THERMODYNAMIC PROPERTIES OF ELECTRONS IN SMALL METAL PARTICLES

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The electronic properties of a collection of small metal particles are determined by the distribution of their discrete electronic energy levels. According to Gorkov and Eliashberg, the concepts of the Random Matrix Theory may be applicable to the problem of the energy level distribution in small metal particles. In this paper we use the Gaussian ensembles instead of Dyson ones. This enables us to obtain 3-level correlation functions. The approach makes possible an extension to a wider temperature range for previous results of the specific heat and spin susceptibility due to Czerwonko.

1. Introduction

Small metal particles have unique physical and chemical properties, different from those of the bulk metal [1]. The physical properties of metals depend characteristically on their excitation spectra. In a bulk metal the thermal broadening of electronic levels effectively produces a continuous spectrum. The energy levels, however, are expected to be separated for small particles when the average spacing δ between levels is much greater than the thermal energy kT. For a finite system the average spacing δ between single-electron states is of the order E_F/N, where E_F is the Fermi energy and N is the number of conduction electrons. The separation of energy levels should occur for particles of diameter less than 100 Å and temperatures below 10 K. Under such conditions, at temperatures so low that only a few electrons are excited above the Fermi level, the statistical characteristics of the spectrum have a direct influence in determining the partition function Z and thermodynamic properties derived from it. The exact counting of the possible electron excitation leads to the difference in behaviour between particles with an even and those with an odd number of conduction electrons. As the thermal energy kT becomes large, compared to the average level spacing δ, the even-odd effects as, well as the discrete nature of the spectrum, are washed out.

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Thus, to calculate the thermodynamics of a collection of small metal particles at low temperatures, one needs the distribution of energy levels about the Fermi level. In the case of a perfect metallic sphere, the distribution of energy levels is not difficult to obtain; the degeneracy in magnetic quantum numbers due to spherical symmetry is proportional to $N^{1/3}$. However, the electronic energy levels of experimentally produced small particles are seen to be random. Kubo [2] 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 assumed a completely random distribution for the energy electron levels, to which corresponds a nearest-neighbour spacing distribution of the Poisson type. Gorkov and Eliashberg [3] using the same qualitative argument as Kubo, considered the concepts of the Random Matrix Theory for nuclear level fluctuations to be applicable to the small metal particle problem. They assumed that surface irregularities of the order of atomic dimensions would lead to a Hamiltonian matrix with random elements, when expressed in a single-electron basis. The electronic energies necessary to compute the partition function Z are the eigenvalues of this Hamiltonian matrix.

The problem of random matrices was further considered by Dyson [4, 5] who showed that the general symmetry requirements provided for a classification into three groups corresponding to respective ensembles of Hamiltonians. For small metal particles the orthogonal ensemble applies when spin-orbit coupling of the conduction electrons is weak and time-reversal invariance holds. The symplectic ensemble describes the case of strong spin-orbit coupling with time-reversal invariance. The unitary ensemble is used for the case of large spin-orbit coupling with no time-reversal invariance, i.e., in large magnetic fields. The criterion that the field or coupling is strong or weak is given by comparison with the average level spacing δ.

Czerwonko [6, 7] obtained the extension of Kubo's and Gorkov–Eliashberg's results. He derived the analytical and numerical formulas for specific heat and spin susceptibility of a collection of small metal particles in two limiting cases: for δ much greater than kT and for δ much smaller than kT, i.e., at low and high temperatures, respectively. At low temperatures he used the 2-level correlation functions of the Dyson ensembles for averaging the thermodynamic properties over the statistical distribution describing the levels in the collection of particles. It has been shown in [8] that the results of Czerwonko are in accordance with the numerical results obtained later by Denton, Mühlschlegel and Scalapino [9].

In this paper we use the Gaussian ensembles instead of the Dyson ones [10, 11] to describe the distribution of energy levels in small metal particles. For these ensembles we can obtain the 3-level correlation functions necessary to extend the low-temperature results of Czerwonko.

2. 3-level correlation functions

According to quantum mechanics, the energy levels of a system are described by the eigenvalues of the Hamiltonian operator. The problem of calculating the eigenvalues of Hamiltonian operators of complicated systems, for which the eigenvalue equation can-

not be solved, was considered in nuclear physics. Wigner [12] first proposed to describe the energy levels of a complex nuclear system statistically as the eigenvalues of a random matrix. The Hamiltonian of a single nuclear system is represented by a matrix for some set of basis states, and in turn an ensemble of matrices would correspond to an ensemble of possible nuclear systems. The elements in the matrices are randon variables whose distributions are restricted only by the general symmetry properties imposed on the ensemble of Hamiltonian operators. The possible ensemble of randon matrices corresponding to various symmetry requirements can then be diagonalized to yield the respective distribution of ordered energy eigenvalues.

It has been shown by Dyson that there are three basic groups of canonical transformations relevant to quantal systems, viz. the orthogonal, the symplectic and the unitary ensembles. In addition to the symmetry classifications, there are two main classes of ensembles: the circular [4] and the Gaussian [13] version of these ensembles. One should note that the assumptions underlying the derivations of the energy eigenvalues are different for these two classes. Dyson's ensembles need only one hypothesis which is loosely connected with the Hamiltonian, while in the Gaussian ensembles one uses two hypotheses connected directly with the Hamiltonian matrix. The circular ensembles of Dyson are esthetically more satisfactory, on the other hand, the Gaussian ensembles have some remarkable properties. Namely, approximations in the Gaussian ensembles for high dimensions lead to results which are identical with the exact results in the circular ensembles for high dimensions. It has also been found empirically that level spacing distributions, for small spacings, computed in the Gaussian ensembles, are nearly independent of matrix dimensions. Even working in two dimensions one obtains for the nearest-neighbour spacing distribution which does not differ very much numerically from the infinite results [10]. Hence it is very useful to obtain results for low dimensional matrices in the Gaussian ensembles. The information on the level spacing distributions obtained in this way may be a good approximation of the exact results in the circular ensembles.

The joint probability distribution function for the eigenvalues of matrices from the Gaussian ensembles [11], is given by

$$P_{N\gamma}(\varepsilon_1, \ldots, \varepsilon_N) = C_{N\gamma} \prod_{j<k} |\varepsilon_j - \varepsilon_k|^{\gamma} \exp\left(-\frac{\gamma}{2} \sum_{j=1}^{N} \varepsilon_j^2\right). \tag{1}$$

It gives the normalized distribution of N ordered eigenvalues for the three ensembles, obtained by diagonalizing the matrices in each ensemble, where $\gamma = 1$ if the ensemble is orthogonal, $\gamma = 4$ if it is symplectic and $\gamma = 2$ if it is unitary. The constant $C_{N\gamma}$ is chosen in such a way that the joint probability function (1) is normalized to unity. Each pair of eigenvalues in the formula above displays a level "repulsion", which expresses the fact that an accidental degeneracy is very unlikely; the perturbations represented by the off-diagonal elements in the random matrices will split apart any eigenvalues which approach one another.

The probability of finding a level (regardless of labelling) in each of the unit intervals around the levels $\varepsilon_1, \ldots, \varepsilon_n$, when the position of the remaining levels is unobserved, is

measured by the n-level correlation function

$$R_{n\gamma}(\varepsilon_1, \ldots, \varepsilon_n) = \lim_{N\to\infty} \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} P_{N\gamma}(\varepsilon_1, \ldots, \varepsilon_N) d\varepsilon_{n+1} \ldots d\varepsilon_N. \tag{2}$$

Because the position of the absolute level is irrelevant, the n-level correlation function (2) may be expressed as a function of the $(n-1)$ level spacings $\Delta_i = \varepsilon_{i+1} - \varepsilon_i$, $i = 1, \ldots, (n-1)$. Thus $R_{2\gamma}(\Delta_1)$ represents the probability that two successive levels are separated by an energy Δ_1, $R_{3\gamma}(\Delta_1, \Delta_2)$ — the probability that three successive levels have the relative spacings Δ_1 and Δ_2, etc. For the nearest-neighbour spacing distributions $R_{2\gamma}(\Delta)$ the exact numerical results as well as the asymptotic form are known. Moreover, the Gaussian ensembles give the same results as the Dyson ones for $N \to \infty$. In the limit where Δ is small compared with the average level spacing δ, the orthogonal, unitary and symplectic distributions vanish as various powers of $\Delta/\delta = x$ reflecting the level repulsion effects

$$R'_{21}(x) = \frac{\pi^2}{6} x, \quad R'_{22}(x) = \frac{\pi^2}{3} x^2, \quad R'_{24}(x) = \tfrac{32}{270} \pi^4 x^4. \tag{3}$$

The exact solution of a general spacing distribution $R'_{n\gamma}(x_1, \ldots, x_{n-1})$ is very difficult to calculate, since the limiting behaviour resulting from integrations taken over $P_{N\gamma}(\varepsilon_1, \ldots, \varepsilon_N)$ must be determined. For the spacing distributions with more than one spacing variable, the exact result is only available for $R'_{31}(x_1, x_2)$; Metha [11] has presented a numerical tabulation of this function for a limited range of the variables. Therefore, it is necessary to obtain simple approximations to the exact formulas. As has been noted by others [10], useful approximations to the exact nearest-neighbour spacing distributions (3) are obtained by taking $N = 2$ in $P_{N\gamma}(\varepsilon_1, \ldots, \varepsilon_N)$, changing variables to the spacing between the two eigenvalues and integrating over the remaining variable. The generalization of this procedure may give approximate formulas for the more complicated distributions [9]. We obtain the approximate formulas for $R_{3\gamma}(x_1, x_2)$ in an analytical way.

In order to obtain the approximate distribution of n spacings, the joint probability density function (1) is restricted to the smallest number of levels needed to have n spacings; thus one uses $P_{(n+1)\gamma}(\varepsilon_1, \ldots, \varepsilon_{n+1})$. The variables of the $(n+1)$ successive levels are changed to n spacing variables given by $\Delta_i = \varepsilon_{i+1} - \varepsilon_i$, $i = 1, \ldots, n$, with the energy variable ε_1 remaining. Integration over this variable produces the spacing distribution from the eigenvalue distribution

$$R_{(n+1)\gamma}(\Delta_1, \ldots, \Delta_n) \equiv \int_{-\infty}^{+\infty} d\varepsilon_1 P_{(n+1)\gamma}(\varepsilon_1, \Delta_1, \ldots, \Delta_n). \tag{4}$$

The distribution (4) satisfies

$$\int_0^\infty d\Delta_1 \ldots \int_0^\infty d\Delta_n R_{(n+1)\gamma}(\Delta_1, \ldots, \Delta_n) = 1.$$

The average values of Δ_i here are generally different, while the average values for the exact spacing distribution are equal. By scaling the variables Δ_i in terms of their average

values $\Delta_i \to \Delta_i/\overline{\Delta}_i \equiv x_i$ we can obtain the properly normalized distribution $R_{(n+1)\gamma}(x_1, \ldots, x_n)$ which then satisfies

$$\bar{x}_i = \int_0^\infty dx_1 \ldots \int_0^\infty dx_n x_i R_{(n+1)\gamma}(x_1, \ldots, x_n) = 1$$

and

$$\int_0^\infty dx_1 \ldots \int_0^\infty dx_n R_{(n+1)\gamma}(x_1, \ldots, x_n) = 1. \tag{5}$$

For the calculations of $R_{2\gamma}(x)$ one sets $N = 2$ in the joint probability density function (1), with spacing Δ_1 defined as $\Delta \equiv \Delta_1 = \varepsilon_2 - \varepsilon_1$. By integrating over ε_1 from $-\infty$ to $+\infty$ one obtains the spacing distribution (4) in the form

$$R_{2\gamma}(\Delta) = \gamma^{\frac{\gamma+1}{2}} 2^{-\gamma} \left[\Gamma\left(\frac{\gamma+1}{2}\right)\right]^{-1} \Delta^\gamma \exp\left(-\frac{\gamma}{4}\Delta^2\right), \tag{6}$$

where Γ is the gamma function. In order to scale $\Delta_i \to x_i$ we compute the average values $\overline{\Delta}_\gamma$ for the different ensembles

$$\overline{\Delta}_\gamma = \gamma^{1/2} \Gamma\left(\frac{\gamma}{2}\right)\left[\Gamma\left(\frac{\gamma+1}{2}\right)\right]^{-1}. \tag{7}$$

Then one obtains the properly normalized approximate distribution which satisfies (5) expressed as

$$R_{2\gamma}(x) = 2\frac{\left[\Gamma\left(1+\frac{\gamma}{2}\right)\right]^{\gamma+1}}{\left[\Gamma\left(\frac{1+\gamma}{2}\right)\right]^{\gamma+2}} x^\gamma \exp\left\{-\left[\frac{\Gamma\left(1+\frac{\gamma}{2}\right)}{\Gamma\left(\frac{1+\gamma}{2}\right)}\right]^2 x^2\right\}. \tag{8}$$

Hence in the limit where $x \ll 1$, the orthogonal, unitary and symplectic distributions are given by

$$R_{21}(x) = \frac{\pi}{2} x, \quad R_{22}(x) = \frac{32}{\pi^2} x^2, \quad R_{24}(x) = (\tfrac{8}{3})^6 \frac{1}{\pi^3} x^4. \tag{9}$$

The coefficients in the exact spacing distributions (3) and in the approximate spacing distributions (9) have a small relative difference of a few percent. One obtains errors of order 4.5%, 1.5% and 0.5% for the orthogonal, unitary and symplectic ensemble, respectively.

For the calculation of $R_{3\gamma}(x_1, x_2)$ one sets $N = 3$ in the eigenvalue distribution (1) with spacings Δ_1, Δ_2 defined as $\Delta_1 = \varepsilon_2 - \varepsilon_1$, $\Delta_2 = \varepsilon_3 - \varepsilon_2$. By integrating over ε_1 from $-\infty$ to $+\infty$ one obtains the spacing distribution (4) in the following form

$$R_{3\gamma}(\Delta_1, \Delta_2) = C'_{3\gamma}[\Delta_1\Delta_2(\Delta_1+\Delta_2)]^\gamma \exp\left[-\frac{\gamma}{3}(\Delta_1^2+\Delta_1\Delta_2+\Delta_2^2)\right]. \tag{10}$$

This spacing distribution is symmetric in the variables Δ_1, Δ_2, hence the average values $\bar{\Delta}_{1\gamma}$ and $\bar{\Delta}_{2\gamma}$ obtained from this distribution are the same and $\bar{\Delta}_{1\gamma} = \bar{\Delta}_{2\gamma} \equiv \bar{\Delta}_\gamma$. Defining a transformation

$$\Delta_1 = u(1-v), \quad \Delta_2 = vu; \tag{11}$$

we find that the set $\{(\Delta_1, \Delta_2) : \Delta_1 \geqslant 0, \Delta_2 \geqslant 0\}$ is mapped onto the plane subset bounded by the lines $v = 0$, $u = 0$ and $v = 1$. The Jacobian of this transformation is u. In terms of these variables we find the expressions for the normalization constant $C'_{3\gamma}$ and for the average values $\bar{\Delta}_\gamma$. For example, for the orthogonal ensemble ($\gamma = 1$) we have

$$(C'_{31})^{-1} = \int_0^1 v(1-v)dv \int_0^\infty u^4 \exp\left[-\tfrac{1}{3}u^2(1-v+v^2)\right]du, \tag{12}$$

and

$$\bar{\Delta}_1 = C'_{31} \int_0^1 v^2(1-v)dv \int_0^\infty u^5 \exp\left[-\tfrac{1}{3}u^2(1-v+v^2)\right]du. \tag{13}$$

Performing the integrations in (12) and (13), we get

$$C'_{31} = \frac{1}{\sqrt{3\pi}} \quad \text{and} \quad \bar{\Delta}_1 = \sqrt{\frac{27}{4\pi}}. \tag{14}$$

Analogously, for the unitary ($\gamma = 2$) and for the symplectic ensemble ($\gamma = 4$), we obtain

$$C'_{32} = \frac{4}{\pi\sqrt{3}} \quad \text{and} \quad \bar{\Delta}_2 = \frac{27}{8\sqrt{2\pi}}, \tag{15}$$

$$C'_{34} = \frac{4^5}{45\pi\sqrt{3}} \quad \text{and} \quad \bar{\Delta}_4 = 13!!\,\frac{37}{25\sqrt{\pi}}\left(\tfrac{3}{20}\right)^6. \tag{16}$$

Now we can compute the properly normalized approximate distributions $R_{3\gamma}(x_1, x_2)$. In the limit where Δ_1, Δ_2 are small compared with the average level spacing, we obtain (from (5) and (14)–(16)) the following expressions for the orthogonal, unitary and symplectic ensemble

$$R_{31}(x_1, x_2) = \frac{3^7}{2^5\pi^3} x_1x_2(x_1+x_2),$$

$$R_{32}(x_1, x_2) = \left(\tfrac{3}{2}\right)^{23} \frac{\sqrt{3}}{8\cdot\pi^5} [x_1x_2(x_1+x_2)]^2,$$

$$R_{34}(x_1, x_2) = \left(\tfrac{9}{2}\right)^{40} \frac{3\sqrt{3}}{32\cdot\pi^8} (13!!37)^{14} 10^{-113} [x_1x_2(x_1+x_2)]^4. \tag{17}$$

The coefficients in the exact spacing distribution (given by Mehta [11])

$$R'_{31}(x_1, x_2) = \frac{\pi^4}{45} x_1 x_2 (x_1 + x_2),$$

and in the approximate spacing distribution $R_{31}(x_1, x_2)$ obtained above, have a small relative difference of 1.8%.

3. *Thermodynamic properties*

To calculate the thermodynamics of a collection of small metal particles, one must also use the appropriate partition function. For the orthogonal and symplectic ensembles the partition function Z in the following form (given by Kubo [2]) is suitable

$$Z = \frac{1}{2\pi i} \oint \frac{dz}{z^{\alpha}} \prod_{\substack{k \geqslant 1 \\ s = \pm 1}} (1 + z e^{sh - \beta \varepsilon_k}) \prod_{\substack{l \leqslant 0 \\ s = \pm 1}} \left(1 + \frac{1}{z} e^{sh - \beta \varepsilon_l'}\right), \tag{18}$$

where α is equal to 1 or 0 for particles with an even or odd number of conduction electrons, respectively; $h = \frac{1}{2} g \beta \mu_B H$, g is the Lande factor of electrons, μ_B is the Bohr magneton $\beta = (kT)^{-1}$ and the magnetic field H is set equal to zero. In the partition function, the energy levels ε_k and ε_l' are ordered with respect to the Fermi level ε_0, where ε_k refers to excited electrons above ε_0 and ε_l' refers to holes created in the levels below ε_0. The ground-state energy is chosen to give $\varepsilon_0 = 0$. In the case of the unitary ensemble, the partition function Z_0 for a spinless system [9] is appropriate and can be obtained from the Kubo's partition function Z in the following form

$$Z_0 = \frac{1}{2\pi i} \oint \frac{dz}{z} \prod_{k \geqslant 1} (1 + z e^{-\beta \varepsilon_k}) \prod_{l \leqslant 0} \left(1 + \frac{1}{z} e^{-\beta \varepsilon_l'}\right). \tag{19}$$

Kubo has also presented an effective method of computing the partition function Z in the two limiting cases of low and high temperatures. Czerwonko [6] has shown that at the extremely low temperature, where only the level ε_1 is significantly populated, for the specific heat and spin susceptibility, the analytical formulas can be obtained. Following the method of Kubo and Czerwonko, using the 2- and 3-level correlation functions of the Gaussian ensembles, we can obtain the specific heat and spin susceptibility in a wider temperature range. The experimental precision is not adequate for distinguishing between the orthogonal and the symplectic behaviour of small metal particles [14] and we will not investigate the case of the symplectic ensemble.

Analogously to results obtained by using the 2-level correlation functions of the Dyson ensembles [6, 8], when $R_{2\gamma}(x)$ is the correlation function of the Gaussian ensemble, the specific heat of particles described by the orthogonal ensemble is given by

$$\frac{\langle C \rangle_1}{k} = 2\beta^2 \frac{\partial^2}{\partial \beta^2} \int_0^{\infty} dx R_{21}(x) \ln (1 + e^{-\beta \delta x}) = \frac{9}{2} \pi \zeta(3) \left(\frac{kT}{\delta}\right)^2 = 16.99 \left(\frac{kT}{\delta}\right)^2, \tag{20}$$

when the number of conduction electrons in a particle is odd. When this number is even we have

$$\frac{\langle C\rangle_1}{k} = \beta^2 \frac{\partial^2}{\partial\beta^2} \int_0^\infty dx R_{21}(x) \ln\left(1+a^2 e^{-\beta\delta x}+e^{-2\beta\delta x}\right)$$

$$= \tfrac{3}{2}\pi \left\{\frac{\pi^2}{3} \ln A + \tfrac{1}{3}\ln^3 A + 4\sum_{n=1}^{\infty} (-1)^n \frac{B^{n+1}}{n^3}\right\} \left(\frac{kT}{\delta}\right)^2 = 28.86 \left(\frac{kT}{\delta}\right)^2, \tag{21}$$

where $\langle \ldots \rangle$ denotes the statistical average, $R_{21}(x) = \dfrac{\pi}{2} x$, ζ is the zeta function $a = 2\cosh \beta\mu_B H$ and A, B satisfy the equations $AB = 1$, $A+B = 4$ for $H = 0$.

In the case where the unitary ensemble describes a system with a large spin-orbit coupling in a sufficiently large magnetic field, there is no longer any energy level degeneracy. The previously two-fold degenerate levels with average level spacing δ are split apart. This produces a system with average level spacing $\delta' = \frac{1}{2}\delta$ and there should be no longer any even-odd distinction. For particles described by this ensemble, we get

$$\frac{\langle C\rangle_1}{k} = \beta^2 \frac{\partial^2}{\partial\beta^2} \int_0^\infty dx R_{22}(x) \ln\left(1+e^{-\beta\delta' x}\right) = \left(\frac{8}{\pi}\right)^2 84\zeta(4) \left(\frac{kT}{\delta}\right)^3$$

$$= 5.89 \times 10^2 \left(\frac{kT}{\delta}\right)^3, \tag{22}$$

where $R_{22}(x) = \dfrac{32}{\pi^2} x^2$ and $\delta' = \frac{1}{2}\delta$.

The spin susceptibility for the orthogonal ensemble, when the number of conduction electrons in a patricle is odd, is given by

$$\frac{\langle \chi\rangle_1}{\chi_P} = \frac{\delta}{2\mu_B^2 \beta} \frac{\partial^2}{\partial H^2} \ln(2\cosh \beta\mu_B H) = \tfrac{1}{2}\frac{\delta}{kT}, \tag{23}$$

where $\chi_P = \dfrac{2\mu_B^2}{\delta}$ is the Pauli spin susceptibility; when the number of conduction electrons in a particle is even, we have

$$\frac{\langle \chi\rangle_1}{\chi_P} = \frac{\delta}{2\mu_B^2 \beta} \frac{\partial^2}{\partial H^2} \int_0^\infty dx R_{21}(x) \ln\left(1+a^2 e^{-\beta\delta x}+e^{-2\beta\delta x}\right)$$

$$= \frac{\pi}{\sqrt{3}} \left\{\tfrac{1}{2}\ln^2 A + \frac{\pi^2}{6} - 2\sum_{n=1}^{\infty} (-1)^{n+1} \frac{B^n}{n^2}\right\} \frac{kT}{\delta} = 3.64 \frac{kT}{\delta}, \tag{24}$$

where $A = 2+\sqrt{3}$, $B = 2-\sqrt{3}$ from equations $AB = 1$, $A+B = 4$ and $a = 2$ for $H = 0$.

The next order of the specific heat approximation for the orthogonal ensemble is given by

$$\frac{\langle C\rangle_2}{k} = -\frac{5\cdot 3^8}{2^4\pi^3}\left(\frac{kT}{\delta}\right)^5 \int_0^1 \frac{ds}{s}\int_0^1 \frac{dt}{t} \ln s \ln t(\ln s + \ln t)$$

$$\times \left\{2\ln\frac{1+s+st}{(1+s)(1+st)} + \ln\frac{1+s+t+st(s+t)+a^2st+s^2t^2}{(1+s)(1+t)}\right\} = 389.48\left(\frac{kT}{\delta}\right)^5, \quad (25)$$

when the number of conduction electrons in a particle is odd; when this number is even we have

$$\frac{\langle C\rangle_2}{k} = -\frac{5\cdot 3^8}{2^4\pi^3}\left(\frac{kT}{\delta}\right)^5 \int_0^1 \frac{ds}{s}\int_0^1 \frac{dt}{t} \ln s \ln t(\ln s + \ln t)$$

$$\times \left\{2\ln\frac{1+a^2s(1+t+st)+s^2+s^2t^2}{1+a^2s+s^2} - \ln(1+a^2st+s^2t^2)\right\} = 304.9\left(\frac{kT}{\delta}\right)^5, \quad (26)$$

where $s = \exp(-\beta\delta x_1)$, $t = \exp(-\beta\delta x_2)$, $a = 2$ for $H = 0$ and we have used the 3-level correlation function $R_{32}(x_1, x_2)$ obtained in the Gaussian ensembles (17). For particles described by the unitary ensemble, we have

$$\frac{\langle C\rangle_2}{k} = \frac{3^{25}\sqrt{3}}{2^{15}\pi^5}\left(\frac{kT}{\delta}\right)^8 \int_0^1 \frac{ds}{s}\int_0^1 \frac{dt}{t} \ln^2 s \ln^2 t(\ln s + \ln t)^2$$

$$\times \left\{2\ln\frac{1+s+st}{1+s} - \ln(1+st)\right\} = 54.5\times 10^5\left(\frac{kT}{\delta}\right)^8, \quad (27)$$

where s and t are the same as above, and we have used the 3-level correlation function $R_{32}(x_1, x_2)$ from (17).

The spin susceptibility in the next order of approximation, for the orthogonal ensemble is given by

$$\frac{\langle\chi\rangle_2}{\chi_P} = -\frac{3^7}{(2\pi)^3}\left(\frac{kT}{\delta}\right)^4 \int_0^1 \frac{ds}{s}\int_0^1 \frac{dt}{t} \ln s \ln t(\ln s + \ln t)$$

$$\times \frac{st}{s(1+s)t^2+(1+4s+s^2)t+(1+s)} = 23.36\left(\frac{kT}{\delta}\right)^4, \quad (28)$$

when the number of conduction electrons in a particle is odd; when this number is even we have

$$\frac{\langle\chi\rangle_2}{\chi_P} = -\frac{3^7}{(2\pi)^3}\left(\frac{kT}{\delta}\right)^4 \int_0^1 \frac{ds}{s}\int_0^1 \frac{dt}{t} \ln s \ln t(\ln s + \ln t)$$

$$\times\left(\frac{st}{1+4s+s^2} \times \frac{(1+s)(1+s^2)-s^2t^2}{s^2t^2+4s(1+s)t+(1+4s+s^2)} - \frac{st}{1+4st+s^2t^2}\right) = -26.8\left(\frac{kT}{\delta}\right)^4. \quad (29)$$

where $s = \exp(-\beta\delta x_1)$, $t = (-\beta\delta x_2)$, χ_P is the Pauli spin susceptibility and $H = 0$. In this order of approximation the integrals were calculated numerically.

Taking into account the results obtained in the first (20)–(24) and in the second (25)–(29) order of approximations, we get the low-temperature behaviour of the specific heat and spin susceptibility of electrons in small metal particles expressed as

$$\frac{\langle C\rangle_o}{k} = 16.99\left(\frac{kT}{\delta}\right)^2 + 389.48\left(\frac{kT}{\delta}\right)^5,$$

$$\frac{\langle C\rangle_e}{k} = 28.86\left(\frac{kT}{\delta}\right)^2 + 304.9\left(\frac{kT}{\delta}\right)^5, \quad (30)$$

$$\frac{\langle\chi\rangle_o}{\chi_P} = 0.5\frac{\delta}{kT} + 23.36\left(\frac{kT}{\delta}\right)^4,$$

$$\frac{\langle\chi\rangle_e}{\chi_P} = 3.64\frac{kT}{\delta} - 26.8\left(\frac{kT}{\delta}\right)^4, \quad (31)$$

for particles described by the orthogonal ensemble. The indices "o" and "e" denote the cases of a particle with an odd and even numbers of conduction electrons, respectively. For particles described by the unitary ensemble, we have

$$\frac{\langle C\rangle}{k} = 5.89\times10^2\left(\frac{kT}{\delta}\right)^3 + 54.5\times10^5\left(\frac{kT}{\delta}\right)^8. \quad (32)$$

At this point it is not evident how large $\frac{kT}{\delta}$ can be for this low-temperature behaviour to remain valid. The lowest order terms in expressions (30)–(32) have the range of validity $\frac{kT}{\delta} \sim 0.1$.

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REFERENCES

[1] I. D. Morokhov, L. I. Trusov, S. P. Chizhik, *Ultradispersnyye metalicheskie sredy*, Atomizdat, Moscow 1977.

[2] R. Kubo, *J. Phys. Soc. Jap.* **17**, 975 (1962).

[3] L. P. Gorkov, G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.* **48**, 1407 (1965).

[4] F. J. Dyson, *J. Math. Phys.* **3**, 140, 157, 166 (1962).

[5] F. J. Dyson, M. L. Mehta, *J. Math. Phys.* **4**, 701 (1963).

[6] J. Czerwonko, *Phys. Status Solidi* **30**, 723 (1968).

[7] J. Czerwonko, *Phys. Status Solidi* **31**, K161 (1969).

[8] K. Weron, *Acta Phys. Pol.* **A53**, 19 (1978).

[9] R. Denton, B. Mühlschlegel, D. J. Scalapino, *Phys. Rev.* **B7**, 3589 (1973).

[10] C. E. Porter, *Statistical Theories of Spectra: Fluctuations*, Academic Press, New York and London 1965.

[11] M. L. Mehta, *Random Matrices and the Statistical Theory of Energy Levels*, Academic Press, New York and London 1967.

[12] E. P. Wigner, *Proc. Camb. Philos. Soc.* **47**, 790 (1951).

[13] C. E. Porter, N. Rosenzweig, *Ann. Acad. Sci. Fennicae* **AVI**, No. 44 (1960).

[14] P. Yee, W. D. Knight, *Phys. Rev.* **B11**, 3261 (1975).