Vol 15 No 5, May 2006
1009-1963/2006/15(05)/1075-06

Chinese Physics

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Electronic spin susceptibility of metallic superconductive nano-particles*

Li Feng(李 凤), Chen Zhi-Qian(陈志谦)†, and Li Qing(李 庆)

School of Materials Science and Engineering, Southwest University, Chongqing 400715, China

(Received 2 January 2005; revised manuscript received 20 February 2006)

We have observed the thermodynamic properties of metallic superconductive nano-particles in the grand canonical ensemble; and the level distribution and the level correlation between the discrete electronic energy levels are considered in the calculation of the electronic spin susceptibility of the ensemble numerically. The quantum effect, even–odd effect and other special effects existing in the metallic nano-particles are also studied in this article.

Keywords: nano-particles, random matrices theory, spin susceptibility
PACC: 7430E

1. Introduction

It is known that the thermodynamic properties of metallic nano-particles are very different from those of the bulk metal.[1−4] The volume and the number of electrons of a bulk sample are usually considered to be infinite, therefore its energy levels have a continuous distribution; but for a metallic nano-particle, its size and electrons cannot be thought to be infinite any more. Hence the energy levels have a discrete distribution, and there is an average level spacing δ between the two nearest-neighbour levels of the single-electron states. A mathematical relation is written as $\delta = 4\varepsilon_{\rm F}/3N \propto V^{-1}$ (here $\varepsilon_{\rm F}$ is the Fermi energy, N is the number of electrons and V is the nano-particle volume).[1] The discrete levels are discovered not only to exist in the nano-particles but also to have effect on the thermodynamic properties of the particles which cannot be neglected especially at low temperatures.[4] Then the conventional BCS theory will not be enough to deal with the superconductive metallic nano-particles. There exist deviation of the thermodynamic properties between the bulk and the superconductive nano-particles, and $\bar{\delta} = \delta/(k_{\rm B}T_{\rm c}) = 1/(N(0)Vk_{\rm B}T_{\rm c})$ is used as a symbol of the departure (here $k_{\rm B}$ Boltzmann constant, $T_{\rm c}$ is the superconductive transition temperature and $N(0)$ is the number of spin energy-states per volume).[2] The simplest view about the level distribution is that the levels are equally distributed. Kubo initially thought that the discrete energy levels of a single-particle appear to be Poisson-distributed.[1] When the surface irregularity of the metallic nano-particles is taken into account, there is a statistical method to describe the distribution: the levels conform to the distributions of three Gauss ensembles, i.e. Gauss orthogonal ensemble (GOE), Gauss symplectic ensemble (GSE), Gauss unitary ensemble (GUE), in the random matrices theory (RMT).[5]

2. Theoretical model

In order to investigate the spin susceptibility χ, we ignore the spin–orbit interaction. Here the spin is still regarded as a good quantum number. According to BCS theory, the reduced Hamiltonian for a nano-particle can be written as

$$\hat{H} = \sum_{j,\sigma} [(\varepsilon_j + h)c_{j\uparrow}^{+}c_{j\uparrow} + (\varepsilon_j - h)c_{j\downarrow}^{+}c_{j\downarrow}] - \lambda\delta \sum_{i,j}{}' c_{i\uparrow}^{+}c_{i\downarrow}^{+}c_{j\downarrow}c_{j\uparrow}\,, \quad (1)$$

where $\uparrow$ and $\downarrow$ mean spin up and down; the indices $i(j)$ labels the single particle energy levels with energy $\varepsilon_i(\varepsilon_j)$, and $c_{j\sigma}$ is the annihilation operator; the states of $|j\uparrow\rangle$ and $|j\downarrow\rangle$ are degenerate; λ is the usual dimensionless phonon-exchange coupling constant which is of an order of 1/4 to 1/2; the prime on the second summation implies a cutoff for states outside an energy shell $\pm\omega_{\rm D}$ (Debye frequency) about the Fermi

*Project supported by the National Natural Science Foundation of China (Grant No 10147207).
†E-mail: chen_zq@swnu.edu.cn

energy; $h = \frac{1}{2}g\mu_{\rm B}H$, where $\mu_{\rm B}$ is the Bohr magneton, H is the external magnetic field and we put g factor equal to 2.

When $H = 0$, the grand canonical partition function of the metallic superconductive nano-particles can be written as

$$Z = {\rm Tr}\exp[-\beta(\hat{H} - \mu N)]\,, \tag{2}$$

with $\beta = 1/k_{\rm B}T$, T is the temperature of the system and μ is the chemical potential.

Introducing a time-independent complex random field $\Delta(\tau) = \Delta^{+}(\tau) + {\rm i}\Delta^{-}(\tau)$, and

$$\Delta^{\pm}(\tau) = \sum_{n} \Delta_{n}^{\pm}\exp(-{\rm i}2n\pi/\beta)$$

with $\tau \in (0, \beta)$, then the Hubbard–Stratonovich transformation allows Eq.(2) to be represented as the path integral[2]

$$\begin{aligned} Z = &\int {\rm d}\Delta\exp\Big[-\pi\int_0^1 {\rm d}\tau|\Delta(\tau)|^2\Big] \\ &\times \prod_j {\rm Tr}\exp\Big[-\int_0^1 {\rm d}\tau\Big\{\beta(\varepsilon_j - \mu)(c_{j\uparrow}^{+}c_{j\downarrow} + c_{j\downarrow}^{+}c_{j\downarrow}) \\ &- (\pi\lambda\beta\delta)^{1/2}(\Delta(\tau)c_{j\uparrow}^{+}c_{j\downarrow}^{+} + \Delta^{*}(\tau)c_{j\downarrow}c_{j\uparrow})\Big\}\Big]\,. \end{aligned} \tag{3}$$

We cannot calculate Eq.(3) directly, so we turn to the static path approximation (SPA) for the integration. SPA includes all the static fluctuation via integrating over all the static path by $\int_0^{\infty}|\Delta_0|{\rm d}|\Delta_0|\int_0^{2\pi}{\rm d}\phi_0$. We observe the static limit of Eq.(3) in which $\Delta(\tau)$ is replaced by a complex number Δ_0. The trace appearing in Eq.(3) can now be performed as

$$\exp[-\beta[(\varepsilon_j - \mu) - E_j](1 + \exp[-\beta E_j])^2\,. \tag{4}$$

Changing the integration variable to $s = \pi\lambda\,|\Delta_0|^2$, we obtain the static approximation for Eq.(2)

$$\begin{aligned} Z = &\frac{1}{\lambda}\int_0^{\infty}{\rm d}s\exp\Big\{-\frac{s}{\lambda} - \sum_j\Big[\beta(\varepsilon_j - \mu) \\ &- \beta E_j - 2\ln(1 + \exp[-\beta E_j])\Big]\Big\}\,, \end{aligned} \tag{5}$$

with

$$\beta E_j = [\beta^2(\varepsilon_j - \mu)^2 + \beta\delta s]^{1/2}\,. \tag{6}$$

If $H \neq 0$, the trace in Eq.(3) can be written as

$$\exp[-\beta[(\varepsilon_j - \mu) - E_j]](1 + \exp[-\beta(E_j + h)])(1 + \exp[1 + \exp[-\beta(E_j - h)]])\,. \tag{7}$$

Now expanding the sum of the logarithms of field-dependent terms to the second order in βh yields

$$\ln\{1 + \exp[-\beta(E_j + h)]\} + \ln\{1 + \exp[-\beta(E_j - h)]\} = 2\ln\{1 + \exp[-\beta E_j]\} + (\beta h)^2 f(\beta E_j)[1 - f(\beta E_j)]\,, \tag{8}$$

where f is the Fermi function.

The interaction cutoff can be easily carried out by Eq.(4) divided by the free-fermion partition function

$$Z_0 = \prod_j \exp(-\beta[(\varepsilon_j - \mu) - |\varepsilon_j - \mu|])(1 + \exp[-\beta|\varepsilon_j - \mu|])^2\,. \tag{9}$$

Now we have

$$\frac{Z(h)}{Z_0} = \frac{Z}{Z_0}\left(1 + \frac{\int_0^{\infty}{\rm d}s\exp[-A(s)](\beta h)^2\sum_j f(\beta E_j)[1 - f(\beta E_j)]}{\int_0^{\infty}{\rm d}s\exp[-A(s)]}\right)\,, \tag{10}$$

where $Z(h)$ is the partition function in a magnetic field H, Z/Z_0 is the zero-field partition function

$$\frac{Z}{Z_0} = \frac{1}{\lambda}\int_0^{\infty}{\rm d}s\exp[-A(s)]\,, \tag{11}$$

which is used to remedy the interaction cutoff, and

$$A(s) = \frac{s}{\lambda} + \sum{}'[\beta|\varepsilon_j - \mu| - \beta E_j + 2\ln(1 + \exp[-\beta|\varepsilon_j - \mu|]) - 2\ln(1 + \exp[-\beta E_j])]\,, \tag{12}$$

where the prime implies a cutoff at $|\varepsilon_j - \mu| \leq \omega_{\rm D}$.

Now we investigate the distribution of the energy levels. Because of the time-reversed Hamiltonian and the existing of an external magnetic field, the three Gauss ensemble distributions within the framework of RMT are suitable for describing the distribution of energy levels. According to the RMT, the distribution functions for the three Gauss ensembles are

$$p(y)=\begin{cases}\dfrac{1}{2}y\exp\left(-\dfrac{1}{4\pi}y^2\right), & \text{(GOE)}\\ \left(\dfrac{64}{9\pi}\right)^3\left(\dfrac{y}{\pi}\right)^4\exp\left(-\dfrac{64}{9\pi^3}y^2\right), & \text{(GSE)}\\ \dfrac{32}{\pi^4}y^2\exp\left(-\dfrac{4}{\pi^3}y^2\right). & \text{(GUE)}\end{cases} \tag{13}$$

The distribution function of the GOE describes the case of weak magnetism and weak spin–orbit coupling. If the coupling interaction is strong, the GSE will be more suitable. If the particles are in a strong magnetic field and have strong spin–orbit coupling, the GUE ought to be used.[5–9] We have known that as magnetic fields increases, the spin degenerate energy levels will be split apart and the average nearest-neighbour level spacing becomes $\delta/2$, but we neglect this problem in this article and still implement the GUE in the two cases, i.e., even-electron and odd-electron systems. Furthermore, the distribution of the electronic energy levels may contain level correlation. According to the RMT, the level correlation functions of the three Gauss ensembles are respectively written as

$$R(x)=\begin{cases}1-\dfrac{\sin^2 x}{x^2}-\dfrac{\mathrm{d}}{\mathrm{d}x}\left(\dfrac{\sin x}{x}\right)\cdot\displaystyle\int_x^\infty\frac{\sin t}{t}\mathrm{d}t, & \text{(GOE)}\\ 1-\dfrac{\sin^2 2x}{(2x)^2}+\dfrac{\mathrm{d}}{\mathrm{d}x}\left(\dfrac{\sin 2x}{2x}\right)\cdot\displaystyle\int_0^x\frac{\sin 2t}{2t}\mathrm{d}t, & \text{(GSE)}\\ 1-\dfrac{\sin^2 x}{x^2}. & \text{(GUE)}\end{cases} \tag{14}$$

In Eqs.(13) and (14), $x=\pi(\varepsilon_i-\varepsilon_j)/\delta$, $y=\pi(\varepsilon_{i+1}-\varepsilon_j)/\delta$, where $(\varepsilon_i-\varepsilon_1)$ is determined by the level correlations $R(x)$, and $(\varepsilon_1-\varepsilon_0)$ is determined by the level distribution functions $p(y)$.[10]

We also consider the difference of the chemical potentials between the even case and the odd case. In this article, we suppose that the distribution of the electrons always enables the particles to possess the lowest energy.[4] The position of the chemical potential is related to the electronic energy levels:[6,8] in the even case the chemical potential lies halfway between the last filled and first empty levels; in the odd case it lies in the half filled level. So we have

$$\mu=\begin{cases}(\varepsilon_0+\varepsilon_1)/2, & s=0;\\ \varepsilon_1, & s=1/2;\\ (\varepsilon_1+\varepsilon_2)/2, & s=1;\\ \varepsilon_2, & s=3/2.\end{cases} \tag{15}$$

We can see that when $s=0$, $x=\pi(\varepsilon_i-\varepsilon_1)/\delta$, $y=\pi(\varepsilon_1-\varepsilon_0)/\delta$; when $s=1/2$, $x=\pi(\varepsilon_i-\varepsilon_2)/\delta$, $x=\pi(\varepsilon_2-\varepsilon_1)/\delta$, etc. Then we find that when $s=0$, $1/2$, 1, $3/2$, ..., the i in x and y is 1, 2, 3, 4, ... respectively; so we can replace $x+y/2$ by $x+(i+1)y/2$, i is for the spin.

3. The calculated results

Based on the above ideas, we calculate the spin susceptibility of an assembly of metallic superconductive nano-particles with integral spin or half integral spin. According to the thermodynamic relation

$$F=-kT\ln Z(h), \tag{16}$$

$$\chi=\left(\frac{1}{kT}\right)^2\frac{\partial^2 F}{\partial H^2}, \tag{17}$$

we obtain

$$\frac{\chi}{\chi_{\mathrm{P}}}=\frac{1}{2}\frac{t}{\bar{\delta}}\frac{\partial^2\ln Z(h)}{\partial h^2}, \tag{18}$$

with $t=T/T_{\mathrm{c}}$ and $\chi_{\mathrm{P}}=2\mu_{\mathrm{B}}^2/\delta$, where χ_{P} is the Pauli paramagnetism susceptibility.

In consideration of the distribution and correlation of energy levels, by taking the dimensionless coupling constant λ to be $1/2$, we calculate the integration (10) at $\bar{\delta}=0.01, 0.1, 1$; for each $\bar{\delta}$, we calculate for four different spins $s=0$, $1/2$, 1, $3/2$. We present the numerical results in Figs.1–3.

As is known, the GUE distribution is suitable for the particles in a strong magnetic field, and we investigate the influence of the field magnetic on the spin

susceptibility as well as the distribution and correlation of the energy levels. We have calculated those at $\bar{\delta}$ =0.01, 0.1 and 1 and for different spins. Here we illustrate those at $\bar{\delta} = 0.1$, $s = 1/2$ or 1 in Fig.4.

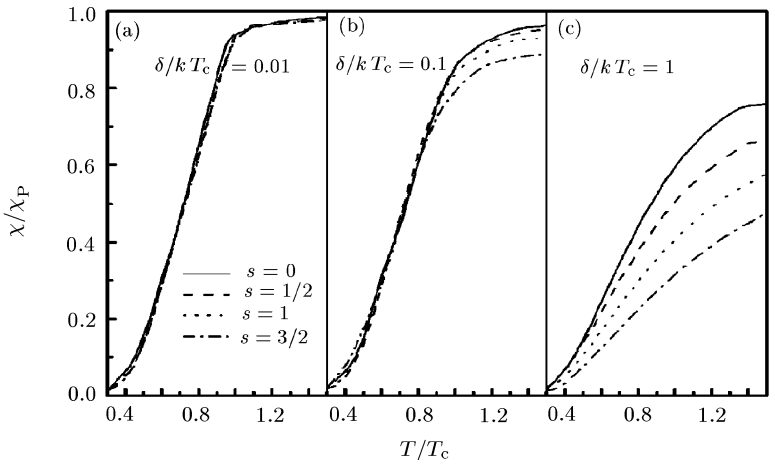


Fig.1. Influence of the energy's Gauss GOE distribution on the spin susceptibility of superconducting nano-particles against T/T_c.

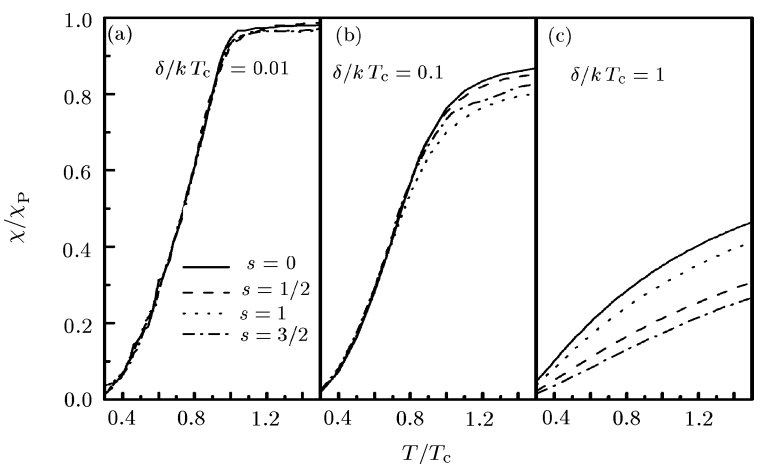


Fig.2. Influence of the energy's Gauss GSE distribution on the spin susceptibility of superconducting nano-particles against T/T_c.

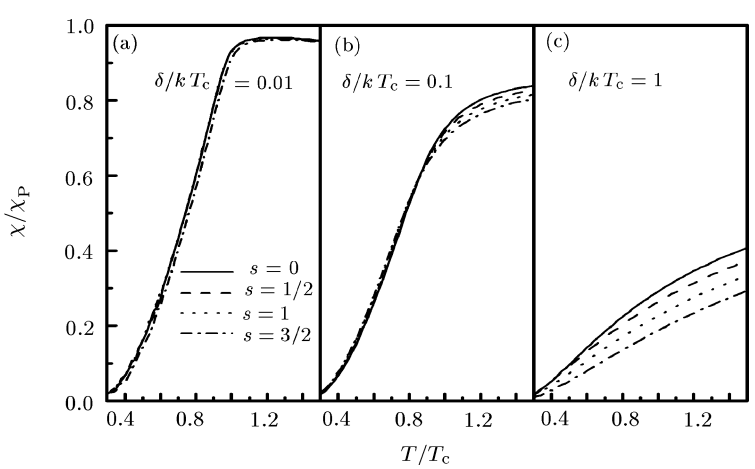


Fig.3. Influence of the energy level's Gauss GUE distribution on the spin susceptibility of superconducting nano-particles against T/T_c.

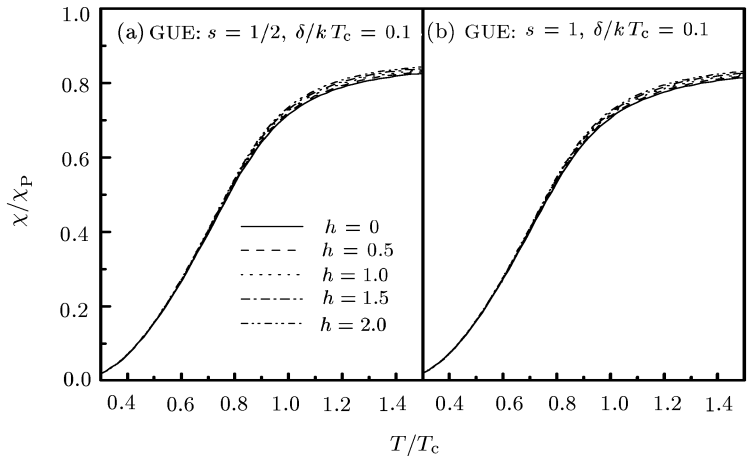


Fig.4. Influence of magnetic fields on the spin susceptibility of metallic superconductive particles against T/T_c.

4. Analysis and discussions

According to the BCS theory, the susceptibility of bulk metallic superconductors satisfies $\chi/\chi_P = 1$ when $T/T_c \geq 1$. However, from Figs.1–3, we find that even when $T/T_c = 1.5$, the susceptibility is still smaller than the Pauli paramagnetism. It is clear that the smaller the size of the particle, the wider the space between the energy levels; the bigger the value of $\bar{\delta}$ in the critical region, the smaller the susceptibility. We also can obtain the idea that for the particles which have the same $\bar{\delta}$ but different spin value, the higher the spin states, the smaller the susceptibility.

We can show that for $\bar{\delta} = 0.01$, $s = 0$, $T/T_c = 1.5$, the χ/χ_P are 0.98564, 0.96709 and 0.95875 for GOE, GSE and GUE respectively, all of them do not yet reach 1. From Figs.1–3, we can conclude that for the particles having the same spin states, the smaller the size, the smaller the susceptibility in the entire temperature region within which we have carried out calculations. That means that the quantum effects, surface effects and fluctuation effects have stronger influence on smaller sized particles.

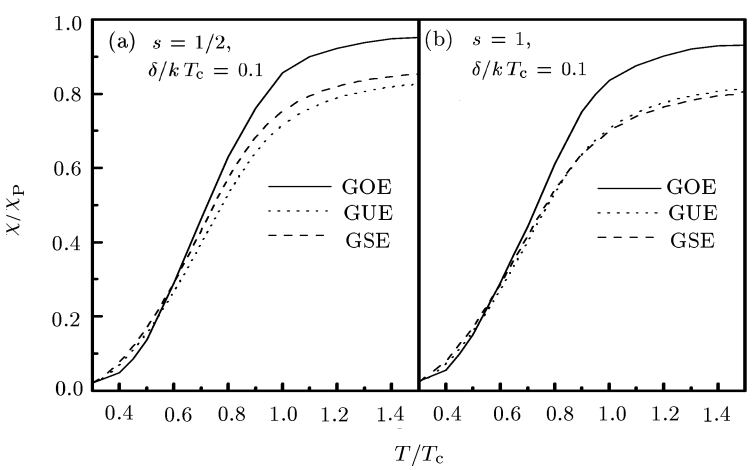


Fig.5. Influence of the three Gauss ensemble distributions on the spin susceptibility of metallic superconductive particles against T/T_c.

The influence of the three Gauss distributions on the susceptibility is shown in Fig.5. For the particles with the same $\bar{\delta}$ and spin, the curves related to the GOE distribution lie always above the curves related to the GSE and GUE distributions. After comparing the curves in Figs.1–3, we know that for the particles

with the same size and same spin, the influence of level distributions on the susceptibility of nano-particles are largest in GOE and smallest in GUE.

Figure 4 suggests that external magnetic fields have an effect on the spin susceptibility. The weak magnetic field leads to the slightly difference among the curves in Fig.4. If we put bigger h in the calculation, greater deviation is expected to appear. But magnetic field has stronger effect on the superconductivity of the nano-particles, a slightly large magnetic field can at once break down the superconductivity. This is the problem we shall discuss in another paper.

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