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Shell Effects in Small Metal Particles

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By assuming periodic discrete electronic spectra, the properties of small metal particles are analyzed. The canonical partition function is obtained exactly. The heat capacity and the electronic magnetic susceptibility are calculated in the presence of a static magnetic field. These results are an extension of the calculations for an equally spaced spectrum. Preliminary considerations of the statistical theory of spectra are included.

KEY WORDS: Metal clusters; electron energy states; shell model; electronic specific heat; magnetic susceptibility; partition functions; electron level density.

1. INTRODUCTION

Atomic clusters or sufficiently *small metal particles* are physical systems which can be studied using discrete single-particle spectra on which fermions or bosons are distributed.(1,2) Generally, a large (but finite) number of delocalized electrons is assumed to move in a finite space region. This region is given by a cluster or a "small particle" of few up to thousands of atoms or molecules. In the recent years, methods of nuclear physics have been applied successfully to these systems (see ref. 3 and contributions in ref. 4). Both aspects have been considered: the methods of random matrices and the shell model. The former has been applied not only to the level spacing distributions as in nuclear physics, but also to the theory of conductance in small conductors.(5) However, this important and vast field will not be contemplated here. Rather, the second aspect concerning shell effects will concern us.

Electronic shell structure in metal clusters is a field of intensive research.(4) This structure was first reported for sodium clusters by Kappes *et al.*(6) and Knight *et al.*(7) For a review on the electronic shell structure

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in metal clusters see ref. 8. More recently, Göhlich *et al.*(9) analyzed the mass spectrum of $Cs_{n+2}(SO_2)$ clusters with a pulsed dye laser and a time-of-flight mass spectrometer. They observed a clear shell structure effect manifested as an abrupt increase or decrease of the mass-peak intensity at certain "magic" values of n ranging from 58 up to 557 ± 5. A simple explanation given by Göhlich *et al.* of the mass spectra is the following. The delocalized electrons move freely in the cluster and occupy subshells of constant angular momentum. Therefore, the clusters will not appear in the mass spectra when one of these subshells is closed and the laser photon energy is smaller than the ionization energy. Also, numerical shell model calculations have been performed by Göhlich *et al.* supporting this approach. For larger clusters, temperature-dependent shell effects can result from the layer packing of the atoms.(10)

The arrangement of atoms in a cluster depends on many factors, for example, on their preparation and their size. The possible kinds of discrete spectra are very diverse and thus a general method is needed to classify spectra according to a small number of mathematical quantities.

Another important similar problem is the study of (isolated) quantum dots. These are small regions on semiconductors where the electrons move in a potential well of parabolic-like form. Typical radii of a quantum dot are of the order of 10^{-7} m, containing ten to hundreds of electrons.(11)

As early as 1937, Fröhlich(12) considered small metallic particles using methods for a bulk metal and studied quantum size effects on the electronic specific heat. The most important observation was that the mean spacing between levels decreases with increasing particle size. In fact, the average level separation δ near the Fermi level ε_F is $\delta = 2/\rho(\varepsilon_F)$, where $\rho(\varepsilon_F)$ is the density of states evaluated at ε_F. For a system of N conduction electrons in a small particle it follows that δ is of order ε_F/N. Thus, for a small metallic particle of size of order 10^{-8} m and containing about 10^5 conduction electrons it would correspond to $\delta \approx 0.1$ meV or equivalently a temperature of $\delta/k_B \approx 1$ K. Fröhlich considered a *constant single-particle spectrum*, but Kubo(13) replaced it by a *random spectrum* (with Poisson spacings distribution). Kubo included additionally the important distinction between an even and an odd number of electrons, first noted by Greenwood *et al.*(14) Finally, Gor'kov and Eliashberg(15) pointed out the possibility of using the more general distributions used in nuclear physics. These considerations are of importance for the low-temperature behavior of the specific heat averaged over the size and shape distributions of all particles in a sample.

But here our point of view departs toward the study of general single-particle spectra and the degree of "bunching" of the single-particle levels into shells. These aspects are necessary to understand the mass spectra of clusters and phenomena such as the density of excited states of individual clusters or also of colloids, gases, and plasmas containing them. We remark that the basic assumption in the nuclear case and in the metal particle case is the existence of an average potential well. In this well, the fermions are considered to move essentially as free particles.

The simplest way to take into account shell effects is to assume a periodic spectrum. As we shall show, this makes it possible to obtain explicit analytic results. This is important for the understanding of experimental results by means of simple phenomenological formulas, instead of involved computer calculations. Of course, in realistic physical models the single-particle spectra are far from being periodic. However, if we are only interested in the excited system not very far from the Fermi level, it becomes reasonable to consider an average constant level spacing. The width of the shell and the distribution of its levels are arbitrary but fixed quantities. The associated parameters could be used to mimic, for example, residual interactions, deformation of the cavities, etc. The validity of this approximation is supported by its extensive use in nuclear physics applications.(16) In problems connected with nuclear reactions, the estimation of the nuclear level density is essential. This quantity is usually calculated assuming a constant single-particle level density. The underlying combinatorial problem is in large part responsible for the importance of the average single-particle level density at the Fermi level and for the exponential increase of the nuclear level density. Shell effects and pairing correlation contributions are included phenomenologically, motivated in part by analytical studies based on periodic spectra. We expect that the analytic results of this work can be applied to find simple formulas for the description of thermodynamic properties of metal clusters. In nuclear physics calculations with realistic shell models there is no unique average potential. There is rather a class of potentials which are able to reproduce experimental data. This fact is an additional motivation to study the simplest possible spectra to distinguish which effects result from nonperiodic spectra.

An important difference between nuclei and metal clusters involves the ionic cores. It is a very difficult task to show for which concrete systems it is appropriate to reduce the influence of the ionic cores to an average smooth potential in the cluster.(17) For this approximation to be reasonable it is necessary to have a weak effective electron–ion potential, considering therefore the valence electrons as delocalized. Many calculations using the jellium model as well as suitably parametrized potentials(17) show that for alkali metal clusters with up to 3000 atoms, the picture of valence electrons in a smooth potential is very adequate. There will be certainly many clusters for which this approximation cannot be applied, but the study of this problem is beyond the objective of this work.

In Section 2 the exact canonical partition function is obtained for arbitrary periodic spectra. The shell structure effects are shown. In Section 3 the density of electronic states of the clusters is considered and an asymptotic formula is given. The transformation properties under modular substitutions are also addressed in this section. In Section 4 the electronic heat capacity and the electronic magnetic susceptibility for a system in a static magnetic field are considered. Preliminary considerations of statistical level spacing distributions of the single-particle levels in a shell are presented in Section 5. The conclusions of this work are given in Section 6.

2. THE CANONICAL PARTITION FUNCTION

Denton *et al.*,(18) based on the studies of Fröhlich and Kubo, considered a system of N electrons in a magnetic field H allocated in a single-particle spectrum with energy levels ε_n. To calculate the heat capacity and the spin susceptibility they studied the canonical partition function

$$Q(N, \beta) = \frac{1}{2\pi i} \int_C dy\, y^{-N-1} \prod_{\substack{n=0 \\ s=\pm 1}} [1 + y \exp(sh - \beta\varepsilon_n)], \qquad \beta = \frac{1}{k_B T} \tag{1}$$

where $y = \exp(\beta\mu)$ is the fugacity and $h = \beta g \mu_B H/2$. The integration contour C encloses the origin. The ground state energy is given by

$$E_0(N) = 2 \sum_{n=1}^{f-1} \varepsilon_n + x\varepsilon_f \tag{2}$$

Here, ε_f is the topmost occupied level and contains $x = 1$ or 2 electrons. Denton *et al.* considered the constant spectrum studied by Fröhlich and showed that $Q(N, \beta)$ can be given in a closed form for $\beta(\varepsilon_f - \varepsilon_0) \gg 1$ using Jacobi theta functions. But the most important part and goal of their calculation was to study the low-temperature behavior of the specific heat and the magnetic susceptibility by averaging single-particle level spacings. They followed the statistical description of the random matrix models of nuclear physics. Since they were not interested in shell structure effects, they analyzed only the constant single-particle spectrum.

We will generalize now the result of Denton *et al.* for the canonical partition function. Instead of a constant single-particle spectrum (with only twofold degenerate levels) we consider now a *periodic single-particle spectrum*. The single-particle energy levels are given as $\varepsilon_{nj} = \delta(n + \nu_j)$, $n = 0, 1, \ldots$, $j = 1, \ldots, e$, where e is the degeneracy of each shell and δ the spacing between adjacent shells. For the single-particle partition function it follows that

$$Z(s) = \sum_{j=1}^{e} \sum_{n \geqslant 0} \exp[-\delta s(n + \nu_j)] = \frac{1}{e^{\delta s} - 1} \sum_{j=1}^{e} \exp[-\delta s(1 - \nu_j)] \tag{3}$$

and using the Bernoulli polynomials $B_n(t)$ defined by

$$\frac{ze^{zt}}{e^z-1}=\sum_{n\geqslant 0}\frac{z^n}{n!}B_n(t), \qquad |z|<2\pi \tag{4}$$

one finds

$$Z(s)=\sum_{j=1}^{e}\sum_{n\geqslant 0}\frac{s^{n-1}}{n!}B_n(1-v_j)=\int_{0-}^{\infty}dt\, e^{-st}g(t) \tag{5}$$

Here $g(t)$ will be called the *single-particle level density* and is defined by

$$g(t)=e/\delta+\sum_{j=1}^{e}\sum_{n\geqslant 0}\delta^k\zeta(-k, v_j)\,\delta^{(k)}(t)/k! \tag{6}$$

where $\zeta(s, a)=\sum (n+a)^{-s}$, $n\geqslant 0$, is the Hurwitz ζ-function. The first term is the usual smooth single-particle level density e/δ. The *smooth ground-state energy* can be calculated using

$$\tilde{E}_0/\delta=\int_{0-}^{\tilde{\varepsilon}_F}dt\, g(t)\, t, \qquad N=\int_{0-}^{\tilde{\varepsilon}_F}dt\, g(t) \tag{7}$$

which yield

$$\frac{\tilde{E}_0}{\delta}=\frac{e\tilde{\varepsilon}_F}{2}-\frac{e}{12}-\frac{e}{2}(\langle v^2\rangle-\langle v\rangle^2) \qquad \text{and} \qquad N=e\tilde{\varepsilon}_F+\frac{e}{2}-\langle v\rangle e \tag{8a}$$

where $\langle v^2\rangle=\sum v_i^2/e$ and $\langle v\rangle=\sum v_i/e$. Therefore

$$\frac{\tilde{E}_0}{\delta}=\frac{N^2}{2e}-\frac{N}{2}+\frac{e}{24}+N\langle v\rangle-\frac{e}{2}(\langle v^2\rangle-\langle v\rangle^2) \tag{8b}$$

But the *exact ground-state energy* is

$$\frac{E_0}{\delta}=\frac{N^2}{2e}-\frac{N}{2}+\frac{e}{2}x(1-x)+\sum_{j=1}^{xe}v_j+(N-xe)\langle v\rangle \tag{9}$$

Here $x\in[0, 1]$ is the filled fraction of the last shell in the ground state. The exact minus the smooth ground-state energies lead therefore to a *shell effect* given as

$$\frac{E_{\text{shell}}(0)}{\delta}=\frac{e}{2}x(1-x)-\frac{e}{24}+\sum_{j=1}^{xe}(v_j-\langle v\rangle)+\frac{e}{2}(\langle v^2\rangle-\langle v\rangle^2) \tag{10}$$

Let us write now for a system of N electrons the *grand canonical partition function* $Z(\alpha, \beta)$ in terms of the *canonical partition function* $Q(N, \beta)$:

$$Z(\alpha, \beta) = \prod_{j=1}^{e} \prod_{n \geqslant 0} (1 + y e^{-\beta\delta n - \beta\delta v_j}) = \sum Q(N, \beta)\, y^N, \qquad y = e^{\alpha} \quad (11)$$

Now, we divide the infinite product into two parts according to whether the single-particle levels are smaller or larger than the topmost occupied energy level $\varepsilon_f = \delta(f + v_f)$, f integer. After rearranging terms and changing the variable $y \to \zeta e^{\beta\delta f}$, it follows that

$$\begin{aligned} Q(N, \beta) = {} & \frac{e^{-\beta E_1}}{\prod_{n>0} (1 - e^{-\beta\delta n})^e} \frac{1}{2\pi i} \int_C d\zeta\, \zeta^{-1 - ex + e/2} \\ & \times \prod_{j=1}^{e} \Bigg[(\zeta^{1/2} e^{-\beta\delta v_j/2} + \zeta^{-1/2} e^{\beta\delta v_j/2}) \prod_{m=1}^{f} (1 + \zeta^{-1} e^{\beta\delta v_j} e^{-\beta\delta m}) \\ & \times \prod_{n>0} (1 - e^{-\beta\delta n})(1 + \zeta e^{-\beta\delta v_j} e^{-\beta\delta n}) \Bigg] \end{aligned} \qquad (12)$$

where

$$E_1 = \delta e f (f-1)/2 + \delta e f \langle v \rangle + \delta e x f + 3\delta e \langle v \rangle/2 + \delta e/8, \qquad \langle v \rangle = \sum_j v_j/e$$

Also $N = ef + ex$, i.e., x is the filled fraction of the last shell. Now, we assume thermal degeneracy $\beta\delta f \gg 1$ and extend the upper limit f in the finite product to infinity. Define $q^2 = \exp(2\pi i\tau) = \exp(-\beta\delta)$, set $\zeta \exp(-\beta\delta v_j) = \exp(2\pi i z_j)$, and look at the infinite product representation of the Jacobi ϑ_2-function$^{(19)}$

$$\vartheta_2(z \mid \tau) = 2q^{1/6} \cos(\pi z)\, \eta(\tau) \prod_{n>0} (1 + q^{2n} e^{2\pi i z})(1 + q^{2n} e^{-2\pi i z}) \qquad (13a)$$

where $\eta(\tau)$ is the Dedekind η-function

$$\eta(\tau) = q^{1/12} \prod_{n>0} (1 - q^{2n}) = \sum_{n \in \mathbb{Z}} (-1)^n q^{3(n+1/6)^2} \qquad (13b)$$

Note that $q^{1/12}/\eta(\tau)$ is a bosonic partition function with $q = \exp(-\delta/2k_B T)$. The canonical partition function will read

$$Q(N, \beta) = \frac{\exp(-\beta E_1 - \beta\delta e/24)}{\eta(\tau)^e} \frac{1}{2\pi i} \int_C d\zeta\, \zeta^{-1 - ex + e/2} \prod_{j=1}^{e} \vartheta_2(z_j \mid \tau) \qquad (14)$$

where we used also the infinite-product representation for the Dedekind

η-function. To integrate the product of theta functions, remember their infinite series representation

$$\vartheta_2(z\,|\,\tau)=\sum_{n\in\mathbb{Z}} q^{(n-1/2)^2} e^{(2n-1)\pi i z} \tag{15}$$

and write

$$Q(N,\beta)=\frac{\exp(-\beta E_1-\beta\delta e/24+\beta e\langle v\rangle)}{\eta(\tau)^e}\sum_{\{n_1,\ldots,n_e\}}\alpha_1\cdots\alpha_e\int_C\frac{d\zeta}{2\pi i}\zeta^{\Sigma n_j-ex-1} \tag{16}$$

where the sums are over the $n_i\in\mathbb{Z}$ and $\alpha_j=\exp[-\beta\delta(n_j-1/2)^2/2-\beta\delta n_j v_j]$. The integration is now immediate and leads to

$$\begin{aligned} Q(N,\beta)&=\eta(\tau)^{-e}\exp(-\beta E_2)\\ &\times\sum_{\{n_1,\ldots,n_{e-1}\}}\exp\left\{-\beta\delta\sum{}'\,[n_i^2-(ex+v_e-v_i)\,n_i]-\beta\delta\sum_{i<j}{}'\,n_in_j\right\} \end{aligned} \tag{17}$$

The primed sums run over $i, j=1,\ldots,e-1$ and

$$E_2=\delta ef(f-1)/2+\delta ef\langle v\rangle+\delta efx+\delta ex(ex-1)/2+\delta e/24+\delta exv_e$$

To transform the infinite multiple sum in (17) into known functions, consider the following symmetric bilinear form:

$$\langle\mathbf{n},\mathbf{m}\rangle=\mathbf{n}'\Omega\mathbf{m} \tag{18}$$

where $\mathbf{n}$ and $\mathbf{m}$ are $(e-1)$-dimensional vectors and the $(e-1)\times(e-1)$ matrix Ω has components $\Omega_{ii}=2$ and $\Omega_{ik}=1$ for $i\neq k$. Let $\mathbf{n}$ and $\mathbf{a}$ be the $(e-1)$-dimensional vectors $(n_1,\ldots,n_{e-1})$ and $(a_1,\ldots,a_{e-1})$ with $a_i=v_i-\langle v\rangle-x$; it follows that

$$\begin{aligned} \tfrac{1}{2}\langle\mathbf{n}+\mathbf{a},\mathbf{n}+\mathbf{a}\rangle&=\sum{}'\,(n_i^2+a_i^2)+\sum_{i<j}{}'\,(n_in_j+a_ia_j)\\ &\quad+2\sum{}'\,n_ia_i+\sum_{i<j}{}'\,(a_in_j+n_ia_j)\\ &=\sum{}'\,(n_i^2+a_i^2)+\sum{}'\,(v_i-v_e-ex)\,n_i+\sum_{i<j}{}'\,(n_in_j+a_ia_j) \end{aligned} \tag{19}$$

where we have used

$$\sum_{i<j}{}'\,(a_in_j+n_ia_j)=\sum{}'\,n_j\left(\sum{}'\,a_i-a_j\right)\qquad\text{and}\qquad a_i+\sum{}'\,a_j=v_i-v_e-ex$$

The only terms in the inner product which are not in the exponential of (17) are

$$\sum{}' a_i^2 + \sum{}' a_i a_j = \frac{1}{2} e(e-1)\, x^2 - ex\langle v \rangle + \frac{e}{2}\left(\langle v^2 \rangle - \langle v \rangle^2\right) + exv_e \tag{20}$$

with $\langle v^2 \rangle = \sum_i v_i^2/e$. But this constant can be allied to the constant E_2 yielding the *final result*:

$$\begin{aligned} Q(N, \beta) &= \exp(2\pi i\tau \tilde{E}_0/\delta)\, \theta_{\mathbf{a},\mathbf{0}}(0 \mid \Omega\tau)/\eta^e(\tau) \\ 2\pi i\tau &= -\beta\delta, \qquad a_i = v_i - \langle v \rangle - x \end{aligned} \tag{21}$$

where $\tilde{E}_0$ is precisely the *smooth ground-state energy*:

$$\tilde{E}_0/\delta = e(f + x + \langle v \rangle - 1/2)^2/2 - e/12 + e\langle v \rangle/2 - e\langle v^2 \rangle/2 \tag{22}$$

as computed above [cf. (8b) with $N = ef + ex$]. We introduced further the *θ-function*, with characteristics **a** and **b**, in $e-1$ variables(20) defined by

$$\theta_{\mathbf{a},\mathbf{b}}(\mathbf{z} \mid \Omega\tau) = \sum_{\mathbf{n}} \exp[\pi i\tau \langle \mathbf{n} + \mathbf{a}, \mathbf{n} + \mathbf{a} \rangle - 2\pi i(\mathbf{z} + \mathbf{b}) \cdot (\mathbf{n} + \mathbf{a})], \qquad \mathbf{n} \in \mathbb{Z}^{e-1} \tag{23a}$$

With relation (21) we have arrived at a closed expression. The most interesting mathematical observation is that (for rational **a**) the canonical partition function is given by a modular form(20) with useful transformation properties. Physically, the most interesting aspect is the appearance of the exponential factor $\exp(2\pi i\tau \tilde{E}_0/\delta)$ containing only the smooth ground-state energy. The dependence on the particle number N is contained only in this prefactor. Note also the bosonic partition function $1/\eta^e(\tau)$. Since $-\beta\delta = 2\pi i\tau$, (21) is given in terms of the inverse of the temperature.

Introduce now the ϑ-function in *one variable* $\vartheta_{\kappa,\lambda}$ with characteristics(19) $\kappa = x + \langle v \rangle - 1/2$ and $\lambda = 0$:

$$\begin{aligned} \vartheta_{\kappa,\lambda}(z \mid \tau) &= \sum_{n \in \mathbb{Z}} \exp\{i\pi(n+\kappa)^2 \tau + 2\pi i(n+\kappa)(z+\lambda)\} \\ &= q^{-1/12}\eta(\tau) \exp[\pi i\kappa^2\tau + 2\pi i\kappa(z+\lambda)] \\ &\quad \times \prod_{n \in \mathbb{Z}} (1 + q^{2n+1} \exp[-2\pi i(z + \kappa\tau + \lambda)]) \\ &\quad \times (1 + q^{2n+1} \exp[2\pi i(z + \kappa\tau + \lambda)]) \end{aligned} \tag{23b}$$

In particular, $\vartheta_{1/2,0}(z \mid \tau) = \vartheta_2(z \mid \tau)$ [cf. (15)].

From (11a), (21), and (22), the grand partition function is

$$Z(\alpha, \beta)=q^{-4\xi}y^{e/2-e\langle v\rangle}\eta^{-e}(\tau)\sum_{xe=0}^{e-1}\theta_{\mathbf{a},0}(0\,|\,\Omega\tau)\,\vartheta_{\kappa,0}(ez\,|\,e\tau) \qquad (24a)$$

where $\xi= -e/24+e\langle v\rangle/4-e\langle v^2\rangle/4$ and $a_i=v_i-\langle v\rangle-x$.

Further, note that the assumption of "thermal degeneracy" $\beta\delta f \gg 1$ to obtain (14) is equivalent to taking the infinite product

$$Z(\alpha, \beta)=\prod_{i=1}^{e}\prod_{n\geqslant 0}(1+q^{2n}e^{2\pi i(z+\tau v_i)})(1+q^{2n+2}e^{-2\pi i(z+\tau v_i)}) \qquad (24b)$$

as grand canonical partition function. This expression can be now interpreted as the partition function of a system of fermions and antifermions. Similar considerations would follow for systems containing bosons and antibosons.

Using now ϑ-functions in one variable with characteristics $v_i-1/2$, it follows that

$$Z(\alpha, \beta)=q^{-4\xi}y^{e/2-e\langle v\rangle}\eta^{-e}(\tau)\prod_{i=1}^{e}\vartheta_{v_i-1/2,0}(z\,|\,\tau) \qquad (24c)$$

In other words, we found two equivalent expressions for $Z(\alpha, \beta)$. Therefore, we arrive at the identity

$$\prod_{i=1}^{e}\vartheta_{v_i-1/2,0}(z\,|\,\tau)=\sum_{xe=0}^{e-1}\theta_{\mathbf{a},0}(0\,|\,\Omega\tau)\,\vartheta_{\kappa,0}(ez\,|\,e\tau), \qquad \kappa=xe+e\langle v\rangle-e/2 \qquad (25)$$

Using the same method, we have derived many other identities which include also θ-functions of higher levels in several variables. Identities of this kind are the result of the underlying *ring structure* of the θ-functions.

The particular case $e=1$ of (21) yields a result by Goudsmit(22):

$$Q(N, \beta)=\exp(2\pi i\tau\tilde{E}_0/\delta)/\eta(\tau) \qquad (26)$$

with $\tilde{E}_0/\delta=f(f-1)/2+1/24$ and $\langle v\rangle=0$.

The next particular case $e=2$ reduces to the result of Denton *et al.*(18) taking here $\langle v\rangle=0$, $v_2= -v_1=g\mu_B H/2\delta$, $a=v_1-x$, and the two values $x=0$, $1/2$. The two corresponding relations are

$$\begin{aligned}Q_{\text{even}}&=\exp[2\pi i\tau(\tilde{E}_{0,\text{even}}/\delta+g^2\mu_B^2H^2/4\delta^2)]\\&\quad\times\vartheta_3(-\tau g\mu_B H/\delta\,|\,2\tau)/\eta^2(\tau) \qquad \text{for} \quad x=0 \qquad (27)\end{aligned}$$

with $\tilde{E}_{0,\mathrm{even}}/\delta = f(f-1) + 1/12 - g^2\mu_{\mathrm{B}}^2 H^2/4\delta^2$; and

$$\begin{aligned} Q_{\mathrm{odd}} &= \exp[2\pi i\tau(\tilde{E}_{0,\mathrm{odd}}/\delta + g^2\mu_{\mathrm{B}}^2 H^2/4\delta^2)] \\ &\quad \times \vartheta_2(-\tau g\mu_{\mathrm{B}} H/\delta \,|\, 2\tau)/\eta^2(\tau) \qquad \text{for} \quad x = 1/2 \end{aligned} \tag{28}$$

with $\tilde{E}_{0,\mathrm{odd}}/\delta = f^2 - 1/6 - g^2\mu_{\mathrm{B}}^2 H^2/4\delta^2$. Here we have written in the background magnetic field dependence in the z argument of the Jacobi ϑ-functions. The ϑ_2-function is given by (15) and ϑ_3 by

$$\vartheta_3(z\,|\,\tau) = \sum_{n \in \mathbb{Z}} q^{n^2} \exp(2\pi i n z) \tag{29}$$

3. TRANSFORMATION FORMULAS AND THE DENSITY OF EXCITED STATES

The transformation formulas for the Jacobi ϑ-functions and the Dedekind η-function under the modular substitution $\tau \to -1/\tau$ can be used to express $Q(N, \beta)$ in the preceding examples in terms of $k_{\mathrm{B}}T = -\delta/2\pi i\tau$. Explicitly,

$$\vartheta_2(z\,|\,\tau) = (i/\tau)^{1/2}\, e^{-i\pi z^2/\tau}\vartheta_0(z/\tau\,|\,-1/\tau)$$

$$\vartheta_3(z\,|\,\tau) = (i/\tau)^{1/2}\, e^{-i\pi z^2/\tau}\vartheta_3(z/\tau\,|\,-1/\tau)$$

and

$$\eta(\tau) = (i/\tau)^{1/2}\,\eta(-1/\tau) \tag{30}$$

The infinite series for the Jacobi ϑ-functions and the Dedekind η-function converge very fast for large $\mathrm{Im}(\tau)$, i.e., for low temperatures. Only few terms are needed for a high numerical precision. For this reason, the transformation formulas are particularly useful for also computing with great accuracy the high-temperature case.

Also a similar modular transformation holds for the general result (21). For the general periodic spectra the needed formula reads

$$\theta_{\mathbf{a},0}(\mathbf{0}\,|\,\Omega\tau) = (-i\tau)^{(1-e)/2}\,|\Omega|^{-1/2}\,\theta_{0,\mathbf{a}}(\mathbf{0}\,|\,-1/\tau\Omega) \tag{31}$$

where $|\Omega|$ denotes the determinant of Ω. In our application $|\Omega| = e$.

In many cases, for a given modular form (defined with respect to a certain subgroup of the modular group) it is possible to obtain the *exact* Fourier coefficients.(23,24) In other words, from (21) we can assert that (for rational ν_i) it is possible to obtain the *exact* Fourier coefficients of the canonical partition function for a system of fermions in a periodic single-particle spectrum. Thus, we have found a way to solve exactly the calculation of the cluster level density for (rational) periodic single-particle spectra and not too high excitation energies. However, let us remark that the explicit calculations depend strongly on the subgroups involved and can become very difficult in general.

For number-theoretic considerations it is convenient to introduce a largest unit d to express (if necessary, only approximately) all single-particle energies as integer multiples of it. Observe that for the periodic spectra $\{\varepsilon_{kj} = (k + \nu_j)\delta\}$ it is not necessarily the case that $d = \delta$ (true only for equidistant spectra with periodically degenerate levels). The Fourier series of the grand canonical partition function for the system of fermions and antifermions [cf. (24b)] reads

$$Z(\alpha, \beta) = \sum_{N \in \mathbb{Z}} \sum_{n \geqslant 0} \rho(N, U)\, x^n y^N, \qquad x = e^{-\beta d}, \quad y = e^{\alpha} \tag{32}$$

with coefficients

$$\rho(N, U) = \frac{1}{(2\pi i)^2} \int_{C_0} dx \int_{C_0} dy\, Z(\alpha, \beta)\, x^{-n-1} y^{-N-1} \tag{33}$$

where the contours C_0 surround the origins. These coefficients will be called the *cluster level density*. It gives the number of excited states of a system of N (>0) fermions (particles), or alternatively of N (<0) antifermions (holes) distributed on the periodic single-particle spectrum $\{\varepsilon_{kj}\}$ with total energy $E = nd = U + E_0$, where U is the excitation energy and E_0 the (exact) ground-state energy. The integral over y in (33) is the canonical partition function $Q(N, \beta)$ as given by (21). Therefore

$$\rho(N, U) = \frac{1}{2\pi i} \int_{C_0} dx\, x^{-[U - E_{\text{shell}}(0)]/d - 1} \theta_{\mathbf{a},0}(0 \mid \Omega\tau)\, \eta^{-e}(\tau) \tag{34}$$

with the ground-state energy shell effect $E_{\text{shell}}(0)$ given by (10). As mentioned above, this integral can be calculated exactly in many cases. However, for now, it is not necessary to give the exact formulas.

As example of the number-theoretic aspects of the last results, consider again the case $e = 1$, i.e., equally spaced levels. Then, from (26)

$$Z(\alpha, \beta) = \prod_{n \geqslant 0} (1 + q^{2n} y)(1 + q^{2n+2} y^{-1}) = \sum_{m \geqslant 0} \sum_{n \in \mathbb{Z}} q^{n(n-1) + 2m} y^n p(m) \tag{35}$$

Here $p(m)$ denotes the number of partitions of the integer m into positive integers. Clearly, $\rho(N, m) = p(m)$ for $N \geqslant m$. The first values are $\rho(N, m) = 1, 1, 2, 3, 5, 7, 11, 15, 22, 30, 42, \ldots$ for $m = 0, 1, 2, \ldots$. Asymptotically

$$\rho(N, m) \approx \frac{\exp(\pi\{[m\delta + E_{\text{shell}}(0)]\, 2e/3\delta\}^{1/2})}{4\sqrt{3}[m\delta + E_{\text{shell}}(0)]\, e/\delta}, \qquad E_{\text{shell}}(0) = -\frac{\delta}{24} \tag{36}$$

More general spectra lead to many interesting problems in additive number theory. The asymptotic formula for $\rho(N, m)$ in the general periodic case is obtainable using the saddle point method or Tauberian theorems. The result is given again by (36) but with $E_{\text{shell}}(0)$ from (10).

4. THE SPECIFIC HEAT AND THE MAGNETIC SUSCEPTIBILITY

Now it is possible to calculate explicitly the thermodynamic properties of the system. In this section, the electronic specific heat C and the electronic magnetic susceptibility χ will be considered. These quantities are important for comparisons with experimental observations.(2) They are given by

$$C = k_{\text{B}} \beta^2 \partial_\beta^2 \ln Q(N, \beta), \qquad \chi = \beta^{-1} \partial_H^2 \ln Q(N, \beta) \tag{37}$$

In general, for arbitrary temperatures, magnetic fields, and periodic spectra, the use of our result (21) for $Q(N, \beta)$ is the simplest way for numerical calculations. This occurs because of the fast convergence of the ϑ-series for large $\text{Im}(\tau)$, i.e., relatively low temperatures. For higher temperatures the transformation formulas simplify the calculations again.

For physical applications let us restrict the general periodic spectrum of the preceding section somewhat. Consider now only periodic shells of degenerate levels (subshells) ε_i. In a weak static magnetic field H, we assume that each level splits into new levels ε_i' according to a certain scheme. Remember now that the levels of the preceding section were $\varepsilon_{nj} = \delta(n + \nu_j)$, $j = 1, \ldots, e$, with ν_j arbitrary. Thus, these numbers are to be selected as to reproduce the new levels ε_i' and therefore they will depend on H. For simplicity, we will consider only a linear dependence and write $\varepsilon_{nj} = \delta(n + \nu_j + \mu_j H)$, where the redefined ν_j and the introduced μ_j do not depend on H and $\langle \mu \rangle = 0$. Quadratic and higher-order terms in H can be introduced easily. The consideration of a spin-orbit interaction using perturbation theory(25,26) leads to quadratic terms in H.

From (22), the smooth ground-state energy will be

$$\begin{aligned} \tilde{E}_0/\delta = {} & e(f + x + \langle \nu \rangle - 1/2)^2 - e/12 + e\langle \nu \rangle/2 - e\langle \nu^2 \rangle/2 \\ & - eH^2\langle \mu^2 \rangle/2 - eH\langle \mu\nu \rangle \end{aligned} \tag{38}$$

in which $e\langle \mu\nu \rangle = \sum \mu_i \nu_i$, $i = 1, \ldots, e$.

The θ-function present in (21) can be now rewritten as

$$\theta_{\mathbf{a}+\boldsymbol{\mu}H,\mathbf{0}}(0\,|\,\Omega\tau)=\exp(\langle\boldsymbol{\mu},\boldsymbol{\mu}\rangle H^2\pi i\tau+\langle\boldsymbol{\mu},\mathbf{a}\rangle H 2\pi i\tau)\,\theta_{\mathbf{a},\mathbf{0}}(\Omega\boldsymbol{\mu}\tau H\,|\,\Omega\tau) \tag{39}$$

where the $a_i=v_i-\langle v\rangle-x$, $i=1,\ldots,e-1$, do not depend on H.

The exponential common factor in $Q(N,\beta)$ gives no contribution to the specific heat. Therefore

$$C=k_{\mathrm{B}}\beta^2\partial_\beta^2[-e\ln\eta(\tau)+\ln\theta_{\mathbf{a},\mathbf{0}}(\Omega\tau\boldsymbol{\mu}H\,|\,\Omega\tau)] \tag{40}$$

For the susceptibility one finds

$$\chi=\beta^{-1}\partial_H^2\ln\theta_{\mathbf{a},\mathbf{0}}(\Omega\tau\boldsymbol{\mu}H\,|\,\Omega\tau) \tag{41}$$

where we used $\langle\boldsymbol{\mu},\boldsymbol{\mu}\rangle=e\langle\mu^2\rangle=\sum\mu_i^2$.

From the definition (23a) for the θ-functions, the quasiperiodicity rule

$$\theta_{\mathbf{a},\mathbf{b}}(\mathbf{z}+\Omega\tau\mathbf{m}\,|\,\Omega\tau)=\exp(-2\pi i\mathbf{m}'\mathbf{b}-2\pi i\mathbf{m}'\mathbf{z}-\pi i\mathbf{m}'\Omega\tau\mathbf{m})\,\theta_{\mathbf{a},\mathbf{b}}(\mathbf{z}\,|\,\Omega\tau),$$
$$\mathbf{m}\in\mathbb{Z}^{e-1} \tag{42}$$

follows. Thus, the specific heat and the magnetic susceptibility are periodic functions of H. The period is given by the smallest h such that $\boldsymbol{\mu}h\in\mathbb{Z}^{e-1}$. This is possible if, for example, the level spacings in a subshell after splitting are constant and rational multiples of the same energy unit for all subshells. However, the situation is in general more complicated.

Consider now the low-temperature limit, i.e., large $\mathrm{Im}(\tau)$. For the specific heat observe first the well-known result

$$\ln\eta(\tau)=\frac{\pi i\tau}{12}-\sum_{n>0}\frac{q^{2n}}{n(1-q^{2n})},\qquad \mathrm{Im}(\tau)>0 \tag{43}$$

Thus, the first term in (40) leads to an exponential decrease $\exp(-\delta/k_{\mathrm{B}}T)$. But the second term leads also to a similar decrease as follows from (23a):

$$C\approx k_{\mathrm{B}}\beta^2\delta^2\{e\cdot e^{-\beta\delta}+\tfrac{1}{2}(\langle\mathbf{n}_1+\mathbf{a}+\boldsymbol{\mu}H\rangle^2-\langle\mathbf{n}_0+\mathbf{a}+\boldsymbol{\mu}H\rangle)$$
$$\times\exp[-\beta\delta(\langle\mathbf{n}_1+\mathbf{a}+\boldsymbol{\mu}H\rangle-\langle\mathbf{n}_0+\mathbf{a}+\boldsymbol{\mu}H\rangle)/2]\}$$

where $\mathbf{n}_0$ and $\mathbf{n}_1$ are the values of $\mathbf{n}\in\mathbb{Z}^{e-1}$ such that $\langle\mathbf{n}+\mathbf{a}+\boldsymbol{\mu}H\rangle$ acquires its minimum value for $\mathbf{n}=\mathbf{n}_0$ and for $\mathbf{n}=\mathbf{n}_1$ leads to the next larger value. If several $\mathbf{n}_1$ fulfil this condition, a degeneracy factor should be included. The result of Denton *et al.*[18] for $e=2$ remains qualitatively valid for the general periodic spectra for all shell fillings.

The susceptibility for low temperatures is also similar to that for $e=2$. If the last occupied subshell (of zero width) is closed, the susceptibility is exponentially attenuated. In the case that it is nonclosed, the susceptibility will follow a Curie law behavior. Note that also those systems with an even number of electrons in the last subshell will lead to a Curie law behavior, if the subshell is nonclosed. However, an odd–even effect could be still considered additionally since in the shell model this effect results from the pairing of electrons in the same shell. If a quadratic term in H is added to the subshell energies, then a nonvanishing susceptibility arises for even systems and a modified Curie law results for odd systems. Further, if a quadratic term in H is added to the subshell splittings, a nonvanishing susceptibility arises for even systems and a modified Curie law results for odd systems.

In the high-temperature limit, $\operatorname{Im}(\tau) \to 0$. From (30) and (31) the expressions

$$\eta(\tau) = -\frac{1}{2}\ln\tau - \frac{\pi i}{12\tau} + O(e^{-\pi i/\tau}) \tag{44a}$$

$$\theta_{\mathbf{a},0}(0\,|\,\Omega\tau) = \frac{1-e}{2}\ln\tau + O(\text{const}) \tag{44b}$$

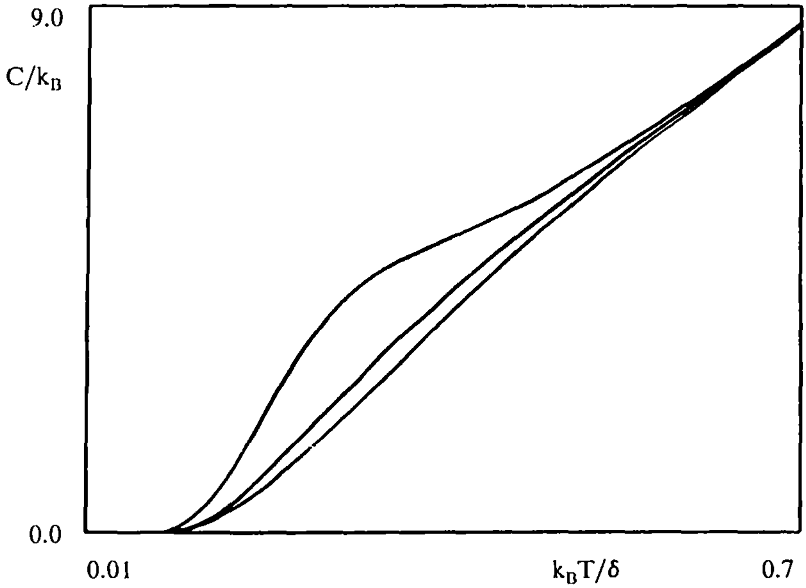

Fig. 1. Specific heat against $k_B T/\delta$ at $H = 0$ for an equally spaced spectrum with fourfold degenerate levels. The top curve corresponds to a closed ground-state shell, the middle curve to 1/4- or 3/4-filled shells, and the bottom curve to half-filled shells.

result. Using these formulas, we arrive at the limits

$$C = \frac{\pi^2 k_B^2 Te}{3\delta} - \frac{k_B}{2} \tag{45a}$$

and

$$\chi = -\partial_H^2 \tilde{E}_0 = \delta e \langle \mu^2 \rangle \tag{45b}$$

Both expressions do not depend on the shell filling at the ground state, i.e., the shell effects have been washed out. The specific heat coincides with the result given by Denton *et al.*(18) if we substitute in their result the level density by e/δ. But the susceptibility given by (45b) differs in general from the Pauli spin susceptibility found by Denton *et al.* not only in the different single-particle level density. Of course, for even e and $\mu_i = \pm g_1 \mu_B / 2\delta$ the Pauli susceptibility follows from (45b) with level density e/δ. But in general the introduction of the shell model assumptions could lead to different constants.

In Fig. 1, the specific heat is shown as a function of the temperature at $H = 0$ for an equally spaced spectrum with fourfold degenerate levels.

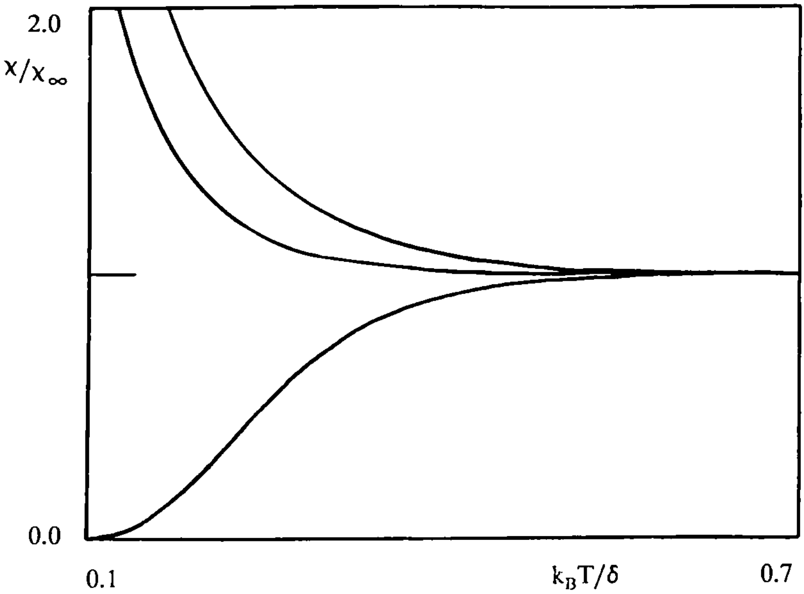

Fig. 2. The magnetic susceptibility against the temperature at $H = 0$ for an equally spaced spectrum with fourfold degenerate levels. The bottom curve is for closed shells, the middle curve for 1/4- or 3/4-filled shells, and the top curve for half-filled shells.

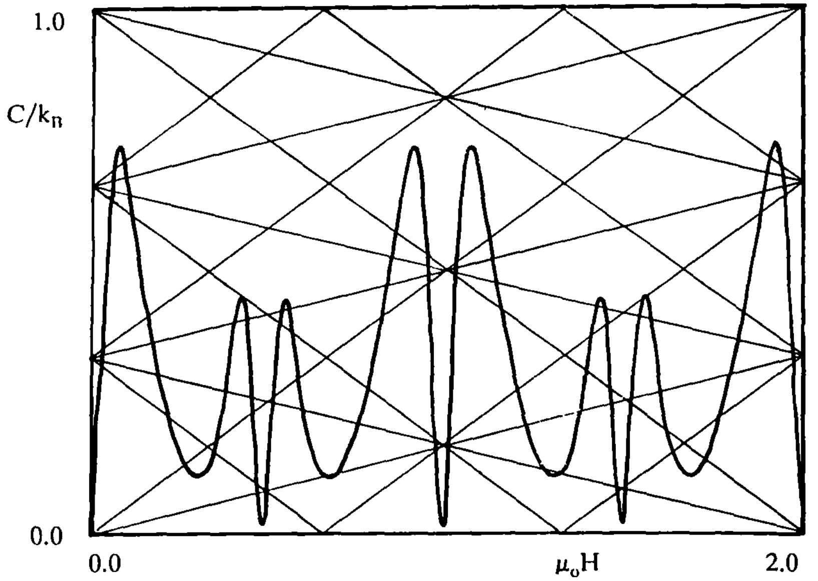

Fig. 3. The specific heat as a function of $\mu_0 H$ at a temperature $k_B T = 0.05\delta$ and a shell filling $x = 1/4$. The magnetic field dependence of part of the underlying fourfold degenerate spectrum is also shown.

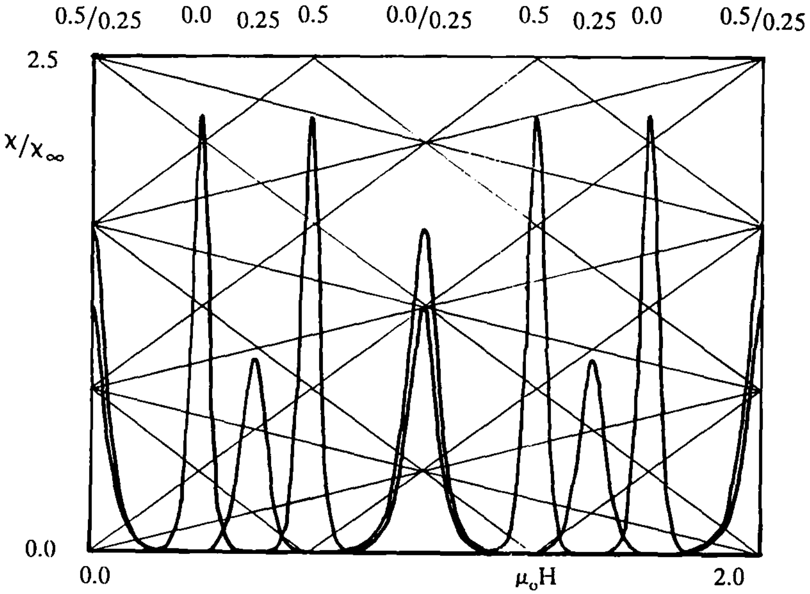

Fig. 4. Same as Fig. 3, for the magnetic susceptibility. The values at the top give the shell fillings ($x = 0$, 0.25, and 0.5) of the respective peaks.

For the same spectrum, Fig. 2 shows the magnetic susceptibility at $H = 0$. In this last figure, the systems with partially filled ground-state shells can be clearly distinguished (Curie-law-type behavior) from the closed shell system (exponential attenuation for $k_B T \to 0$). Finally, in Figs. 3 and 4 the magnetic field dependences for the specific heat and the magnetic susceptibility are shown for a temperature $k_B T = 0.05\delta$. The underlying straight lines show schematically some levels of the fourfold degenerate spectrum and its magnetic field dependence. For the specific heat only the shell filling $x = 1/4$ is shown for more clarity.

5. STATISTICAL LEVEL SPACING DISTRIBUTIONS

As mentioned in the introduction, Kubo(13) and Gor'kov and Eliashberg(15) proposed to consider statistically distributed level spacings. Their motivation was the existence of surface irregularities as well as the presence of impurities. Having in mind an ensemble of small particles, it was argued that the resulting perturbations should be taken as uncorrelated. Then it was considered adequate to invoke the theory of random matrices(27) to average the single-particle level spacings near the Fermi level. Kubo performed the calculations with a Poisson distribution and Gor'kov and Eliashberg considered the so-called Gaussian ensembles.

Denton *et al.*(18) realized numerical calculations taking as zeroth-order approximation their equal-level-spacing results, the nth-order approximation being defined as an average over n adjacent level spacings around the Fermi energy. They compared the three kinds of Gaussian ensembles. They found that the high-temperature limit approaches the equal-level-spacing results and the low-temperature behavior depends only on the low-lying states.

It seems therefore natural to expect for the general periodic spectra a similar behavior following the same methods. However, the dependence on the shell structure needs to be analyzed carefully. In particular, for relatively small clusters we would expect that the perturbations would not wash out the original shell structure of the spectra as strongly as for very large systems.

6. CONCLUSIONS

The canonical partition function for a set of electrons in a periodic single-particle spectrum has been found exactly. The electronic specific heat and the electronic magnetic susceptibility were calculated. There are still many possibilities to fix the parameters which characterize the periodic spectra used. In principle, by letting the width of the periodic shell take a sufficiently large value, any kind of spectrum (also nonperiodic) could be studied for not too high temperatures. Certainly, it would be of interest to compare the theoretical results with experimental data. Also the cluster level density (34), (36) could be important for the study of excited clusters and their reaction mechanisms.

The relationship with analytic number theory would also be worth further study. Additionally, the symmetries associated with the symmetric bilinear form (18) and the canonical partition function (21) could allow an interesting link with affine Kac–Moody algebras.(20)

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