned, the grand canonical ensemble has been used throughout these calculations. An effort to project to the canonical ensemble has been made by Mühlschlegel *et al.* [14] for a BCS model Hamiltonian using the functional averaging method. It remains an open problem to include the constancy of the number of electrons in each small superconducting particle for the strong-coupling case. However, when $D/k_B T_c$ is small, we expect the corrections with respect to our results to be extremely small.

We shall now turn our attention to the effect of spectrum fluctuations on some observable properties of small particles. To start with, let us consider in some detail the spectrum fluctuations by themselves.

III. THE NATURE OF ELECTRONIC SPECTRUM FLUCTUATIONS

Since spectrum fluctuations are of an intrinsic statistical nature, we introduce an ensemble of small particles to describe them. This corresponds to actual experimental conditions, since experiments are always performed using not only one small particle, but a very large set ($\sim 10^{14}$) of them. Furthermore, it is extremely difficult to produce experimentally two identical small particles and therefore, each one will have a slightly different

electronic spectrum. Once the ensemble of spectra with a mean spacing D (corresponding to mean volume v) and with the desired fluctuation properties is defined, the properties of a powder of small particles are obtained via an ensemble average. Let us now discuss what kind of spectrum fluctuations we can expect.

In a small particle the electron energy levels ϵ_k will be influenced by the particle's surface. In the simplest possible approach, that of the free-electron model, the ϵ_k are obtained after solving Schrödinger's equation

$$\left[\frac{\hbar^2 \nabla^2}{2m_e} + \epsilon_k\right] \psi_k(\mathbf{r}) = 0 \tag{3.1}$$

with the condition

$$\psi_k(\mathbf{r}) = 0 \tag{3.2}$$

when $\mathbf{r}$ is a point at the surface. This follows from the fact that electrons should not leave the particle.

When the powder of small particles is produced, we can not have a direct control over the surface irregularities, for example, there could be defects at the surface. This will destroy any systematic behaviour in the electron spectrum and some randomness might appear. In 1962, Kubo [1] assumed that the spectrum is completely random and, in 1965, Gor'kov and Eliashberg (GE) [2] argued that surface irregularities would induce random interactions between the energy eigenstates; they introduced a random-matrix description of the electron spectrum, similar to that considered in nuclear physics to deal with slow-neutron resonances [15]. Since the work of GE, random matrices have been thought to be a suitable description for electron levels in small particles. We have given recently evidence against this belief.

In a completely random spectrum, the nearest-neighbour spacing distribution $p(s/D)$ (which equals the probability of having a level at $\epsilon_i + s$ if there is another level at ϵ_i with no levels in between) is equal to a Poisson distribution

$$p_{\mathrm{P}}(s/D) = e^{-s/D} \tag{3.3}$$

Random matrix ensembles, on the other hand, produce spectra with correlated levels [15]. The type of correlation, and therefore of spacing distribution, depends on the precise definition of the ensemble. We shall

here restrict ourselves to what is called the Gaussian Orthogonal Ensemble (GOE), in which the matrix elements are independent Gaussian random numbers. In this case, the nearest-neighbour distribution is closely approximated by Wigner's formula [15]

$$p_W(s/D) = \frac{\Pi}{2}\left(\frac{s}{D}\right) \exp\left[-\frac{\Pi^2}{4}\left(\frac{s}{D}\right)^2\right] \tag{3.4}$$

which shows what is known as "level repulsion", i. e. $p_W(0) = 0$, so the probability of having two closely lying levels vanishes.

As we intended to make clear above, both Kubo and GE based their assumptions on the same argument, which is clearly of a qualitative nature. Since spectrum fluctuations are such a basic ingredient for the theory of electrons in small particles, it is clear that a close analysis of these assumptions is worthwhile. We have done precisely that in the last few years, both from the theoretical standpoint [4, 5, 6] as well as from comparison with available experimental data (see section IV).

Although the situation is not completely cleared up, present evidence indicates that a completely random spectrum provides a better description of most available data.

III.1 Qualitative arguments

As we have already mentioned, Gor'kov and Eliashberg claim a similarity between the small metallic particle problem and that of the nuclear spectrum at high excitations. It is useful here to quote from Mehta's book on random matrices [16]. According to Mehta, one can justify the use of random matrices in small particles in the following way:

The electronic energies are the eigenvalues of a fixed Hamiltonian but with random boundary conditions that can be incorporated into a random matrix through the use of fictitious potentials. The ensemble of random matrices to be used depends on the particular conditions of the powder: i) if the number of electrons is even and there is no magnetic field the orthogonal ensemble is applicable since time reversal holds; ii) when the number of electrons is odd and no magnetic field is present the symplectic ensemble applies, and iii) when there is a magnetic field H, the Hamiltonian is no longer invariant under time reversal, and the ensemble of random matrices should be of the unitary type if $\mu H >> D$, where μ is the electron magnetic moment.

Here we find the first conceptual difficulty, which has to do with the difference in description for a particle with an even or an odd number of electrons. Since the surface is so irregular, the problem will not show

spherical symmetry and, therefore, GOE will only be appropriate to small particles with an even number of electrons, the odd particles being described by the symplectic ensemble. But this clearly is an awkward situation, particularly so if one thinks of building the particle atom by atom, to the point of having 10^4 or so atoms. No reasonable description, using the methods of molecular physics, would lead to such a big difference between particles with even or odd number of atoms.

A second problem appears if we recall what is done in the nuclear case in order to compare random matrix predictions with experimental results. These latter are obtained from slow-neutron experiments, in which care is taken to include only *s*-wave resonances [17]. Then one is sure that only states with total angular momentum $J = 1/2$ are included when bombarding an even nucleus in its ground state. Resonances corresponding to *p*-wave scattering are carefully avoided. As a matter of fact, a host of statistical tests have been developed to detect these "intruder" states and to eliminate them from consideration. In other words, random matrix results are compared only with corresponding properties of pure sequences of states, all having the same good quantum numbers. If many of these pure sequences are mixed at random, it is known that a completely random spectrum will evolve [18].

But in dealing with the thermal properties of small metallic particles no such care is possible. We do not have any control as to which excited states are seen. The situation would be similar as if we had neutron scattering in many partial waves and we had no way of detecting how impure the sequence of observed neutron resonances is. This argument points in favor of a completely random spectrum.

A somewhat more formal argument goes back to the question of representing the effect of a random surface in terms of matrices, as suggested by Mehta. For this we have to compute the matrix elements on a single-electron wave function basis. Referring to Eq. (3.1), what we need is to obtain ψ_k in terms of an unpertubed set of wave functions φ_k, defined by the same boundary condition, but on an unperturbed surface S', as indicated in Fig. 4. In order to ensure that ψ_k be zero on S, so that no electrons can leave the small particle, we need to introduce a potential barrier between S and S', which eventually has to be of infinite value. As φ_k is different from zero in this region, this will demand infinite matrix elements, and no matrix description of the boundary perturbation is possible.

Tavel *et al.* [19, 20] have however gone around the above argument, in much the same way the hard core nucleon-nucleon force is dealt with in nuclear many-body theory: by introducing an effective interaction.

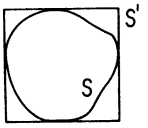

Figure 4 The unperturbed region R' surrounded by the surface S' is deformed into a perburbed region *R* with surface *S*.

Their argument goes as follows:

An equivalence is established between the eigenvalue problem for a simple operator (i.e. the kinetic energy) in a complicated domain (i.e. the pertubed region *R* bounded by *S*) and that of a complicated operator in the simple domain *R'*. If one assumes a mapping $\mathbf{r} \to \mathbf{r} = \mathbf{r}'(\mathbf{r})$ which is one-to-one, has an inverse and maps *R* into *R'* in a continuous fashion, the Hermitian transformed Hamiltonian is

$$H'(\mathbf{r}') = J^{-1/2}(\mathbf{r}')\, H[\mathbf{r}(\mathbf{r}')]\, J^{-1/2}(\mathbf{r}') \tag{3.5}$$

where *J* is the Jacobian which characterizes the mapping.

For a slightly deformed spherical region, we have[2]

$$\mathbf{r}' = \mathbf{r}_0 [1 + \lambda \sum_{\ell m} \{a_{\ell m}(Y_{\ell m} + Y^*_{\ell m}) + i b_{\ell m}(Y_{\ell m} + Y^*_{\ell m})\}] \tag{3.6}$$

where $\mathbf{r}_0$ is the average radius and λ is the parameter that adjusts the height of the deformation. The eigenvalues of (3.5) can then be obtained as a power series in λ.

Althought the preceeding formalism has all the drawbacks of perturbation theory, it is interesting for our purposes, since some results obtained with it favor the random matrix approach. As these are numerical results, we shall discuss them along with some of the numerical evidence we have obtained; this will be the content of the next subsection.

III.2 Numerical evidence

Using their perturbation theory approach, Tavel *et al.* [20] have computed directly the nearest-neighbour spacing distribution of the perturbed energy levels. They use a non perturbed spherical surface and restrict themselves to study the non-degenerate energy levels arising from a single

2. It seems that direct experimental evidence is now being accumulated which shows that small metallic particles are not at all spherical, but rather have well defined edges and faces [21].

unperturbed ℓ-state. The question of convergence at different perturbation orders is analyzed, although no proof of convergence is given. In the case in which the coefficients $a_{\ell m}$ and $b_{\ell m}$ of Eq. (3.6), which are taken as random numbers to simulate the assembly of small particles, all have the same random distribution, the perturbed eigenvalues (up to first order in λ) are such that a nearest-neighbor spacing distribution of the Wigner type follows. This is no longer the case when coefficients with larger values of ℓ are less and less important, and an akward shape for $p(s/D)$ is obtained.

We have proceeded along different lines. If one uses a different version of boundary perturbation formalism [22], no convergence is found for Dirichlet boundary conditions. On the other hand, if the assumption is made that spacing distributions are not strongly affected by the boundary conditions, the perturbation series can be obtained for Neumann boundary conditions and convergence can be proved [4]. However, the resulting eigenvalues are incorrect for electrons in a two-dimensional rectangular platelet, as shown in figure 5.

One could actually take the platelet (or the cube) shape seriously and compute the spacing distributions directly, since in this case the energy values can be obtained exactly. Using an ensemble of such platelets (or cubes) a Poisson distribution is obtained. Since this disagrees with Tavel's results it would be important to use their approach in this same example and understand the discrepancy; unfortunately this has not been done up to now. An important point should be made here. Tavel *et al.* obtain

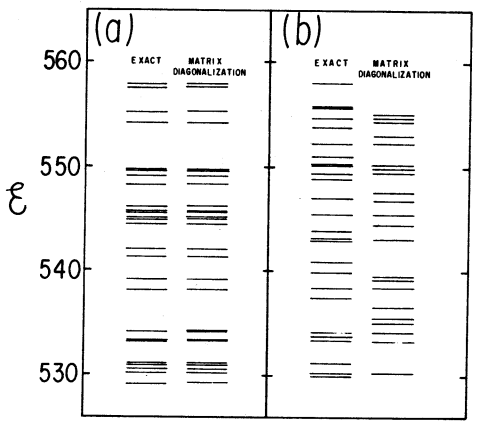

Figure 5 Comparison of the exact eigenvalues and those obtained after diagonilizing the matrix corresponding to perturbation theory. The perturbed region R is a square of sides 1 and 1-η. Case (a) corresponds to η = 0.001 and (b) to η = 0.01. A typical electron wavelength in this energy region is of the order of 0.08.

$p(s/D)$ along a single spectrum. To compare with our result (or with experiment, for that case) one has either to assume or to prove that what is known as ergodicity holds [23]. In the case of the ensemble of platelets this has been done numerically [4].

We have also computed the spacing distribution of electron energy levels in very small clusters [5]. For two microparticles, one of a rather arbitrary shape and the other of a very regular structure, we have obtained $p(s/D)$ from the energy levels computed by other authors, which took into account electron-electron and electron-nuclei Coulomb interactions. For both "realistic" calculations a Poisson distribution was obtained, once an "unfolding" procedure which maps the spectrum into one with constant level density was performed.

As far as our present knowledge goes this is the status of direct theoretical evidence regarding electronic fluctuations in small particles.

We shall now present some of the indirect evidence, in which experimental data are compared with the results of theoretical calculations based either of the two types of spectra we have been discussing, the completely random Poisson case and the GOE spectrum.

IV. EFFECTS OF THE ELECTRONIC SPECTRUM FLUCTUATIONS

IV.1 Specific heat of normal metallic particles

Equilibrium properties, such as the thermodynamics of small particles, depend strongly on level fluctuations only at very low temperatures. It is therefore interesting to calculate exactly in this temperature region quantities such as the specific heat of normal metallic particles. This can be done on the computer by simulating an assembly of particles by their spectra. To each particle we associate a one-electron spectrum that follows a given level spacing distribution, either Poisson or GOE. The calculation proceeds as follows First we calculate the partition function in the canonical ensemble for $\mathcal{N}$ particles.

$$Z = \prod_{\alpha=1}^{\mathcal{N}} \sum_{\ell} g_{\ell}^{(\alpha)} \exp(-E_{\ell}^{(\alpha)}/k_B T) \tag{4.1}$$

with $E_{\ell}^{(\alpha)}$ and $g_{\ell}^{(\alpha)}$ the energy and degeneracy of the ℓth excited state of one particle containing $n^{(\alpha)}$ electrons. Second, we obtain the specific heat $\mathcal{C}_v$ per particle from

$$\frac{\mathcal{C}_v}{k_B} = \frac{1}{\mathcal{N}} \beta^2 \frac{\partial^2}{\partial \beta^2} (\ln Z) \text{ where } \beta = (k_B T)^{-1} \ . \tag{4.2}$$

The results for an assembly of 2000 P or GOE spectra are plotted in the morphologic chart [6] of figure 6. The curves are even-odd averages on 1000 particles of each kind. In the case of GOE spectra this is not correct, because as stated before, this ensemble applies only for particles with even number of electrons. In any case, the GOE curve in Fig. 6 must be understood as characteristic of a system with level repulsion. Indeed, Fig. 6 allows for a comparison between GOE results and those coming from an uncorrelated Wigner (UW) set of spectra. Both $\mathscr{C}_\nu$ curves differ very little, although in the UW spectra part of the correlation contained in a GOE spectra is lost.

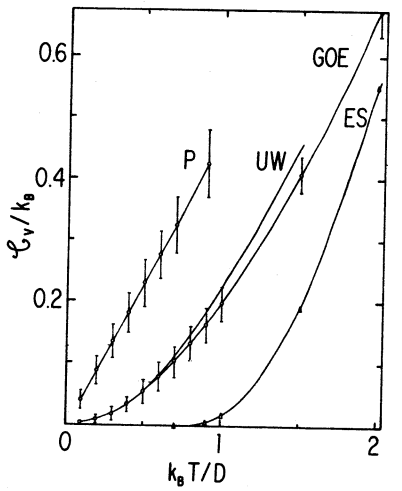

Figure 6 A morphologic chart for the specific heat.

The specific heat for a Poisson ensemble exhibits a linear dependence at low temperatures both for particles with even and odd number of electrons as seen from figure 7. As expected, the slope is smaller in the odd case because the number of excitations compatible with a given temperature is less than in the even case. For Poisson spectra it is therefore possible to define a Grüneissen constant which is smaller than in the bulk.

Unfortunately, the specific heat for normal metallic particles has not been measured; up to our knowledge, it is known only in one case, that of superconducting vanadium small particles [24]. Mühlschlegel *et al.* [14] calculated theoretically under certain approximations the behaviour of $\mathscr{C}_\nu$ for superconducting particles. However these authors neglect the variation of T_c with D, which renders their work rather incomplete. This is one line of work that should be pursued.

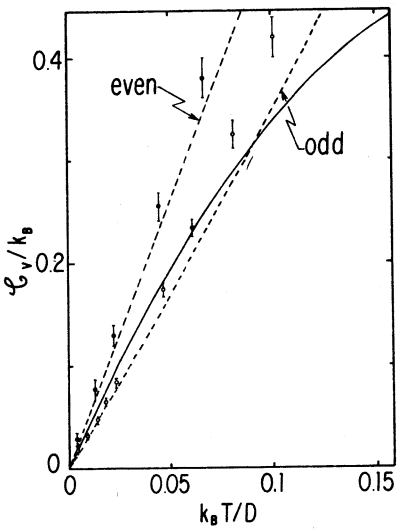

Figure 7 The specific heat as a function of temperature. Full and empty dots stand for samples of 1000 P spectra with even and odd number of electrons, respectively. The dotted lines correspond to Kubo's calculation[1] and the solid line to Denton *et al.*[8] approximation for the P even-odd average.

IV. 2 Properties of small superconducting particles

Turning back to the problem stated in section II.2 we want now to investigate if spectrum fluctuations can give extra contributions to the variation of $\Delta(0)$ and of the critical temperature with D. We proceed as follows: a given average spacing D is fixed and an ensemble of spectra with the desired fluctuation properties is generated numerically. For each spectrum, either Eq. (2.2) or (2.7) is solved and an average over the en-

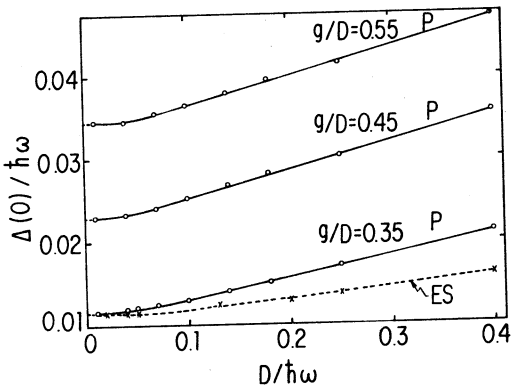

Figure 8 The gap parameter at $T = 0$ as a function of D for different values of g/D and for different type of spectra.

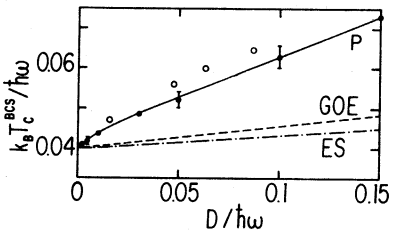

Figure 9 Dependence of T_C for a BCS small particle on the mean level spacing D for P, GOE and ES spectra, the value $g/D = 0.3$ was used and averages over 200 spectra for the P and GOE cases was taken. The open data dots correpond to experimental values for Aℓ (ref. 25).

semble is taken thereafter. Thus we obtain $\Delta(0)$ or T_c as a function of D in BCS theory and T_c in the strong coupling limits. The results are shown in Figs. 8 and 9 for BCS particles (such as Al) and in Fig. 10 for intermediate and strong coupling materials such as V, In and Pb. From these figures it is clear that the spectrum fluctuations have a large effect on the values of $\Delta(0)$ and $k_B T_c$, effect which has been disregarded up to know. The dots in Figs. 9 and 10 are experimental data [24, 25] for several small

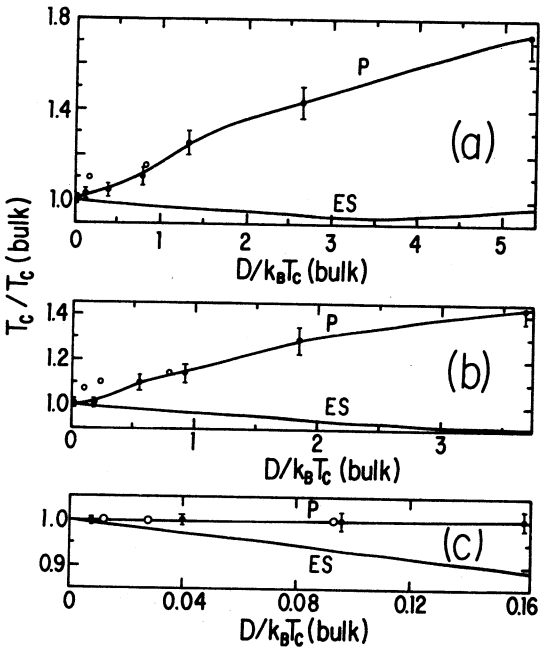

Figure 10 Dependence of T_C on D in strong-coupling superconducting small particles for P and ES spectra. The open dots correspond to experimental values for V(ref. 24), In and Pb (ref. 25). In (a) $\lambda = 0.6$ and 300 spectra were used; for (b) $\lambda = 0.69$ and 500 spectra and in (c) $\lambda = 1.12$ and the average over 300 Poisson spectra was taken. In all cases $\mu^* = 0.1$. $\langle\omega\rangle/\hbar\omega = 0.5$ and $\hbar\omega_0$ was fitted to give the correct bulk limits. Continuous lines are traced to guide the eyes.

superconductors. Although no effort whatsoever has been made to fit the data to the parameters of the theoretical calculation, it certainly looks as if results based on random spectrum follow the experimental points much more closely than do the GOE or ES assumptions.

V. FURTHER PROBLEMS

Let us finally comment on those conclusions and open questions which we feel are the most important when considering electronic spectrum fluctuations in a powder of many small systems.

Throughout our study, except for the analysis in microclusters [5], we worked under the assumption that in each small particle the electronic spectrum is free-electron like and that fluctuations on it may arise from slight changes on the surface of each member of the assembly of $\sim 10^{14}$ small particles. In section III we have given qualitative and numerical evidence favoring a random electronic spectrum (Poisson distribution law). The matter of which level spectrum distribution is the best, is nevertheless still under controversy. Indeed, the calculation of Tavel *et al.* [19, 20] based on the introduction of an effective interaction to represent a perturbed boundary, points to a GOE spectrum. However, these authors assume an assembly of almost spherical particles, which might not be a realistic assumption [21]. Furthermore, Tavle's assembly of spectra has not been proved to be ergodic and convergence of their perturbation series has only been analyzed slightly. Evidently, more work along these lines is necessary, although the discussion would be ended if the eigenvalues of a system of $\sim 10^4$ electrons, were calculated exactly for slightly different conformations of the ions. Even if this were the case, the spacing distribution would be a convenient tool to calculate averages over the assembly of small particles, which could then be compared to experimental values.

The importance of spectrum fluctuations was illustrated in section IV, which discusses their influence on the specific heat of normal particles and on the superconducting transition temperature in both weak and strong-coupling limits. These are just two examples of a broad kind of problems which can be dealt with. In fact, experimental data are now beginning to accumulate for several properties and several materials [27].

We think that our calculation of C_ν is complete and accurate, but then no experimental values up to now are available for comparison. When using the morphologic chart of figure 6 we should remark, however, that the GOE average over even and odd number of electrons is not strictly valid, because GOE is not applicable for odd particles. We note that C_ν is linear with temperature only for Poisson spectra, implying that these

statistical fluctuations lead to a thermodynamics of finite but large Fermi systems not too different from that of the bulk.

On the other hand, the calculation of the critical temperature for superconducting particles is subject to improvement. To start with, we have not taken into account any changes in the phonon spectrum such as the addition of surface modes. This will affect, among other things, the value of the electron-phonon coupling constant λ as has been indicated by Novotny *et al.* [26] and later on by Matsuo and coworkers [25]. In our calculation we adapted Eliashberg equations to include the effect of spectrum fluctuations. These equations are a generalization of Migdal's treatment of the coupled electron-phonon system in normal metals [28], based on the existence of the small parameter $(m_e/M_{\text{ion}})^{1/2}$. This parameter is the same in the bulk as in the small particle, because the electron number density is not changed. However, the number density fluctuations may be different from the bulk, in which case attention should be focused on which ensemble in statistical mechanics should be used to relate the thermodynamic functions to the model Hamiltonian of the many small-particle assembly. In this context, one of the problems that may arise is the use of the grand canonical ensemble in the definition of the one-particle thermodynamic Green's functions in the Nambu scheme [29]. What we have done to be consistent with this picture, is to fix a chemical potential as

$$\mu = E_0(\bar{N}+1) - E_0(\bar{N}) \propto \frac{1}{\bar{N}}$$

where $E_0(\bar{N})$ is the ground state energy of a system with $\bar{N}$ electrons, $\bar{N}$ being the average over the assembly of 10^{14} particles. In all our calculations $\bar{N} \sim 10^4$, so μ has a rather constant value. In any case, further work along these lines should include the fluctuations of μ.

Another and very direct way to study the differences between a grand canonical and a canonical statistical description of small particles, is to compute the particle-hole occupation number distribution $n(\epsilon)$ in each particle for both ensembles. Denton *et al.* [8] have obtained $n(\epsilon)$ for an ES spectrum, without including spectrum fluctuations. Even in this case one sees that for $D < k_B T$ the function $n(\epsilon)$ resembles closely the Fermi distribution, in which case a canonical or grand canonical description should not lead to significant differences.

In the specific heat calculation there was a difference between the values obtained for even and odd number of particles. In what concerns the superconducting transition temperature, if the initial mean number of electrons $\bar{N}$ is even, and the addition of an odd particle results in the

appearance of one quasi-particle k_0 in the ground state of the $\bar{N}+1$ system, without modification of the quasi-particle even distribution, then no differences between odd and even transition temperatures will be obtained [30].

Even and odd values of $\bar{N}$ certainly matter for the magnetic susceptibility, for which many experimental results are now available [27]. Unfortunately, the theoretical calculations of χ show many deficiencies. The calculations of Kubo [1] and later on of Denton *et al.* [8] were done using the free-electron model without including spin-orbit effects or any other interactions. On the other hand, Shiba included the spin-orbit effect only in an average way; furthermore, his calculation was done using a grand-canonical ensemble and for an ES spectrum. Therefore, the calculation χ in which a reasonable model Hamiltonian is considered and spectrum fluctuations are included remains a completely open problem. A similar situation occurs for other electromagnetic properties, such as the optical absorption of small metallic particles.

As we hope to have shown in this paper, the field of electrons in small particles offers a large number of theoretical open problems, whose solution will certainly be of importance in many applications.

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RESUMEN*

En este testimonio se analizan los efectos del tamaño finito y de las fluctuaciones en el espectro electrónico de partículas pequeñas. Se dan argumentos cualitativos respecto a la naturaleza de estas fluctuaciones. Se describen cálculos teóricos, así como comparaciones con resultados experimentales disponibles, para distintas propiedades de sistemas pequeños. Finalmente se comenta sobre algunos problemas abiertos en este campo.

* Traducido del inglés por la Redacción.