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Studies on the Problem of Small Metallic Particles. I. — Spectrum Fluctuations in a Two-Dimensional Model and the Associated Specific Heat

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It is shown that the qualitative arguments given up to now in the literature, are not enough to justify the applications of Random Matrix Theory to the small metallic particle problem. Using a two-dimensional model we show that the spacing distributions approach Poisson's law, as originally assumed by Kubo, who computed the specific heat for this case. By means of a numerical calculation we show, however, that Kubo's result is only valid for $k_B T/\delta \lesssim 0.025$, where δ is the mean spacing and k_B is Boltzmann's constant.

1. INTRODUCTION

The physical properties of an assembly of small metallic particles differ from those of the metal in bulk. In particular, the thermodynamic properties of electrons reflect directly the fact that the single-particle spectrum is discrete, with a mean spacing δ between states around the Fermi level of the order of 10^{-4} eV (or the energy $k_B T$ at 1 K) for a particle consisting of 10^5 atoms. Under these conditions, at low temperatures only a few electrons are excited above the Fermi level; as a consequence, the statistical characteristics of the spectrum have a direct influence in determining the partition function Z and thermodynamic properties derived from it, such as the specific heat at constant volume C_v.

Historically, the first attempt to determine the specific heat of a powder of small metallic particles at low temperatures was due to Fröhlich [1], who assumed the electronic levels of each particle to be equally spaced, thereby obtaining an exponential behavior of C_v with temperature. Twenty-five years later, Kubo [2] again tackled the

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problem, but now assuming a completely random distribution for the electron energy levels: a spacing s between two levels and containing k levels in between follows the Poisson distribution

$$p_P(k; x) = x^k e^{-x}/k! \tag{1.1}$$

where $x = s/\delta$. Kubo argued that the random character of the spectra arises from surface irregularities which remove degeneracies or any other systematic spectral property which could be present in a particle of regular shape. He calculated explicitly the partition function and obtained a linear dependence of C_v with T at low temperatures, the coefficient of T being, however, smaller than the one corresponding to the metal in bulk; this coefficient is also different according to whether the number of electrons in the particle is even or odd.

But Gor'kov and Eliashberg [3] (GE), using the same qualitative argument as Kubo, assumed that surface irregularities of the order of atomic dimensions would lead to a Hamiltonian matrix with random elements when expressed in the single-electron basis. In other words, GE considered the ideas of Random Matrix Theory (RMT), as developed by Wigner [4], Dyson [5], Mehta [6], Porter [7], and others [8] for nuclear level statistical fluctuations, to be applicable to the small metallic particle problem.

According to Mehta [6], one could justify the assumption of Gor'kov and Eliashberg in the following way. The electronic energies, relevant to compute the partition function, are the eigenvalues of a fixed Hamiltonian but with random boundary conditions, which may be incorporated into a random matrix through the use of fictitious potentials. The appropriate ensemble of random matrices to be used depends on the particular conditions of the powder (a) if the number of electrons is even and there is no magnetic field, the orthogonal ensemble is applicable, since time reversal holds;[1] (b) when the number of electrons is odd and no magnetic field is present, the symplectic ensemble applies; and (c) when there is a magnetic field H, the Hamiltonian is no longer invariant under time reversal, and the ensemble of random matrices suitable to represent the metallic powder should be of the unitary type if $\mu H \gg \delta$, μ being the electron magnetic moment.

In any case, independent of which of the ensembles of RMT is to be used, level repulsion holds: $p(0; x) \to 0$ when $x \to 0$, and a lack of small spacings occurs. In particular, for the orthogonal ensemble of case (a), the nearest neighbor spacing distribution is closely approximated by Wigner's distribution [9]

$$p_W(0; x) = (\pi x/2) \exp(-\pi x^2/4). \tag{1.2}$$

This contrasts with Poisson's law (1.1) where the value $x = 0$ is the most probable one for $k = 0$, and leads to a different T-dependence for C_v at low temperatures. For the orthogonal ensemble C_v varies as T^2, for the symplectic ensemble a T^5 variation is obtained, and for the unitary case C_v is proportional to T^4.

[1] The orthogonal ensemble also applies if the number of fermions is either even or odd and the interaction is invariant under both rotations and time reversal; however, in our case, the interaction due to surface irregularities is not invariant under rotations.

As we see, the same qualitative argument has led to different results concerning the statistical spectral properties of a powder of small metallic particles. It would certainly be interesting to analyze more closely from a quantitative point of view the various assumptions involved in previous works.

In this paper we shall give evidence that it is not possible, in general, to formulate the boundary perturbation problem in matrix form; this we shall do in Section 2. This implies that RMT is not always applicable to the problem and the question of what is the effect of a boundary irregularity on the statistical properties of the electronic spectrum remains, therefore, open. We answer this question in a particular case by considering, in Section 3, a simple two-dimensional model for which Schrodinger's equation is exactly soluble. We find that Poisson's law holds. A model for which this law is followed exactly is used in Section 4 to obtain numerical values for the specific heat at finite temperatures.

2. Is It Possible to Describe the Problem of Random Boundary Perturbations in the Language of Random Matrix Theory?

Up to now, the application of RMT to the small metallic particle problem has been justified [3], as we already noted, by an argument of a qualitative nature. It is assumed that irregularities of the order of atomic dimensions on the boundary of the small particle would destroy any systematic behavior of the electronic energy levels and cause the statistical properties of the spectrum to be properly described by an ensemble of random matrices.

Two basic assumptions are implicitly made in the above argument. First, one supposes that the problem of a boundary perturbation can indeed be formulated as a matrix problem; and, second, that the assembly of matrices associated with the various small metallic particles is well represented by one of the conventional ensembles of RMT, thus giving rise to a repulsion of energy levels. We shall now study the first assumption.

The problem of perturbations of the boundary shape can be stated, in the free-electron picture, in the following way. Consider a region R' in which the solution to the differential equation

$$(\nabla^2 + k_n^2)\,\phi_n = 0 \tag{2.1}$$

is known. The eigenfunctions ϕ_n obey given conditions on the boundary S' of R'. A region R contained in R' (Fig. 1) is then obtained by perturbing S' and the problem is to determine the new eigenvalues and eigenfunctions, which now satisfy the same boundary conditions as ϕ_n, but on the surface S, the boundary of R.

When Neumann boundary conditions apply, the problem can indeed be formulated in matrix language, using the unperturbed wavefunctions ϕ_n as a basis. This is done, for example, in the book by Morse and Feshbach [10], where perturbation-iteration procedures are applied to the eigenvalue equations; the analysis of convergence is also included. However, for an impenetrable small metallic particle, it is Dirichlet con-

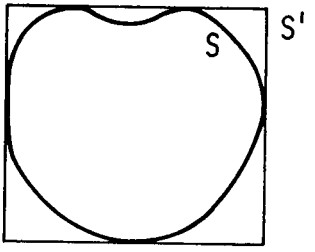

FIG. 1. The problem of the perturbation in the shape of the boundary. Solutions of Schrödinger's equation in region R bounded by S are to be obtained from those in region R' bounded by S'.

ditions that should be obeyed, since the electronic wavefunctions should vanish at the particle boundary. But then difficulties arise to cast the boundary perturbation problem as a matrix one, as we now intend to demonstrate.

The reason for the difficulties in the Dirichlet case can be seen qualitatively in a very simple way. Consider, in region R', the equation

$$(\nabla^2 - V + K_m^2)\,\psi_m = 0 \tag{2.2}$$

with

$$\begin{aligned} V(\mathbf{r}) &= V_0 \qquad \text{for} \quad \mathbf{r} \in R' \quad \text{but} \quad \mathbf{r} \notin R, \\ &= 0 \qquad \text{for} \quad \mathbf{r} \in R, \end{aligned} \tag{2.3}$$

and such that

$$\psi_m(\mathbf{r}) = 0, \qquad \mathbf{r} \in S'. \tag{2.4}$$

It is now clear that, when V_0 increases, ψ_m decreases exponentially in the region between S and S'. The function ψ_m will become zero on S only when $V_0 \to \infty$. Therefore, in order that ψ_m obey Dirichlet conditions on S, the matrix elements of V with respect to the unperturbed wavefunctions ϕ_n become infinite.

Notice that the same argument does not hold true for Neumann boundary conditions. A simple illustration of this can now be given for a one-dimensional problem.

It is our purpose to write the matrix equation determining the eigenvalues K_m^2 of

$$(d^2\psi_m/dx^2) + K_m^2\psi_m = 0 \tag{2.5}$$

in the interval $\{0, 1 - \epsilon\}$ with $\epsilon > 0$ and

$$\psi_m(0) = \psi_m(1 - \epsilon) = 0, \tag{2.5a}$$

in terms of the eigenfunctions ϕ_m satisfying the differential equation

$$(d^2\phi_m/dx^2) + k_m^2\phi_m = 0 \tag{2.6}$$

with boundary conditions

$$\phi_m(0) = \phi_m(1) = 0. \tag{2.6a}$$

The solutions ψ_m are

$$\begin{aligned} \psi_m(x) &= (2/(1-\epsilon))^{1/2} \sin(m\pi x/(1-\epsilon)) \qquad 0 < x < 1-\epsilon, \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad 1-\epsilon < x < 1, \end{aligned} \tag{2.7}$$

with $K_m^2 = (\pi^2 m^2/(1-\epsilon)^2)$ while the ϕ_m are given by

$$\phi_m = 2^{1/2} \sin(m\pi x). \tag{2.8}$$

In order to obtain the Hamiltonian matrix, we construct the operator

$$\mathscr{H} = \sum_{m=1}^{\infty} |\psi_m\rangle K_m^2 \langle\psi_m| \tag{2.9}$$

whose eigenvalues are indeed K_m^2 and which differs from the Hamiltonian by the factor $h^2/(2m_e)$.

The desired matrix elements of $\mathscr{H}$ with respect to the unperturbed wavefunctions are then

$$\begin{aligned} \langle\phi_r|\mathscr{H}|\phi_s\rangle = {} & \frac{4}{1-\epsilon} \sin\{\pi r(1-\epsilon)\} \sin\{\pi s(1-\epsilon)\} \\ & \times \sum_{m=1}^{\infty} m^4\{m^2 - (1-\epsilon)^2 r^2\}^{-1} \{m^2 - (1-\epsilon)^2 s^2\}^{-1} \end{aligned} \tag{2.10}$$

where 1 and $1-\epsilon$ are assumed to be incommensurable, for convenience. As the dummy index m tends to infinity, each term in this series approaches a constant, and the series does not converge.

On the other hand, for Neumann conditions, the corresponding series would be (for $r, s \neq 0$)

$$\begin{aligned} \langle\phi_r|\mathscr{H}|\phi_s\rangle = {} & 4(1-\epsilon)\, rs \sin\{\pi r(1-\epsilon)\} \sin\{\pi s(1-\epsilon)\} \\ & \times \sum_{m=1}^{\infty} m^2\{m^2 - (1-\epsilon)^2 r^2\}^{-1} \{m^2 - (1-\epsilon)^2 s^2\}^{-1} \end{aligned} \tag{2.11}$$

and no convergence problems arise, since each term of the series goes as m^{-2} when $m \to \infty$.

Thus, when Dirichlet conditions are required, the matrix elements of $\mathscr{H}$ are infinite and the problem of boundary perturbations cannot be cast in matrix form. As a consequence, a random boundary perturbation is not appropriately represented by RMT. It seems that the conclusions of Gor'kov and Eliashberg should be revised. In view of the generality of spacing distributions [11, 12] and since we know that there are examples (such as the two-dimensional example considered at the end of this section) in which the spectrum fluctuations are independent of the boundary conditions, it is of interest to analyze Neumann's problem in matrix form.

To obtain the eigenfunctions ψ_m whose normal derivative $\partial\psi_m/\partial n$ vanishes on the surface S, the Hermitian matrix

$$\mathscr{H}_{rs} = k_r^2 \cdot N_{rs} + A_{rs} \tag{2.12}$$

must be diagonalized [10]. Here k_r are the eigenvalues of the unperturbed problem, N_{rs} is the overlap

$$N_{rs} = \int_R \phi_r \phi_s \, dV \tag{2.13}$$

of the unperturbed functions in the perturbed region R and A_{rs} is given by

$$A_{rs} = \oint_S \frac{\partial \phi_r}{\partial n} \phi_s \, d\sigma, \tag{2.14}$$

S being the boundary of R.

Before discussing the results of the diagonalization of (2.12), let us proceed via perturbation theory for nonorthogonal wavefunctions [10]; one has, up to second order, the following expression for the new eigenvalues K_m^2

$$(K_m^2 - k_m^2) N_{mm} = A_{mm} + \sum_{p(\neq m)} \{A_{mp} - (K_m^2 - k_m^2) N_{mp}\}$$

$$\times \{A_{pm} - (K_p^2 - k_p^2) N_{pm}\}\{N_{pp}(K_m^2 - k_p^2) - A_{pp}\}^{-1}. \tag{2.15}$$

In the same example as before, when the original region is the interval $\{0, 1\}$ and the perturbed one is the interval $\{0, 1 - \epsilon\}$ we get from (2.15)

$$K_m^2 = k_m^2 + \frac{\pi m}{1 - \epsilon} \sin(2m\pi\epsilon)$$

$$+ \frac{4\pi m^2}{1 - \epsilon} \sin^2(m\pi\epsilon) \sum_{p(\neq m)} \frac{\cos^2 p\pi\epsilon}{\pi(1 - \epsilon)(m^2 - p^2) - p \sin 2p\pi\epsilon}. \tag{2.16}$$

We learn from this formula that, for small m, ϵ indeed plays the role of an expansion parameter. However, for large m, which is the case of interest when discussing the eigenvalues around the Fermi level for a small metallic particle, it is no longer clear what the expansion parameter is and the perturbation series is no longer meaningful. We thus turn to the diagonalization method.

We first fix our attention on a given energy $\mathscr{E}$ and take d unperturbed wavefunctions ϕ_m with $k_m^2 \sim \mathscr{E}$; using Eqs. (2.12) to (2.14) we construct a d-dimensional matrix and study whether the eigenvalues obtained after diagonalizing it approach a definite limit as d grows. For the one-dimensional example we dealt with above, no problem seems to arise. For example, when $\epsilon = 0.1$ the first 19 eigenvalues were obtained correctly by taking $d = 21$, as is shown in Fig. 2. The situation is quite different in a closely related two-dimensional problem. If we take as the unperturbed problem a square of side 1 (region R'), while region R is taken to be a rectangle of sides $1 - \epsilon$

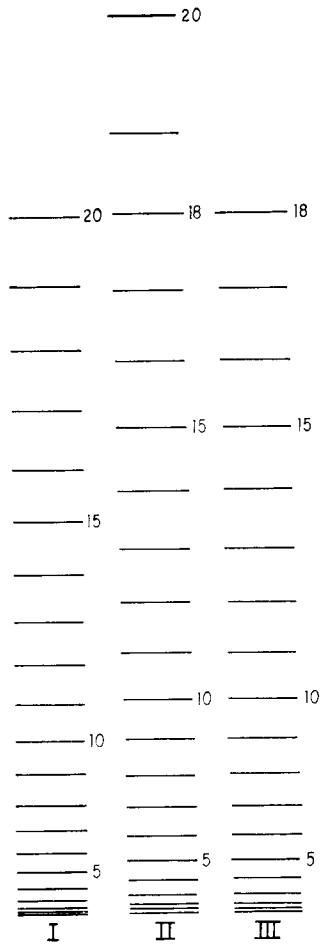

FIG. 2. Columns I and II show the first 21 levels of the single-particle spectrum for the one-dimensional Neumann problem in the interval {0, 1} and {0, 0.9}, respectively. Column III shows the first 19 eigenvalues obtained by diagonalizing matrix (2.12) in the basis provided by the 21 unperturbed states of column I.

and 1, we find a good approximation only when ϵ is much smaller than a typical wavelength in the region of the spectrum we are studying. If this condition is not fullfilled, no trace of convergence is observed, even if a value d as large as 82 is used, as in Fig. 3. We expect this situation to be even worse for a three-dimensional problem, since then the level density increases with k_n.

From the discussion presented up to now, we can draw the following conclusions. A problem of boundary perturbations with Dirichlet conditions cannot even be formulated in terms of matrices; on the other hand, a problem with Neumann's conditions leads to finite matrix elements; this, however, does not mean that we have

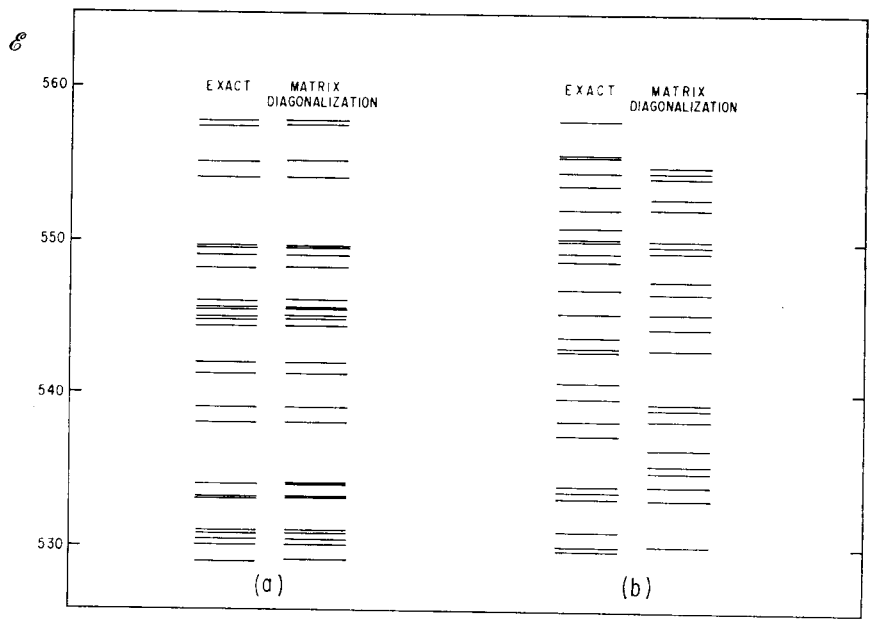

FIG. 3. A portion of the spectrum for the two-dimensional model calculated exactly (Eq. (3.3)) and by diagonalizing the matrix (2.12) with $d = 82$ for two cases (a) $\epsilon = 0.001$ and (b) $\epsilon = 0.01$. A typical wavelength in this energy region is of the order of 0.08.

achieved a convergent matrix formulation of the problem. In fact, the numerical example shows no trace of convergence to the exact eigenvalues.

The problem will then be analyzed from a different point of view in the following section.

3. Level Spacing Distribution and the Specific Heat of an Assembly of Small Metallic Platelets: A Simple Model

Since RMT cannot be applied, in general, to describe random boundary perturbations, the spacing distribution appropriate to the small metallic particle problem remains to be investigated. We thus proceed to analyze it by means of a simple two-dimensional soluble model, which simulates an assembly of platelets.

Consider an assembly of small platelets, in which platelet x contains $n^{(x)}$ electrons. To obtain the eigenvalues of the one-electron Schrödinger equation

$$(\nabla^2 + K_n^2)\,\psi_n = 0 \tag{3.1}$$

with

$$\psi_n(\mathbf{r}) = 0, \qquad \mathbf{r} \in S \tag{3.2}$$

is clearly a very difficult problem for a boundary S of arbitrary shape. However,

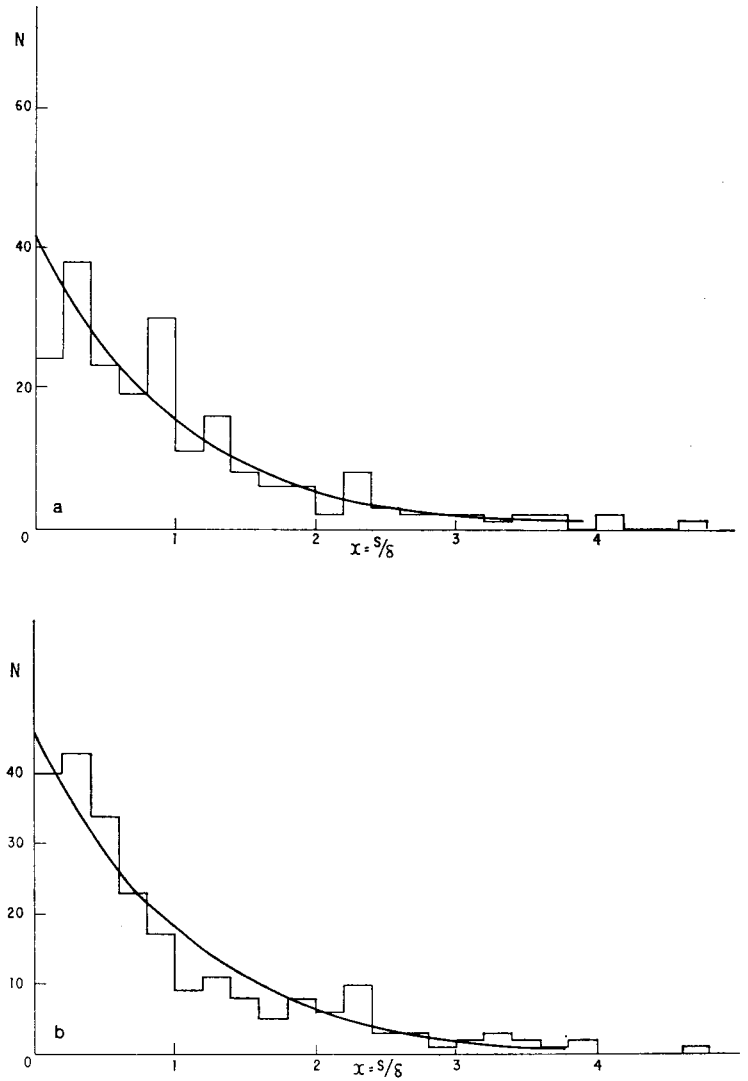

FIG. 4. Nearest neighbor spacing distribution in two different regions of the spectrum defined by Eq. (3.3) for $\epsilon = 0.015$. (a) Region from level 1 to 209; (b) region from level 965 to 1200.

there are simple cases for which the boundaries can be varied at random and yet the eigenvalue problem can be solved exactly. For example, suppose that the small metallic platelets are simulated by rectangles of sides $1 - \epsilon$ and 1, ϵ being the quantity that generates the assembly. The eigenvalues are then known, being

$$E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2m_e} \left\{ \frac{n_1^2}{(1-\epsilon)^2} + n_2^2 \right\}. \tag{3.3}$$

We shall first discuss the spacing distribution for *one* such rectangle, defined by a fixed value of ϵ. The histograms for the spacing between successive levels are shown in Fig. 4 for two different regions in the spectrum. We see that in both cases the distributions are not consistent with Eq. (1.2), since they show no level repulsion; they rather approximate the Poisson nearest-neighbor distribution (1.1), with $k = 0$. A much better idea of how closely the historgams of Fig. 4 follow Poisson's law is obtained through the value of the statistic ω; the value of ω arises from a least-squares fit of the curve

$$p_\omega(x) = \alpha x^\omega e^{-\beta x^{\omega+1}} \tag{3.4}$$

to the histogram [13]. Here α and β are chosen so that the mean value of x equals one and $p_\omega(x)$ is normalized. When $\omega = 0$, (3.4) reduces to Poisson's distribution, and when $\omega = 1$ to Wigner's distribution (1.2). For case (a) in Fig. 4, $\omega = 0.209 \pm 0.084$ and for case (b) $\omega = 0.023 \pm 0.035$, indicating that as we go up in energy in the spectrum and the electron wavelengths involved approach the size of the perturbation, $p(0; x)$ tends to a Poisson distribution.

Therefore, in this example a perturbation on the boundary does not produce level repulsion, but rather a completely random distribution.

We next construct an *assembly* of N rectangles by varying the number $n^{(\alpha)}$ ($\alpha = 1,..., N$) of electrons, keeping the electronic density constant (therefore varying the size of each platelet). The assembly is such that for $\epsilon = 0$, $n^{(\alpha)} = 800$, and $n^{(\alpha)}$ varies from 750 to 850. The histogram shown in Fig. 5 for the spacing between the Fermi level and the next one for the assembly of platelets is again of the Poisson type,[2] as evidenced by the value $\omega = 0.003 \pm 0.05$. We then conclude that the assembly of platelets shows a spacing distribution different from those predicted by conventional RMT; in particular, perturbing the boundary does not induce level repulsion in the spectrum. Our result then agrees with what was first assumed by Kubo [2].

By assuming an energy-independent level density and a completely random sequence of levels, Kubo [2] obtained the specific heat C_v at low temperatures. He found

$$C_v = k_B \left\{5.024 \left(\frac{k_B T}{\delta}\right) + 0.76 \left(\frac{k_B T}{\delta}\right)^2 + \cdots\right\}, \qquad n^{(\alpha)} \text{ even}, \tag{3.5a}$$

$$= k_B \left\{3.290 \left(\frac{k_B T}{\delta}\right) + 2.33 \left(\frac{k_B T}{\delta}\right)^2 + \cdots\right\}, \qquad n^{(\alpha)} \text{ odd}, \tag{3.5b}$$

with an even–odd average

$$C_v = k_B\{4.157(k_B T/\delta) + 1.55(k_B T/\delta)^2 + \cdots\} \tag{3.6}$$

up to second order in $(k_B T/\delta)$, where k_B is Boltzmann's constant.

[2] Notice that we have analyzed the spacing distributions in two different ways. First, we considered many spacings all belonging to a single platelet and, second, a single spacing from the spectra of many platelets at a fixed energy. Since we have found the same distribution in both instances, we say that the system of platelets shows the ergodic property for level fluctuations [12].

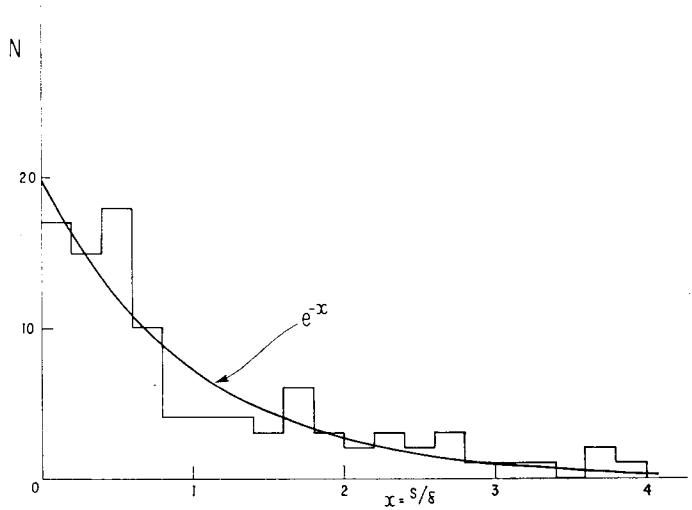

FIG. 5. Histogram for the spacing between the Fermi level and the next one for the assembly of platelets described in the text.

Since we know that the fluctuations in the levels of our model are those of a Poisson type, we shall extend Kubo's result by computing numerically the partition function Z and the thermodynamic properties derived from it, for an assembly of N single-electron spectra constructed with a random number generator in such a way that it has constant level density and that it follows Poisson's law (1.1) for spacing distributions exactly.[3]

For any given temperature, Z contains a finite number of terms if a numerical accuracy is fixed. This allows us to extend Kubo's results (3.5) to higher values of $k_B T/\delta$.

The partition function for the assembly of N particles is

$$Z = \prod_{\alpha=1}^{N} Z^{(\alpha)} \tag{3.7}$$

where

$$Z^{(\alpha)} = \sum_{\lambda} g_{\lambda}^{(\alpha)} \exp -\{\mathscr{E}_{\lambda}^{(\alpha)}/k_B T\}. \tag{3.8}$$

Here $g_{\lambda}^{(\alpha)}$ is the degeneracy of the λ level of the αth particle, $\mathscr{E}_{\lambda}^{(\alpha)}$ being the corresponding energy. From this, the specific heat is given by

$$C_v/k_B = (1/N)(1/k_B T)^2 \sum_{\alpha=1}^{N} S_0^{(\alpha)-2}\{S_0^{(\alpha)} S_2^{(\alpha)} - S_1^{(\alpha)2}\} \tag{3.9}$$

[3] We recall that the level density is assumed independent of the energy in the calculation by Kubo which, incidentally, is also true in our two-dimensional model.

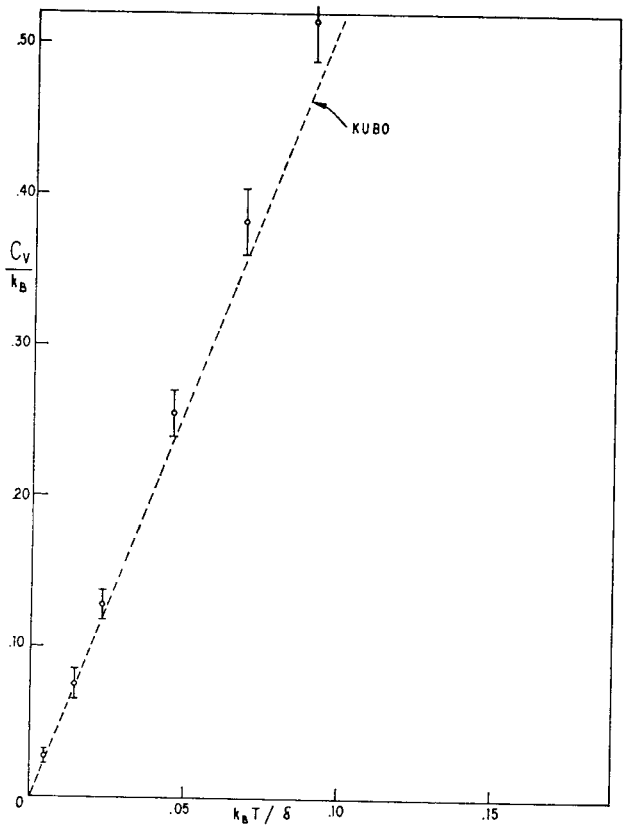

FIG. 6. Average and standard deviation of the specific heat C_v for an even number of electrons, for a sample of 1000 single-electron spectra obeying Poisson's distribution (1.1). The dashed curve is Kubo's result (3.5a).

where

$$S_l^{(\alpha)} = \sum_\lambda g_\lambda^{(\alpha)} \mathscr{E}_\lambda^{(\alpha)l} \exp -\{\mathscr{E}_\lambda^{(\alpha)}/k_B T\} \qquad l = 0, 1, 2. \tag{3.10}$$

The results of the numerical calculation for the specific heat are shown in Figs. 6 and 7 for an even and an odd number of electrons, respectively. In both cases $N = 1000$ spectra were used; the average value of C_v corresponds to the dots and the error bars give the standard deviation for a sample of 1000 spectra. Notice that our result deviates from Eq. (3.5) when $k_B T/\delta \gtrsim 0.025$; this is so, since at higher temperatures more many-electron configurations, not taken into account in Kubo's calculation, start to be important. It is also interesting to calculate analytically the standard deviation of C_v (i.e., $(\langle C_v^2 \rangle - \langle C_v \rangle^2)^{1/2}$, where the bracket indicates an average over the spectra), within the same approximation used by Kubo. As an example we show in Fig. 8, in the odd case, a comparison between the standard deviation of C_v obtained

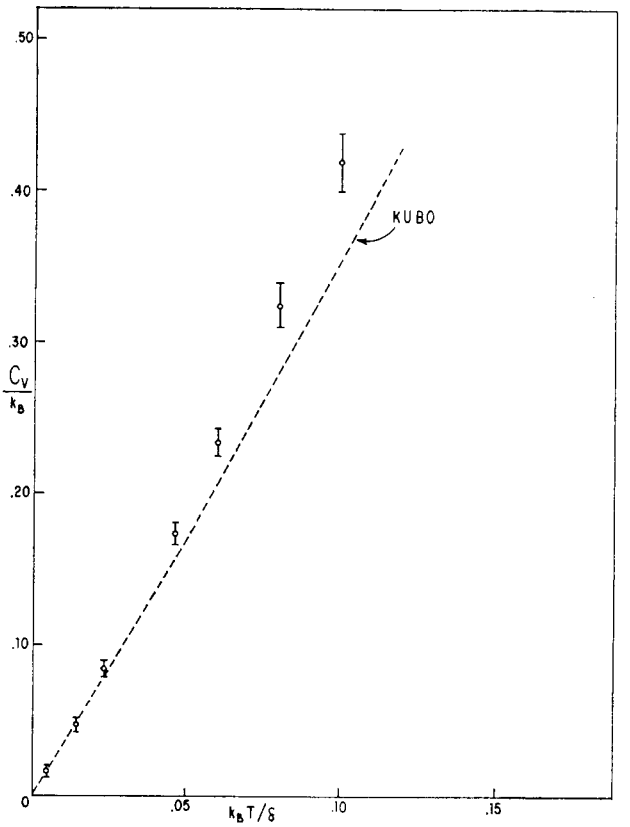

FIG. 7. Average and standard deviation of the specific heat C_v for an odd number of electrons, for a sample of 1000 single-electron spectra obeying Poisson's distribution (1.1). The dashed curve is Kubo's result (3.5b).

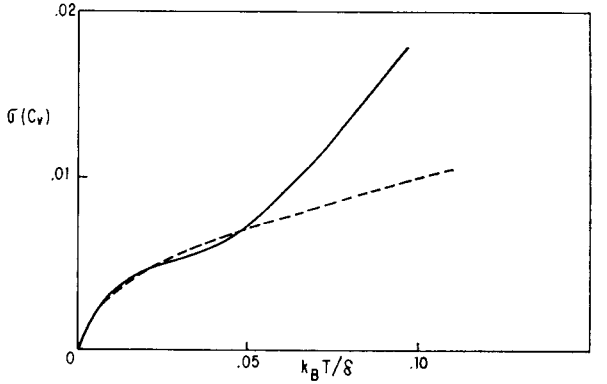

FIG. 8. Theoretical (dashed line) and numerical (solid line) standard deviation of the specific heat C_v of Fig. 7.

analytically, which is proportional to $(k_B T)^{1/2}$, and the one obtained numerically and shown as the error bars in Fig. 7. We see that both results agree once more only when $k_B T/\delta \lesssim 0.025$. Another calculation of C_v has been given by Denton *et al.* [14]; a comparison with our results is given elsewhere [15].

4. Conclusions

Several points emerge from this paper. First, it seems that RMT is not applicable, at least not in general, to the problem of boundary perturbations, since this problem cannot be formulated in matrix form. Second, the analysis of a simple two-dimensional model tells us that the spacing distributions of an assembly of small particles are not of the type encountered in RMT but rather of a Poisson nature, as originally assumed by Kubo and as was known in acoustical problems [16]. This is contrary to what is normally believed [17], even on the grounds of experimental evidence concerning the magnetic susceptibility of small metallic particles. This evidence is, however, scanty and somewhat unreliable at very low temperatures, since impurities and other effects could play a significant role [18, 19].

In any case, assuming a Poisson spacing distribution for an assembly of N spectra, we computed numerically an exact value for the specific heat. The calculation shows that Kubo's original analytical result is correct only for $k_B T/\delta < 0.025$, a rather small value.

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