Vol 13 No 9, September 2004
1009-1963/2004/13(09)/1549-04

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

The heat capacity of small metallic grains studied by the random matrices theory*

Chen Zhi-Qian(陈志谦)†, Cheng Nan-Pu(程南璞), and Shi Zhen-Gang(施振刚)

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

(Received 18 February 2004; revised manuscript received 5 March 2004)

The random matrices theory is applied to a study of the heat capacity of small metallic grains. The numerical calculations indicate that the level distribution and the difference between the particles respectively with an even and an odd numbers of electrons are important for the heat capacity of the small metallic grains at a low temperature and the level correlation mainly affects the heat capacity at a high temperature.

Keywords: heat capacity, small metallic grains, random matrices theory
PACC: 7430E, 7115P, 7155D

Since Black, Ralph and Tinkham[1,2] found the superconductivity in a single small metallic grain, it has been studied deeply by various approaches,[3−12] whereas other properties, such as the heat capacity, have been nearly neglected in recent years. Due to their small size, compared with the bulk metal, the small metallic grains have different properties. For bulk samples, the volume and the number of electron number are considered to be infinite. The single-particle energy levels will form a quasi-continuum. But for the small metallic grains, their sizes and electron number are finite. There exists a mean nearest-neighbour level spacing δ, which is of the order of $\varepsilon_{\rm F}/N$, between the single-electron states, where $\varepsilon_{\rm F}$ is Fermi energy, N the number of electrons. Then the discrete feature of the single-particle energy levels will enter and affect the thermodynamic properties of the small metallic grains at a low temperature (LT).[13] In the simplest cases, one often considers the spacings of the single-particle energy levels to be equal (EQU) or Poisson-distributed (Poisson) and discusses the thermodynamic properties.[14] But when the surface irregularity of the small metallic grains is taken into account, the energy levels will distribute statistically and conform to the three Gauss ensemble distributions, i.e. Gauss orthogonal ensemble (GOE), Gauss unitary ensemble (GUE) and Gauss symplectic ensemble (GSE), of the random matrices theory (RMT)[15] which was developed in nuclear physics in the 1950s. Besides the discrete energy levels, another feature of the small metallic grains at a low temperature is the difference between the particles respectively with an even and an odd number of electrons, but this difference will vanish at a high temperature (HT).[16] Based on these ideas, we firstly calculate the heat capacity of an assembly of small metallic grains with an even or an odd number of electrons by using the level distribution functions. For the reason that only a few energy levels near the Fermi surface will strongly affect the heat capacity at low temperatures, as mentioned above, we calculate the heat capacity by considering the level distribution of only four energy levels near the Fermi surface with the level spacings of the other energy levels remaining equal. Furthermore, the distribution of the electronic energy levels may contain level correlation, so we bring the level correlation functions into the question. Our purposes are to reveal the properties of the heat capacity, the effects of the level distribution and the level correlation, and the difference between the odd-electron and the even-electron systems.

The number of electrons in the small metallic grains is finite and denoted by N. If the eigen values are E_j $(j = 1, 2, \ldots)$, the canonical partition function is

$$Z = \sum_{j=1,2,\ldots} \exp(-E_j/(k_{\rm B}T)). \qquad (1)$$

When the interactions among electrons are neglected,

*Project supported by the National Natural Science Foundation of China (Grant No 10147207) and the Chongqing Commission of Science & Technology.

†E-mail: chen_zq@swnu.edu.cn

each eigen value E_j can be regarded as the sum of each single particle's energy ε_i, i.e. $E_j = \sum_i n_i\varepsilon_i$. The number N of electrons in the small metallic grains can be written as

$$N = \sum_{ij} n_{ij}. \tag{2}$$

Hence the canonical partition function is

$$Z(N,T) = \sum_{j}^{(N)} \exp[-\beta(n_{1j}\varepsilon_1 + n_{2j}\varepsilon_2 + \cdots)]. \tag{3}$$

We introduce Lagranian λ and construct a creation function:

$$f(\lambda) = \sum_{N=0}^{\infty} Z(N,T)\lambda^N. \tag{4}$$

After several transformations, we obtain

$$Z(N,T) = \frac{1}{2\pi}\oint \frac{f(\lambda)}{\lambda^{N+1}}\mathrm{d}\lambda. \tag{5}$$

According to general thermodynamics, the heat capacity is determined by the following formula:

$$c/k_{\mathrm{B}} = \beta^2\frac{\partial^2 \ln Z}{\partial\beta^2}. \tag{6}$$

In correspondence with the RMT, there is an average level spacing δ and all levels present some distributions:[13]

$$w_N^{\gamma}(\varepsilon_1 \ldots \varepsilon_N) = C_N^{\gamma}\exp\left(-\frac{\gamma}{2}\sum_{i=1}^{N}\varepsilon_i^2\right)\prod_{j<k}|\varepsilon_j - \varepsilon_k|^{\gamma}, \tag{7}$$

where γ=0, 1, 2, 3 represent the Poisson distribution, the gauss orthogonal ensemble (GOE), the Gauss unitary ensemble (GUE), and the Gauss symplectic ensemble (GSE), respectively, and the C_N^{γ} is the normalization factor. The distribution function of level spacings ($\Delta_i = \varepsilon_{i+1} - \varepsilon_i$) is written as

$$p_{n-1}^{\gamma}(\Delta_1 \ldots \Delta_n) = \int_{-\infty}^{\infty} \mathrm{d}\varepsilon_1 w_{n+1}^{\gamma}(\varepsilon_1, \Delta_1, \ldots \Delta_n)$$

and

$$\int_0^{\infty}\mathrm{d}\Delta_1 \ldots \int_0^{\infty}\mathrm{d}\Delta_n p_{n-1}^{\gamma}(\Delta_1 \ldots \Delta_n) = 1. \tag{8}$$

Hence

$$\langle \ln Z\rangle = \int_0^{\infty}\mathrm{d}\Delta_1 \ldots \int_0^{\infty}\mathrm{d}\Delta_n p_{n-1}^{\gamma}(\Delta_1 \ldots \Delta_n)\ln Z. \tag{9}$$

Finally, we obtain

$$c/k_{\mathrm{B}} = \beta^2\frac{\partial^2 \langle \ln Z\rangle}{\partial\beta^2}. \tag{10}$$

Excessive levels make the calculation of Eqs.(5), (8) and (10) very difficult. However, at a low temperature, only a few levels near Fermi surface can make a considerable impact on the properties of the small metallic grains. Therefore we consider the distribution of the few levels and regard the others as the ones with equal level spacing (EQU). The electron configurations of the first to the fourth level are shown in Fig.1. The left column manifests the even electron case, and the right column manifests the odd case.

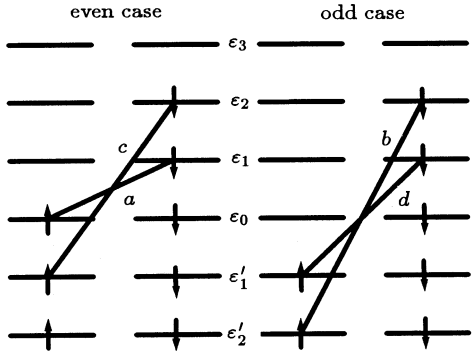


Fig.1. Configurations for even and odd numbers of electrons in the small metallic grains.

The calculations of Eq.(10) including 200 levels for Poisson, GOE, GUE, GSE and EQU are plotted in Fig.2. Figure 3 gives the curves in detail at a very low temperature, i.e. $k_{\mathrm{B}}T/\delta \leq 0.1$

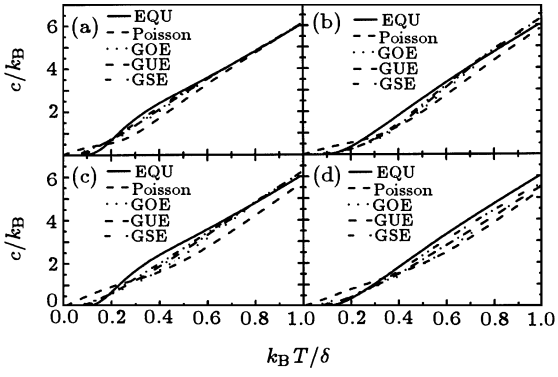


Fig.2. Variation of c/k_{B} vs $k_{\mathrm{B}}T/\delta$ for EQU, Poisson and other Gauss ensembles respectively with even (a, c) and odd (b, d) numbers of electrons.

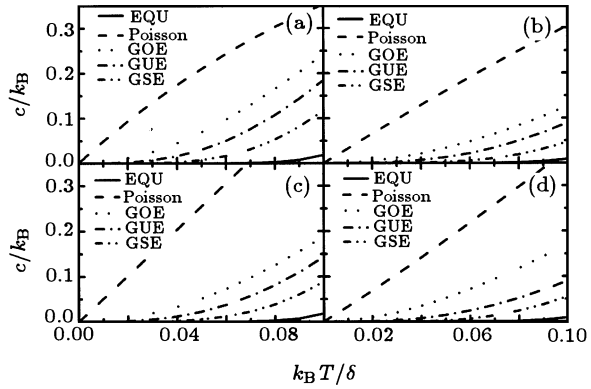


Fig.3. Variation of c/k_B vs k_BT/δ for EQU, Poisson and other Gauss ensembles respectively with even (a, c) and odd (b, d) electrons at a very low temperature.

Now we fit the various curves at a high temperature ($k_BT/\delta \geq 0.6$) and a very low temperature ($k_BT/\delta \leq 0.05$) in Table 1 and 2.

Table 1. Low and high temperature limits for EQU.

c/k_B	very low temperature	high temperature
even	$\to 0$	$6.1236k_BT/\delta$
odd	$\to 0$	$6.8623k_BT/\delta$

From Fig.2 we see that the lines of the heat capacity in all the cases are linear at high temperatures when $k_BT/\delta > 0.6$. But at low temperatures, namely $k_BT/\delta < 0.4$, the heat capacity except in the cases of Poisson-distributed and EQU, varies nonlinearly with the temperature. The heat capacity in the even case increases more quickly than that in the odd case at all the temperatures. From Table 2 we find that the heat capacity of the Poisson and the other three Gauss ensembles varies with the factor $(k_BT/\delta)^{\gamma+1}$ and increases in line with the law EQU→GSE→GUE→GOE→ Poisson at a very low temperature ($k_BT/\delta \leq 0.05$) for the corresponding level distribution. In the low temperature limit $k_BT/\delta \ll 1$, the nearest-neighbour level spacing Δ, compared with the average level spacing, is small, and only the first order of the level distribution functions is important. At this point, the probability density of finding two energy levels with a given nearest-neighbour level spacing is proportional to $(k_BT/\delta)^{\gamma}$ and exactly embodied in the level repulsion between the nearest-neighbour energy levels for different statistical ensembles. The energy variation of these levels is $\propto k_BT$, so the heat capacity complies with the power law $T^{\gamma+1}$. That is to say, the level distribution is very important and should be considered at low temperatures. At high temperatures, the lines of the heat capacity for the different distributions are roughly parallel and change following the rule Poisson →GSE→GUE→GOE→EQ, but in the even and odd cases they tend to be consistent in the high temperature limit (the case of the Poison-distributed is unreasonable at this point; when all the energy levels are considered, this will be corrected, see as follows). It suggests that, at high temperatures, the energy levels will form a quasi-continuum spectrum, then the effect of the level distribution and the difference between the particles respectively with an even and an odd number of electrons will vanish.

Table 2. Low and high temperature limits for Fig.2 (a, b, c, and d) in which $\alpha = k_BT/\delta$.

c/k_B	a		b		c		d	
	LT	HT	LT	HT	LT	HT	LT	HT
Poisson	4.334α	7.09α	5.1α	7.94α	3.22α	7.87α	3.45α	7.32α
GOE	$27.8\alpha^2$	6.61α	$20.6\alpha^2$	7.77α	$13.5\alpha^2$	7.84α	$21.2\alpha^2$	7.86α
GUE	$244.5\alpha^3$	6.51α	$180\alpha^3$	7.34α	106α	7.41α	$117\alpha^3$	6.86α
GSE	$3\times10^4\alpha^5$	6.42α	$1.7\times10^4\alpha^5$	7.05α	$8\times10^3\alpha^5$	7.1α	$7\times10^3\alpha^5$	6.52α

In Fig.2 and Table 2, when the level correlation is considered, the variations of the heat capacity for all the different level distributions at low temperatures are very small. At high temperatures, although all the lines of the heat capacity are linear and parallel, the values increase a little more in accordance with the rule GSE→GUE→GOE→EQU→Poisson (the Poisson case changes a lot comparatively) and they tend to be more consistent in the high temperature limit. Here we know that the contributions of all the energy levels are taken into account, so it could be considered as an accurate result. In order to reveal to what extent the level distribution of only four energy levels near the Fermi surface is accurately considered, one can make comparisons as follows. For GOE (even case),

$$\begin{cases} 28.36(k_BT/\delta)^2/28.5(k_BT/\delta)^2 \approx 0.995 & k_BT/\delta \leq 0.05 \\ 6.63(k_BT/\delta)/6.18(k_BT/\delta) \approx 1.073 & k_BT/\delta \geq 0.60 \end{cases} . \tag{11}$$

Hence, without any strict requirement, it is reasonable to take only the effect of the level distribution of the four levels near the Fermi energy into account in the low temperature limit and consider the energy levels to be equal at a higher temperature.

Here we should mention the experimental results of Pd and Fe.[14,15] In Ref.[17], the authors found that the heat capacity of Pd particles (with weak magnetism and weak spin-orbit coupling) with a diameter $d \approx 15$nm was $\propto T^2$ at a low temperature and $\propto T$ at a high temperature. In Ref.[18], it was indicated that the heat capacity of the Fe particles with an average size of 40nm was $\propto T^2$ at a low temperature. Our theoretical results, including the values and $T^{\gamma+1}$ law of the heat capacity, of GOE qualitatively coincide with those experimental results well.

From the above analyses, we can draw the conclusions as follows: (1) level statistics should be considered in small metallic grains due to the discrete electronic energy levels; (2) at low temperatures, only several energy levels are important for the heat capacity; (3) the level distribution and the difference between the particles respectively with an even and an odd number of electrons are important for the heat capacity of the small metallic grains at a low temperature, but these effects will vanish at a high temperature; (4) the level correlation mainly affects the heat capacity at a high temperature.

References

[1] Black C T, Ralph D C and Tinkham M 1996 *Phys. Rev. Lett.* **76** 688

[2] Ralph D C, Black C T and Tinkham M 1995 *Phys. Rev. Lett.* **74** 3241

[3] von Delft J *et al* 1996 *Phys. Rev. Lett.* **77** 3189

[4] Smith R A and Ambegaokar V 1996 *Phys. Rev. Lett.* **77** 4962

[5] Matveev K A and Larkin A I 1997 *Phys. Rev. Lett.* **78** 3749

[6] Berger S D and Halperin B I 1998 *Phys. Rev.* B **58** 5213

[7] Chen Z Q *et al* 2000 *Chin. Phys. Lett.* **17** 762

[8] Chen Z Q *et al* 2000 *Acta Phys. Sin.* **49** 969 (in Chinese)

[9] Chen Z Q *et al* 2001 *Chin. Phys. Lett.* **18** 592

[10] Chen Z Q *et al* 2001 *Chin. Phys.* **10** 1149

[11] Chen Z Q *et al* 2002 *Acta Phys. Sin.* **51** 649 (in Chinese)

[12] Chen Z Q *et al* 2001 *Chin. Phys.* **12** 1445

[13] Denton R, Mühlschlegel B and Scalapino D J 1973 *Phys. Rev.* B **7** 3589

[14] Kubo R 1962 *J. Phys. Soc. Jap.* **17** 975

[15] Mehta M L 1991 *Random Matrices* (Boston, MA: Academic)

[16] Denton R, Mühlschlegel B and Scalapino D J 1973 *Phys. Rev.* B **7** 3589

[17] Volokitin Y, Sinizig J, De Jongh L J *et al* 1996 *Nature* **384** 621

[18] Bai H Y, Luo J L and Jin D 1996 *J. Appl. Phys.* **79** 361