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Thermodynamic properties of ultra-small metallic particles*

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The thermodynamic properties of ultra-small metallic particles within an ensemble are affected by the level distribution and the level correlation between the discrete electronic energy levels. The specific heat and spin susceptibility of ultra-small metallic particles in the canonical ensemble with an odd or even number of electrons are numerically calculated by considering the effects of the level statistics, and their behaviour at low and high temperatures is also discussed. As an example, the specific heat and spin susceptibility of nano-Al particles are calculated numerically in this paper.

Keywords: ultra-small metallic particles, specific heat, spin susceptibility, level statistics
PACC: 6540, 6740K

1. Introduction

Ultra-small metallic particles, with their special physical and chemical properties, are widely used in aircrafts, transportation vehicles and electronic industries in powder metallurgy. Also some physicists have devoted attention to the thermodynamic properties of the ultra-small metallic particles.[1−9] With their small and finite sizes, compared with the bulk metal, the ultra-small metallic particles have different properties/characteristics. The volume and the number of electrons of the bulk metal are often considered to be infinite, so the single-particle energy levels will form a quasi-continuum. However, the sizes and numbers of electrons of the ultra-small metallic particles are finite, and there is an average nearest-neighbour level spacing $\delta = \dfrac{4\varepsilon_{\rm F}}{3N}$ between the single-electron states, where $\varepsilon_{\rm F} = \dfrac{\hbar^2}{2m}\left(3\pi^2 n_{\rm e}\right)^{2/3}$ is Fermi energy, $N = n_{\rm e}V = n_{\rm e}\dfrac{4}{3}\pi\left(\dfrac{d}{2}\right)^3$ (the particle is supposed to be spherical) is the total number of the conduction electrons contained in a single metallic particle, m is the mass of electron, $n_{\rm e}$ is the density of electrons and d is the effective diameter of the ultra-small metallic particles. Then the single-particle energy levels show the discrete feature that will affect the thermodynamic properties of the ultra-small metallic particles at low temperature (LT).[6,7] Another feature of this kind of system consisting of ultra-small particles, at low temperature, is the parity of the electrons contained in the metallic particles due to their finite sizes.[8] But the effects that come from the two features mentioned above will vanish at high temperatures.[7,8] Furthermore, due to the localized impurities and the surface states of these ultra-small metallic particles, the level correlation between two arbitrary energy levels should be considered in the questions discussed in this paper.[9] In order to calculate the thermodynamic properties conveniently, one used to regard the nearest-neighbour level spacings of the single-electron energy levels as to be equal (EQ) or Poisson-like (Poisson).[7] But when the surface irregularity of the ultra-small metallic particles (especially the light metal) is considered, according to random-matrix-theory (RMT),[10] the energy levels conform to the Gauss orthogonal ensemble (GOE): namely, the Wigner-like-distributed one. Our purposes in this paper are to reveal (1) the properties

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of the specific heat and spin susceptibility; (2) the effects of the level statistics; (3) the differences between the odd-electron and the even-electron systems; (4) numerical calculation of the variation of the specific heat and spin susceptibility with temperature and (5) the effects of the sizes of the ultra-small metallic particles on their thermodynamic properties.

2. Theoretical model

Considering an assembly that consists of ultra-small metallic particles with the same size and conserved electrons, we discuss the problems in canonical ensemble based on the principles of thermodynamics. On the assumption that the eigenvalues are E_j ($j = 1, 2...$), the canonical partition function of the observed systems reads as[6]

$$Z = \sum_{j=1,2...} \exp\left(-E_j/k_{\mathrm{B}}T\right). \tag{1}$$

If the interaction between the electrons is not taken into account, each eigenvalue E_j will be replaced by the sum of the single-electron energy ε_i, i.e. $E_j = \sum_i n_{ij}\varepsilon_i$. Here $\sum_{i,j} n_{ij} = N$ is the total number of electrons in the observed particle. Then the partition function is represented by

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

with $\beta = 1/k_{\mathrm{B}}T$.

Using the Lagrangian multiplier, one can obtain the generating function[6]

$$f\left(\lambda\right) = \sum_{N=0}^{\infty} Z\left(N,T\right)\lambda^N. \tag{3}$$

Now we substitute $Z\left(N,T\right)$ into Eq.(3) and obtain

$$f\left(\lambda\right) = \sum_{N=0}^{\infty}\left(\sum_{j}^{(N)} \exp\left[-\beta n_{ij}\varepsilon_i\right]\lambda^{n_{ij}}\right). \tag{4}$$

The generating function $f\left(\lambda\right)$ is analytic in the whole complex plane and the partition function will change its form into

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

If there exists an external magnetic field H, the partition function Eq.(5) is represented by[6]

$$Z\left(N,T,H\right) = \frac{1}{2\pi\mathrm{i}}\oint \frac{\mathrm{d}\lambda}{\lambda}\lambda^r \prod_{\substack{l=0\\ s=\pm1}}^{p-1}\left[1+\left(\frac{1}{\lambda}\mathrm{e}^{sh}\mathrm{e}^{-\beta\varepsilon_l'}\right)\right] \times \prod_{\substack{k=1\\ s=\pm1}}^{\infty}\left[1+\left(\lambda\mathrm{e}^{sh}\mathrm{e}^{-\beta\varepsilon_k}\right)\right] \tag{6}$$

with $h = \frac{1}{2}\beta g\mu_{\mathrm{B}}H$, where g is the Lande factor (as for Al, $g = 2$), and μ_{B} the Bohr magneton. $r = 0$ or 1 represents the case of the even or odd number of electrons contained in a metallic particle. Here we must point out that the first product in Eq.(6) contains all the energy levels below the Fermi energy (the ground state) and the second one describes the contribution of all the levels above the Fermi energy. But it is very difficult to make sure of the value of p in the first product. Fortunately, for convenience in the numerical calculation, the first product can be reasonably extended to infinity because of the thermal degeneracy $p\delta\beta \gg 1$. In this paper, the effects of external magnetic field are not considered, namely, $H = 0$ in Eq.(6). According to thermodynamics, the specific heat and the spin susceptibility are respectively defined as

$$\begin{aligned} c =& -T\frac{\partial^2 F}{\partial T^2} \\ =& T\frac{\partial^2\left(k_{\mathrm{B}}T\ln Z\right)}{\partial T^2} \\ =& k_{\mathrm{B}}\beta^2\frac{\partial^2 \ln Z}{\partial\beta^2}, \end{aligned} \tag{7}$$

$$\begin{aligned} \chi =& -\lim_{H\to 0}\frac{\partial^2 F}{\partial H^2} \\ =& \lim_{H\to 0}\beta^{-1}\frac{\partial^2 \ln Z}{\partial H^2}, \end{aligned} \tag{8}$$

where $F = -k_{\mathrm{B}}T\ln Z$ is the free energy.

The nearest-neighbour level spacings of the energy levels are defined as $\Delta_i = \varepsilon_{i+1} - \varepsilon_i$ ($i = 0, 1, 2, \cdots$), and they should be normalized as $x_i = \Delta_i/\delta$,[10−16] Where δ is the average nearest-neighbour level spacing, and x_i is the normalized nearest-neighbour level spacing. According to RMT, the level distribution functions of the normalized nearest-neighbour level spacings (the probability density for finding two adjacent levels with normalized level spacing x) for the Poisson distribution (random spectra) and the Gauss orthogonal ensemble (GOE) respectively are[10−16]

$$p\left(x\right) = \begin{cases} \mathrm{e}^{-x}, & \text{Poisson,} \\ \dfrac{\pi}{2}x\mathrm{e}^{-\frac{\pi}{4}x^2}, & \text{GOE.} \end{cases} \tag{9}$$

The level correlation function between two arbitrary energy levels is defined as[10−17]

$$R(\varepsilon) = \delta \left\langle \sum_i \delta\left(\varepsilon - (\varepsilon_i - \varepsilon_0)\right) \right\rangle, \tag{10}$$

where the symbol δ in the bracket $\langle \cdots \rangle$ represents the δ function. According to RMT, the level correlation functions in the Poisson and GOE case are respectively given by[10−17]

$$R(y) = \begin{cases} 1, & \text{Poisson}, \\ 1 - \left(\dfrac{\sin(\pi y)}{\pi y}\right)^2 - \dfrac{\mathrm{d}}{\mathrm{d}y}\left(\dfrac{\sin(\pi y)}{\pi y}\right) \displaystyle\int_y^\infty \frac{\sin(\pi t)}{\pi t}\mathrm{d}t, & \text{GOE}. \end{cases} \tag{11}$$

Substituting the level distribution and the level correlation functions ($p(x)$ and $R(y)$) into the partition function $Z(N,T)$ Eq.(5), we may change the form of the products in the partition function as

$$\prod_k f(\varepsilon_k) = \mathrm{e}^{\sum_k \ln f((\varepsilon_k - \varepsilon_1) + (\varepsilon_1 - \varepsilon_0))}. \tag{12}$$

Consequently, $\varepsilon_i - \varepsilon_1$ term in $Z(N,T)$ is determined by the level correlations $R(y)$, and $\varepsilon_1 - \varepsilon_0$ (let the Fermi energy ε_0 be 0) is described by the level distribution functions $p(x)$. So, after considering the effects of level distribution and level correlation, the ensemble averages of specific heat and spin susceptibility of ultra-small metallic particles are represented by

$$c/k_\mathrm{B} = \beta^2 \frac{\partial^2 \langle \ln Z \rangle}{\partial \beta^2}, \tag{13}$$

$$\chi = \lim_{H \to 0} \beta^{-1} \frac{\partial^2 \langle \ln Z \rangle}{\partial H^2}. \tag{14}$$

3. Theoretical results

As for the light metal, according to RMT, using GOE to describe the observed system is suitable due to the weak magnetism and weak spin–orbit coupling.[10] But we also give the results of the cases that the energy levels are equal to each other or Poisson-distributed for comparison. The general results (the size of the particle is not concretely determined) of specific heat and spin susceptibility (compared with the Pauli susceptibility $\chi_\mathrm{p} = 2\mu_\mathrm{B}^2/\delta$) are plotted in Figs.1 and 2, and the numerical fitting for low temperature (LT) and high temperature (HT) limits are given in Tables 1 and 2, respectively. Then we calculate the specific heat and spin susceptibility of the ultra-small Al particles with a definite size within GOE. In this paper we only consider three cases of $d = 16, 20, 24$nm, and the numerical results of the molar specific heat and susceptibility are shown in Figs.3 and 4, respectively.

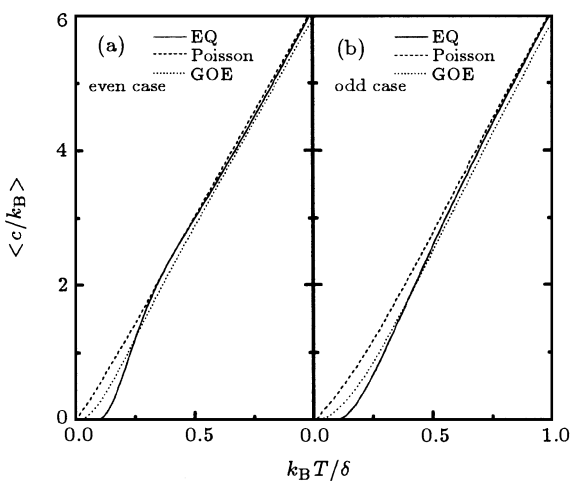


Fig.1. Variations of c/k_B vs $k_\mathrm{B}T/\delta$ for equal, Poisson, and GOE distributions. (a) Even case; (b) odd case.

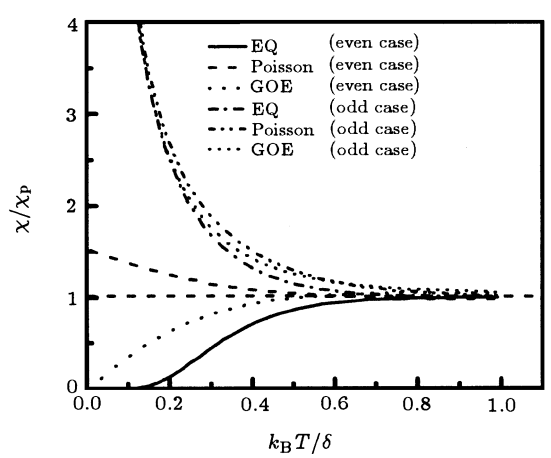


Fig.2. The variations of χ/χ_p vs $k_\mathrm{B}T/\delta$ for EQ, Poisson, and GOE distributions.

Table 1. The fitting results of c/k_B vs $k_BT/\delta = \alpha$ in Fig.1 at low ($k_BT/\delta \leq 0.05$) and high ($k_BT/\delta \geq 0.6$) temperatures (LT and HT).

	EQ		Poisson		GOE	
	LT	HT	LT	HT	LT	HT
Even	$1650.05e^{-\frac{1}{\alpha}}$	6.03α	5.07α	6.21α	$28.5\alpha^2$	6.18α
Odd	$825.024e^{-\frac{1}{\alpha}}$	6.86α	3.38α	6.64α	$16.8\alpha^2$	6.8α

Table 2. The fitting results of χ vs $k_BT/\delta = \alpha$ in Fig.2 at low ($k_BT/\delta \leq 0.05$) and high ($k_BT/\delta \geq 0.9$) temperatures (LT and HT).

	EQ		Poisson		GOE	
	LT	HT	LT	HT	LT	HT
Even	$40.6\chi_p e^{-\frac{1}{\alpha}}$	χ_p	$1.\ 521\chi_p(1-\alpha)$	χ_p	$3.565\chi_p\alpha$	χ_p
Odd	$\chi_p/2\alpha$	χ_p	$\chi_p/2\alpha$	χ_p	$\chi_p/2\alpha$	χ_p

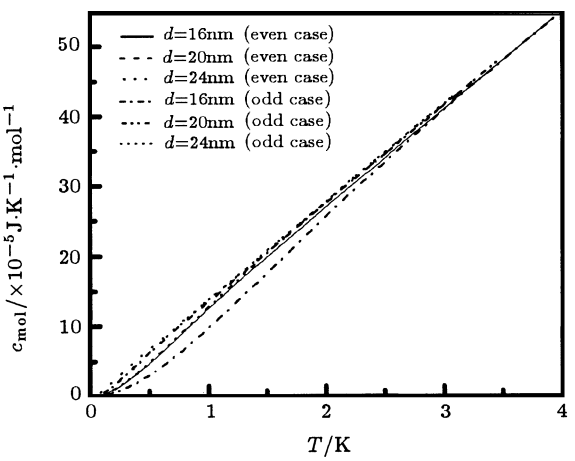


Fig.3. The variation of the molar specific heat c_{mol} vs T for Al particles with d=16, 20 and 24nm (in GOE).

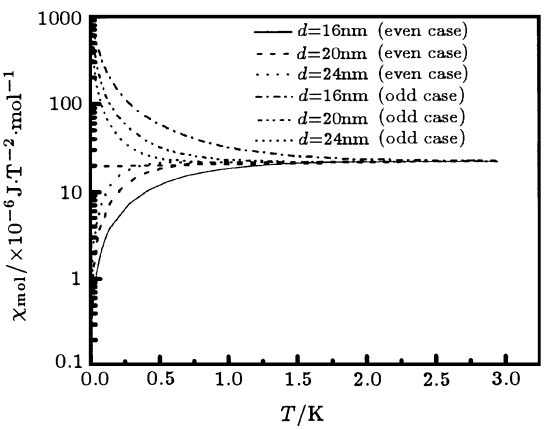


Fig.4. The variation of the molar spin susceptibility χ_{mol} vs T for Al particles with d=16, 20 and 24nm (in GOE).

4. Discussion

From Figs.1 (a) and 1(b) and Table 1, we find that, at low temperatures, the specific heat increases with the rule EQ→GOE→Poisson, but it changes to GOE→EQ→Poisson at high temperatures. The specific heat in the even case increases more quickly than that in the odd case in the whole range of temperatures. At low temperatures, $k_BT/\delta < 0.6$, the specific heat, except for the cases of Poisson, varies nonlinearly with the temperature, while at high temperatures $k_BT/\delta > 0.6$, the lines of the specific heat vary linearly with temperature and tend to be coincident with each other in the high temperature limit. The level distribution functions in Eq.(9) contain a factor x^γ that represents the form of the short-range level repulsion ($\gamma = 0$: Poisson, $\gamma = 1$: GOE).[10,13] In the low temperature limit $k_BT/\delta \ll 1$, the nearest-neighbour level spacing Δ in its definition, compared with the average level spacing, is very small and only the first order of the level distribution function $p(x)$ is important. At this time, the probability density to find two energy levels with a given nearest-neighbour level spacing is proportional to $(k_BT/\delta)^\gamma$. The energy variation unit of these levels is $\propto k_BT$, so the specific heat of Poisson and GOE complies with the power law $T^{\gamma+1}$ in the low temperature limit ($k_BT/\delta \leq 0.05$).

From Fig.2 and Table 2 we see that the spin susceptibilities increase with the law EQ→GOE→Poisson at low temperatures, and tend to the Pauli susceptibility χ_p in the high temperature limit. But there exists an important phenomenon that the susceptibilities in the odd case exhibit the Curie-law behaviour at low temperatures, while that in the even case rises with the temperature. The presence of unpaired spins on odd-electron particles causes these odd–even effects.[6] So, from Figs.1 and 2 (also Tables 1 and 2) we know that the effects of the distributions of the discrete energy levels and the parity of the electrons are much more important at low temperatures.

However, all these discrepancies will vanish because the energy levels will form a quasi-continuum spectrum at high temperatures.

Our numerical results of specific heat and susceptibility within GOE shown in Figs.1 and 2 coincide with the experimental results of ultra-small Pd particles. So we calculate the molar specific heat and susceptibility of ultra-small Al particles within GOE for different sizes (d=16, 20, 24nm) and plot the numerical results in Figs.3 and 4. Now, we find that the laws of the molar specific heat and susceptibility are similar to that of GOE in Figs.1 and 2. That is to say, $c \propto T^2$, $\chi^{\rm o} \propto 1/T$ and $\chi^{\rm e} \propto T$ in low temperature limit, and $c \propto T$ and $\chi^{\rm e/o} \rightarrow$ constant at high temperatures. At the same time, the molar specific heat increases with the increasing of the size of Al particles. The molar susceptibility in the even case increases with the size while that in the odd case decreases. But, for different sizes, the molar susceptibilities tend to the same constant at relatively high temperatures. That means the quantum size effects will vanish at high temperatures. Our numerical results of specific heat and susceptibility for Al particles within GOE in our calculation are qualitatively similar to the experimental results of Pd and Fe,[18,19] but they need to be further corroborated by experiments.

5. Conclusions

From the numerical calculations and analysis of specific heat and susceptibility of ultra-small metallic particles given above, we can draw the conclusions as follows: (1) level statistics should be considered in dealing with ultra-small metallic particles due to the discrete electron levels; (2) the variations of the specific heat and susceptibility with the temperature are: $c^{\rm e/o} \propto T^2$, $\chi^{\rm e} \propto T$ and $\chi^{\rm o} \propto 1/T$ in the low temperature limit, and $c^{\rm e/o} \propto T$ and $\chi^{\rm e/o} \rightarrow$ constant in the high temperature limit; (3) the molar specific heat increases with the size of the Al particles, while the molar susceptibility in the odd case decreases and that in the even case increases with the size at a given temperature; (4) the effects of the discrete electronic levels and the parity of electrons are important for the thermodynamics of the ultra-small Al particles at low temperatures, but they will vanish at high temperatures.

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