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REMARKS ON THE THERMODYNAMICS AND PARAMAGNETIC PROPERTIES OF ELECTRONS IN SMALL METAL PARTICLES

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In this note an expression for the low-temperature specific heat in the unitary ensemble is obtained by using the canonical partition function for a system of spinless fermions. A comparison with the numerical results presented by Czerwonko and Denton, Mühlschlegel and Scalapino is given.

Fröhlich [1] was the first to point out that the condition electrons in small metal particles inhabit quantized energy levels. Kubo [2] shoved that the average spacing δ between the levels near the Fermi surface is just the inverse of the density of states for the spin direction of the free electron gas

$$\delta = \tfrac{4}{3}\frac{E_F}{N} = \frac{2\pi^2\hbar^2}{Vm^*k_F},$$

where V is the volume of the particle, m^* is the effective mass of the electrons, N is the number of free electrons in the particle, k_F and E_F are the Fermi momentum and energy. The spectrum of a particle will appear discrete so long as the level width is less than the average spacing between the levels. This is satisfied when the average level spacing δ is much greater than the thermal energy kT, i. e., at low temperatures. Kubo argued that small metal particles at low temperatures remain electrically neutral, lacking sufficient energy to become charged. The constancy of electron number then implies that particles can be categorized as being even or odd, depending on whether they contain total even or odd numbers of conduction electrons. The even and odd particles are supposed to exhibit different thermodynamics and paramagnetic properties. Kubo considered, also, a system of particles and solved the statistical problem treating the level structure as a random variable with neighbor spacings following a Poisson distribution. Unfortunately, the

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probability distribution used by Kubo is not suitable, since in this distribution we have mutual "attraction" between levels. On the other hand, he presented an effective method of computing the partition function in a canonical ensemble.

The problem of averaging over ensembles of randomly separated energy levels has been extensively studied for the case of level statistics in large nuclei. Dyson [3] discussed this for various symmetries; he found three distinct ensembles. Gorkov and Eliashberg [4] applied these to the case of small metal particles to calculate, among other things, the spin susceptibility and the free energy for a vanishing magnetic field at low temperatures. 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 enseble 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 [5, 6] obtained the extension of Kubo's [2] and Gorkov-Eliashberg's [4] 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 kT much greater than δ and for kT much smaller than δ, i. e., at high and low temperatures, respectively. Independently, Denton, Mühlschlegel and Scalapino [7] have given, also, the extension of the results from [2, 4] in the whole temperature range. They calculated the specific heat and spin susceptibility by numerical methods and an interpolation scheme.

In this note we give an addendum to the papers [5, 6] after which one obtains the concordance, in limiting cases for high and low temperatures, with results obtained later in [7].

To calculate the thermodynamics and paramagnetic properties for a collection of small metal particles, one must use the appropriate partition function. For the magnetic field $H = 0$ the statistical distribution of energy levels is described by the orthogonal ensemble for weak spin-orbit coupling and by the symplectic ensemble as this coupling is increased [3]. These ensembles have levels which are twofold degenerate, for the orthogonal ensemble there are two spin directions and in the symplectic case there is the twofold Kramers degeneracy. Therefore in these cases the partition function Z in the form given by Kubo [2] is suitable

$$Z = \frac{1}{2\pi i} \oint \frac{dz}{z^{\alpha}} \prod_{\substack{k\geq 1 \\ s=\pm 1}} (1+ze^{sh-\beta\varepsilon_k}) \prod_{\substack{l\leq 0 \\ s=\pm 1}} \left(1+\frac{1}{z}e^{sh-\beta\varepsilon'_l}\right),$$

where α is equal to 1 and 0 for particles with even and odd N, 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 Fermi level ε_0, where ε_k referred to excited electrons above ε_0 and ε'_l referred to holes created in the levels below ε_0. The ground-state energy is chosen to give $\varepsilon_0 = 0$.

A using of the partition function Z in [6] for calculating low-temperature specific heat in the unitary ensemble is not appropriate, because the unitary ensemble describes a system with a large spin-orbit coupling in a sufficiently large magnetic field [3]. This should occur when $\frac{1}{2}g\mu_B H$ becomes of the order of the average level spacing δ. In this case there is no longer any energy level degeneracy, since the previously twofold degenerate levels with average level spacing δ are split apart, which produces a system with average level spacing $\delta' = \frac{1}{2}\delta$ and there would be no longer any even-odd distinction. Thus, in this case, the partition function for a spinless system is appropriate.

Now we calculate the low-temperature specific heat by using the canonical partition function for a system of spinless fermions, which is obtained from the Kubo partition function Z

$$Z_0 = \frac{1}{2\pi i}\oint \frac{dz}{z} \prod_{k\geq 1} (1+ze^{-\beta\varepsilon_k}) \prod_{l\leq 0}\left(1+\frac{1}{z}e^{-\beta\varepsilon'_l}\right).$$

If we calculate only the lowest order terms in the expansion of Z_0, when the temperature is much smaller than the average level spacing, then we obtain

$$Z_0 \sim \frac{1}{2\pi i}\oint \frac{dz}{z}(1+z^{-1})\left(1+z\sum_{k\geq 1} e^{-\beta\varepsilon_k}+\frac{1}{z}\sum_{l\leq -1} e^{-\beta\varepsilon'_l}+\ldots\right).$$

Performing the integration, we get

$$Z_0 = 1+\sum_{k\geq 1} e^{-\beta\varepsilon_k}+\ldots.$$

Hence the partition function Z_0 for the single level ε_1 has the form

$$Z_0 = 1+e^{-\beta\delta' x_1}$$

where $\varepsilon_1 = x_1\delta'$ and $\varepsilon_0 = 0$.

Denoting the statistical average over the specific heat as $\langle C_v\rangle$, we have

$$\langle C_v\rangle = k\beta^2 \frac{\partial^2}{\partial\beta^2}\int_0^\infty dx R_2(x)\ln Z_0,$$

where $R_2(x)$ is the two-level correlation function. For the unitary ensemble $R_2(x)$ is approximately given by $\frac{\pi^2 x^2}{3}$ for small x [8].

The last equation becomes

$$\langle C_v\rangle = \frac{\pi^2}{3}k\beta^2\frac{\partial^2}{\partial\beta^2}\int_0^\infty x^2\ln(1+e^{-\beta\delta' x})dx = -\frac{\pi^2}{3}k\delta'\beta^2\frac{\partial}{\partial\beta}\int_0^\infty \frac{x^3}{e^{\beta\delta' x}+1}dx.$$

The interval of integration can be reduced to (0, 1) by substituting $y = e^{-\beta\delta' x}$. Thus, performing the integration, we obtain the low-temperature specific heat in the unitary ensemble

$$\langle C_v \rangle = 8\pi^2 k \left(\frac{kT}{\delta'}\right)^3 \sum_{l=1}^{\infty} (-1)^{l+1} l^{-4} = 5.98 \times 10^2 k \left(\frac{kT}{\delta}\right)^3,$$

where $\delta' = \frac{1}{2}\delta$. This result coincides which the one stated in [7].

Finally, we note that two formulas in [5] for low temperatures are incorrectly calculated and must be exchanged. The formula (22) for the magnetization must read

$$\langle M \rangle = \frac{\mu_B}{2} \operatorname{th}(2\xi) + \frac{\mu_B \pi^2 \operatorname{sh}(4\xi)}{3(\varphi - \psi)} \left(\frac{kT}{\delta}\right)^2 \left[\tfrac{1}{2} \ln \varphi + \frac{\pi^2}{6} - 2 \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\psi^l}{l^2}\right],$$

where

$$\varphi = \psi^{-1} = \operatorname{ch}(4\xi) + 1 + \{\operatorname{ch}(4\xi)\,[\operatorname{ch}(4\xi) + 2]\}^{1/2}, \qquad \xi = \frac{\mu_B H}{2kT}.$$

Consequently the spin susceptibility in the orthogonal ensemble (cf. (24)) for $H = 0$ is

$$\chi = \chi_\infty \left[0.25 \left(\frac{\delta}{kT}\right) + 1.906 \left(\frac{kT}{\delta}\right)\right], \qquad \chi_\infty = \frac{2\mu_B^2}{\delta}.$$

The formula (35) for energy must read

$$\langle E \rangle = \frac{16\pi^4 \delta}{135} \left(\frac{kT}{\delta}\right)^6 \left[\tfrac{31}{126}\pi^6 + \tfrac{7}{12}\pi^4 \ln^2 \varphi + \tfrac{5}{12}\pi^2 \ln^4 \varphi + \tfrac{1}{12} \ln^2 \varphi\right]$$

and consequently the specific heat in the symplectic ensemble (cf. (36)) for $H = 0$ is

$$C_v = 2.415 \times 10^4 k \left(\frac{kT}{\delta}\right)^5.$$

After the above remarks one obtains the complete concordance of [5] with the numerical results given in [7].

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