Energy-level statistics of metallic fine particles: Computer simulations

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It is believed that metallic fine particles usually have some roughness or irregularity at their surfaces. We investigate how the surface irregularity affects the electronic energy levels by means of computer simulations. For results, we obtain the formula $\omega \sim \omega_0(1-c/R^{\eta})$ showing the relation between the level-repulsion exponent ω and the parameter R, which stands for the degree of surface irregularity; here $\omega_0 \simeq 1.0$, $\eta \simeq 2.0$, and c is a positive constant. We further discuss the level statistics of actual fine particles in comparison with this formula.

I. INTRODUCTION

Random matrix theory[1-6] (RMT), originated by Wigner in order to interpret statistical behavior of highly excited states of heavy nuclei, has been developed and applied to problems, which can be classified into three categories: (1) complex many-body problems, such as highly excited electronic states of heavy atoms[7] (and of course highly excited states of nuclei), (2) nonintegrable systems, such as vibrational states of complex molecules[8-10] and quantum billiard problems,[11-13] and (3) random systems, such as one-electron states of metallic fine particles.[14,15] Categories (1) and (2) are different from (3) in that the former are concerned with deterministic systems which are described by a unique Hamiltonian, while the latter is concerned with undeterministic systems described by Hamiltonians that are stochastic.

In this paper we pay attention to the statistical behavior of energy levels of metallic fine particles belonging to category (3). We deal with ensembles of metallic fine particles consisting of N atoms. In practical terms, we are interested in the particles of size $10^2 \lesssim N \lesssim 10^6$. Each atom is assumed to have one valence electron. One of the important features of fine particles is discreteness of the quasiparticle energy spectra due to the system being finite. Now we assume that the mean level spacing $\langle\delta\rangle_{\rm ens}$ is much greater than the width of an energy level $\hbar/\tau_{\rm quasi}$, where $\tau_{\rm quasi}$ is a lifetime of a quasiparticle and $\hbar$ is Planck's constant. Another important feature is the existence of irregularity of morphology of the particles. Roughly speaking, this irregularity is classified into two types. One is microscopic irregularity at the surfaces, say steps, kinks, and adsorbed atoms. Another is deformation of the shapes of the particles as a whole. In both cases the particles with different morphology have about the same energy and, therefore, these irregular shapes are uncontrollable or random. Perhaps the latter irregularity will be important for discussing the electronic states when the particles are rather large in size, say $N \gtrsim 10^6$, where a free-electron picture serves as a good approximation. This case might be related to the quantum billiard problem, the examples of which show chaotic behavior in a classical picture.[11-13] On the other hand the former irregularity may be more important when we are concerned with fine particles of somewhat smaller size, where the continuum model does not work but the discreteness such as lattice structures must be taken into account. In the present paper we concentrate on this microscopic irregularity at the surfaces of fine particles. From now on we call it simply surface irregularity.

The energy-level statistics were first applied by Kubo[16] to discuss thermodynamics of metallic fine particles. Then he assumed the distribution of the energy levels to be purely random. This comes from assuming the uncorrelated distribution without any repulsion between different energy levels. Later Gor'kov and Eliashberg[14] considered the level statistics of fine particles as the problem of random boundary conditions coming from surface irregularity, and assumed applicability of RMT to the level statistics of fine particles. It has been revealed by many authors[14-16] that the level statistics are important in describing low-temperature properties of metallic fine particles such as specific heat, spin susceptibility, and so on. At low temperature, where $kT \ll \langle\delta\rangle_{\rm ens}$ is valid, only a few low-lying levels are important. Here, k, T, and $\langle\delta\rangle_{\rm ens}$ represent Boltzmann's constant, absolute temperature, and mean level spacing near Fermi level, respectively. Therefore statistical behavior of these levels, especially a distribution of the nearest-neighbor level spacings determines the low-temperature properties of metallic fine particles. By using results of RMT, Denton *et al.*[15] have shown that the specific heat is proportional to $T^{1+\beta}$ if $kT \ll \langle\delta\rangle_{\rm ens}$, where the values of β are confined to only 1, 2, and 4 according to the symmetry of random matrices: the random matrix ensemble is orthogonal, giving $\beta=1$, when time-reversal invariance holds and the spin-orbit coupling of valence electrons is weak. The ensemble is symplectic, giving $\beta=4$, when the spin-orbit coupling is strong and the system is time-reversal invariant. It is unitary, giving $\beta=2$, when the time-reversal invariance is lost and the spin-orbit coupling is strong.

However, the assumption that level statistics is applicable to fine particles does not seem to stand on a rigid theoretical basis. We put great emphasis on this point. Actually, nobody has succeeded in making clear the relation between the statistical behavior of the energy levels and surface irregularity. Barojas *et al.*[17] have tried to clarify the relation. They have solved Schrödinger equa-

tions with Dirichlet or Neumann boundary conditions which the electron confined to a rectangle has to obey. Then they found the distribution of energy-level spacings, regarding an ensemble of metallic fine particles, to be that of rectangles with various rates of side lengths. They showed that the level spacings are subject to a Poisson-like distribution. We are not persuaded by their conclusion of the absence of energy-level repulsion in the fine particles. Since their basic equations are separable, the energy levels are composed of two independent sequences between which levels never repel each other. Therefore, it is natural that the level-repulsion exponent becomes much smaller than unity when they fit their distribution to a Brody distribution. Here we would like to point out the fact that actual metallic find particles are nonseparable systems because of the lack of symmetry due to the surface irregularity.

Ratcliff[18] has considered the problem of a free electron confined in a slightly deformed spherical region. He introduces surface irregularities in his model differently than ours, that is, he assumes that the deviations of the shape from a sphere can be expanded in terms of spherical harmonics with random coefficients, which generate the assembly of deformed surfaces. He obtains interesting results: When higher harmonics are as important as lower ones, in other words, when the surfaces are rough enough, the behavior of the energy levels is just that predicted by RMT. On the other hand, the behavior becomes quite different from that predicted by RMT, when the higher harmonics are less effective, as in the case of smoother surfaces. Unfortunately, his approach is valid only when the magnitude of the surface deformation is very small, as he employs the perturbation theory. Further his calculation is restricted within the manifold of the $2L+1$ eigenstates belonging to the eigenvalue of angular momentum L.

Now we refer briefly to the standard Gaussian ensembles[5,19] of the random matrices, that is, each real matrix element H_{ij}^{α} obeys a Gaussian distribution with zero average and equal variance. These relations are given as follows:

$$\langle H_{ij}^{\alpha}\rangle_{\text{ens}}=0\ , \tag{1.1a}$$

$$\langle H_{ij}^{\alpha}H_{kl}^{\gamma}\rangle_{\text{ens}}=[\delta_{ik}\delta_{jl}+(2\delta_{\alpha 0}-1)\delta_{il}\delta_{jk}]\delta_{\alpha\gamma}\ . \tag{1.1b}$$

Here $\langle A\rangle_{\text{ens}}$ means ensemble average of A and δ_{ij} is Kronecker's delta. Greek letters run from 0 to $\beta-1$, where $\beta=1$, 2, and 4 according to the ensembles being orthogonal, unitary, and symplectic, respectively. It is important that the matrix elements are statistically independent of each other. This assumption has made the problem unrealistic. Even if the cluster surface is rough enough, matrix elements of the Hamiltonian should not be statistically independent of each other, because a valence electron cannot be directly transferred from one atom to another if it is separated far enough. In other words, the realistic matrix elements are so correlated that the characteristics, say, a specific density of states, distinguishing a specific material from others have to be observed. Furthermore we want to emphasize the fact that, in general, randomness in the Hamiltonian never justifies the statistical independence of matrix elements. Actually the energy eigenvalues of a one-dimensional electronic system with a random potential were exactly proved by Molchanov[20] to obey the Poisson distribution, but not the distribution expected by RMT. Finally we point out that the density of states has to show a profile characteristic of the Hamiltonian under consideration, while RMT always gives Wigner's semicircle law for the ensemble-averaged density of states. The purpose of the present work is to examine by the use of a computational method whether the surface irregularity of metallic fine particles really causes some of the statistical behavior of the energy levels discussed in RMT.

II. METHODS

We have no detailed knowledge about the growing process of metallic fine particles yet. Therefore, we cannot make a computer algorithm governing the growth of realistic metallic fine particles. We pay attention to some specific properties of metallic fine particles, that is, surface irregularity. Though there may be various kinds of algorithms creating random clusters, we have devised an algorithm which creates two-dimensional clusters free from overhangs at the surface and holes inside the clusters. Let us consider the two-dimensional triangular lattice. We grow clusters of size N on the lattice sites. The cluster of size $N'+1$ is grown from the N' cluster as follows. We add one particle at one of the unoccupied sites neighboring the occupied sites with the probability $Q(\xi)$ given by

$$Q(\xi)=\frac{e^{\alpha\xi}}{\sum_{\xi=1}^{z}e^{\alpha\xi}}\ , \tag{2.1}$$

where ξ, z, and α represent, respectively, the number of occupied sites around the site under consideration, the number of nearest-neighbor lattice sites, and the parameter which governs the surface irregularity of clusters (see Fig. 1). The cluster grown in such a manner tends to have a smooth surface when parameter α is large enough, while it has a rough surface when α is small. When $\alpha\lesssim 0.5$ one obtains clusters having holes inside them. Therefore, we have assumed $\alpha\gtrsim 0.5$.

Now we introduce another parameter R which represents the surface roughness more definitely than α does. We define surface irregularity R in our two-dimensional cluster by the following equation:

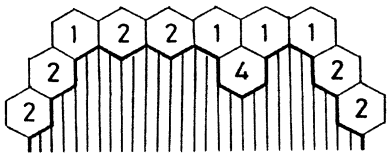

FIG. 1. Occupied sites in the hatched region and unoccupied sites neighboring the occupied sites shown as hexagons. ξ values, which are the numbers of occupied sites around the unoccupied sites, are given inside the hexagons.

$$R=\frac{L^2}{48N}-1\ , \tag{2.2}$$

where L stands for the perimeter of the cluster and the integer 48 comes from a normalization such that $R=0$ if L takes the minimum value, i.e. if the cluster is a regular hexagon. It is evident that the cluster is more irregular as R increases. We assume that all the clusters containing N atoms with the same R or L belong to the same ensemble denoted by (N,R).

Our goal is to obtain statistical properties of electronic energy levels of the clusters in ensemble (N,R). Our program is carried out according to the following three steps:

(i) Grow a cluster belonging to ensemble (N,R). In practical terms, clusters are grown by using a fixed value of parameter α. Then the clusters with the same value of R are collected.

(ii) Diagonalize the tight-binding Hamiltonian H of an electron in the cluster defined by

$$H=-\sum_{\langle i,j\rangle} C_i^{\dagger}C_j\ , \tag{2.3}$$

where $\langle i,j\rangle$ represents the i site as the nearest neighbor of the j site, and $C_i^{\dagger}$ and C_i are the creation and the annihilation operators, respectively. In addition we choose an energy scale which makes the value of the transfer integral unity. For simplicity the spin is neglected. Accordingly, only the orthogonal ensemble is considered. Note that we never deal with the Gaussian orthogonal ensemble given as in Eqs. (1.1a) and (1.1b) with $\beta=1$.

(iii) Repeat procedures (i) and (ii) 600 times and examine the distribution of the level spacings.

We are interested in the fluctuation of energy levels due to surface irregularity. For the purpose of seeing only the fluctuation of energy levels, we define the unfolded level spacing x as the relation

$$x=\frac{E_{\nu+1}-E_\nu}{\langle\delta_\nu\rangle_{\rm ens}}\ , \tag{2.4}$$

where E_ν is the νth energy eigenvalue and $\langle\delta_\nu\rangle_{\rm ens}$ an ensemble average of level spacing $E_{\nu+1}-E_\nu$. From now on for brevity we will call x the level spacings. We examine closely the properties of distributions of the unfolded level spacings mainly around the middle of the energy band.

In addition to the two-dimensional case just mentioned, we have also carried out simulations for three-dimensional clusters on simple-cubic lattice sites. In this case, the surface irregularity parameter R is defined as

$$R=\frac{S^{1.5}}{6^{1.5}N}-1\ , \tag{2.5}$$

where S is the surface area of the cluster. Such an extension of the method is straightforward, so that the detailed descriptions are omitted in this paper.

III. RESULTS

First, we talk about the results in the two-dimensional case. We show figures of some representative clusters with $N=1200$ created in the manner mentioned in the previous section [see Figs. 2(a)–2(c)]. It is found that the degree of surface roughness increases as parameter R becomes large.

Next we show results of the calculation of the electronic states of the clusters. In this calculation, we have assumed rather small sizes, $N=100$, 200, and 300. Figures 3(a) and 3(b) show the ensemble-averaged density of states for ensembles $(N,R)=(300, 0.034)$ and (300, 0.210) consisting of almost regular clusters and fairly irregular ones, respectively. Comparing these two, we find that the surface irregularity has few effects on the gross feature of the averaged density of states. The roughness of the histogram in Fig. 3(a) is due to a limited number of different clusters belonging to ensemble (N,R): We say that two clusters are different if their energy spectra are not identical. Actually the number of different clusters is only about 20 for ensemble (300, 0.034) while it is much greater than 20 for ensemble (300, 0.210). This number increases rapidly as N and/or R increases. We form an ensemble by taking 600 samplings, but we discard the ensembles which contain at least two of the same clusters, as the shortage of the number of different clusters does not seem to justify the level statistics. We emphasize the point that the event looks equally probable in any different cluster belonging to ensemble (N,R) grown by means of our algorithm, as no identical cluster appears in

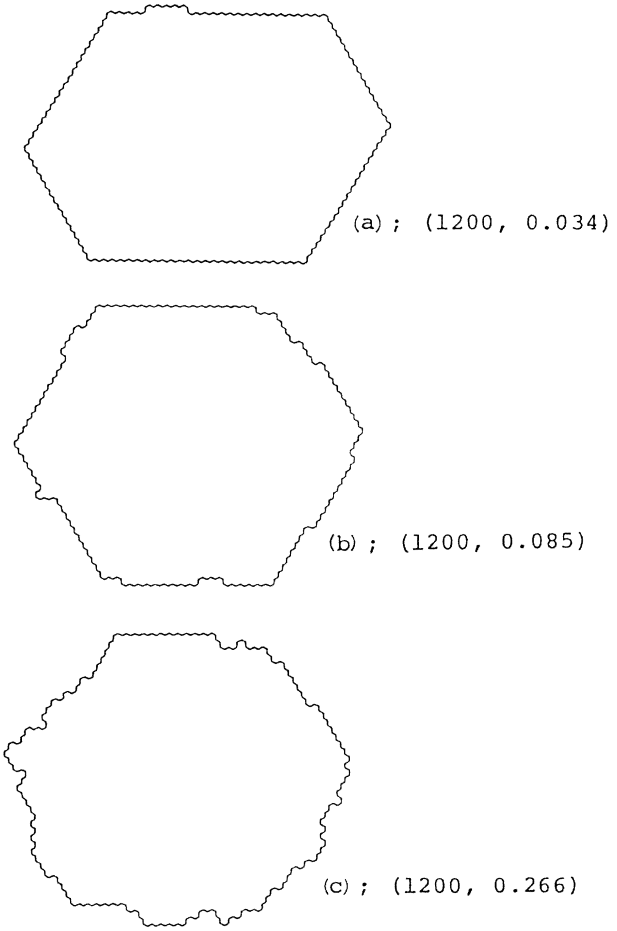

FIG. 2. Some representative two-dimensional clusters shown in (a), (b), and (c) belonging to ensembles (1200, 0.034), (1200, 0.085), and (1200, 0.266), respectively. It is found that the degree of surface roughness increases as parameter R increases.

the adopted ensembles. Note that the semicircle-profile averaged density of states expected from RMT is not attained.

In the analysis, as is usually done in studying quantum chaos,[9-13,21,22] we compare the level-spacing distributions obtained from our simulations with Brody distributions[23] defined by the following form:

$$P_B(x;\omega)=(\omega+1)\kappa(\omega)x^{\omega}\exp[-\kappa(\omega)x^{\omega+1}]\,, \tag{3.1a}$$

$$\kappa(\omega)=\left[\Gamma\left[\frac{\omega+2}{\omega+1}\right]\right]^{\omega+1}, \tag{3.1b}$$

where $\Gamma(x)$ is the Γ function of x and parameter ω evidently corresponds to the exponent representing the degree of level repulsion. This distribution is devised as an interpolation formula connecting the Wigner distribution ($\omega=1$) and the Poisson distribution ($\omega=0$). The Wigner distribution is known to be an excellent approximate formula for the results of RMT in the orthogonal ensemble. Therefore, we may well conclude that RMT is applicable for discussing the statistical behavior of electronic energy levels of metallic fine particles if the Wigner distribution is realized in our calculation. The relation between variance

$$\sigma_j=[\langle(x_j-1)^2\rangle_{\rm ens}]^{1/2} \tag{3.2}$$

and order of energy level j is shown in Fig. 4 for ensemble (300, 0.210). We see constant σ with small fluctuations over the wide range around the middle of the energy band. This fact is thought to reveal that the level-spacing distribution is nearly independent of j. Therefore, we take into account about 100 level spacings around the middle of the band, for the purpose of increasing the sampling number, in order to obtain level spacing distributions. Nevertheless, we are interested in the statistical behavior near Fermi level only. In what follows it will be shown that the calculated level-spacing distributions agree with Brody distributions if appropriate values of ω are chosen. Histograms of Figs. 5(a), 5(b), and 5(c) show the level-spacing distributions in the ensembles (300, 0.068), (300, 0.102), and (300, 0.210), respectively. The level repulsion exponent ω is obtained by using the relation between ω and σ as

$$\sigma=\frac{1}{\Gamma\left[\frac{\omega+2}{\omega+1}\right]}\left[\Gamma\left[\frac{\omega+3}{\omega+1}\right]-\Gamma^2\left[\frac{\omega+2}{\omega+1}\right]\right]^{1/2}. \tag{3.3}$$

Here σ is a variance of level spacings. This procedure gives $\omega=0.795$, $\omega=0.884$, and $\omega=0.967$ for (300, 0.068), (300, 0.102), and (300, 0.210), respectively. Solid curves of Figs. 5 show Brody distributions with ω's given here and, for comparison, the Wigner distribution is shown as a dashed curve.

Next we exhibit the change of ω with respect to R in the three cases of N, that is, $N=100$, 200, 300 in Fig. 6. This figure shows that if surface irregularity R is small, the level repulsion is weak, in disagreement with the level statistics expected from RMT. The theory, however, successfully describes the fluctuation of electronic energy lev-

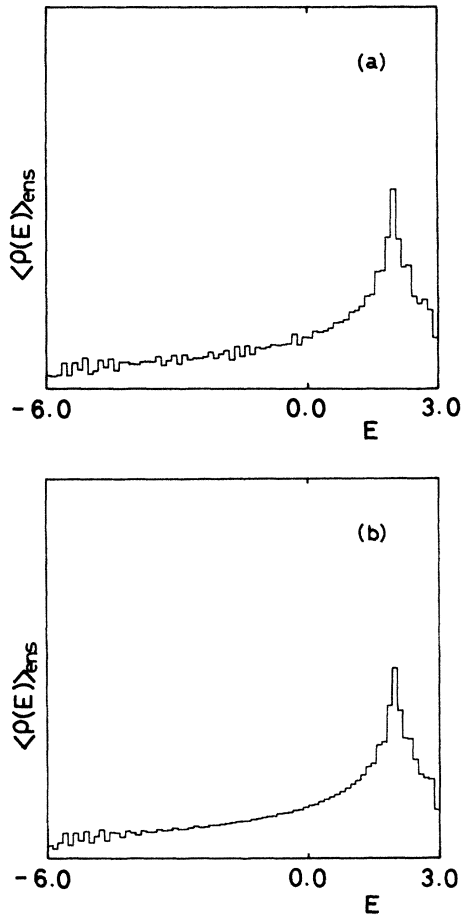

FIG. 3. Ensemble-averaged density of states $\langle\rho\rangle_{\rm ens}$ versus energy E in the two-dimensional case. $\langle\rho(E)\rangle_{\rm ens}$ of ensemble (300, 0.034) and (300, 0.210) are shown in (a) and (b), respectively. $\langle\rho(E)\rangle_{\rm ens}$ of (a) is not so smooth as that of (b) due to the shortage of sample clusters.

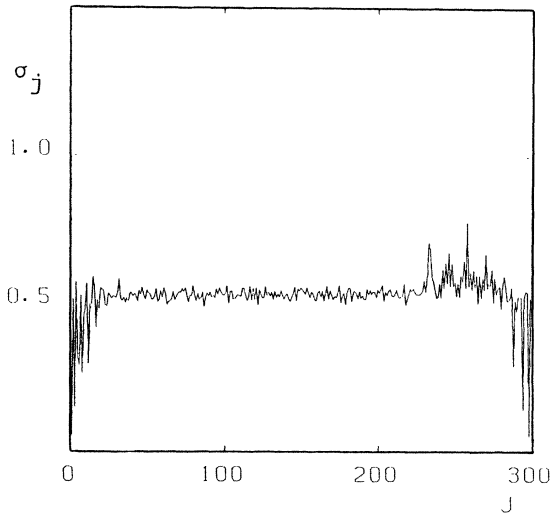

FIG. 4. Variance σ versus the order of energy levels j in ensemble (300, 0.210) of two-dimensional clusters. We find constant σ with small fluctuations over the wide range around the middle of the energy band.

els as long as the cluster morphology is irregular enough, because ω approaches unity. It is seen from Fig. 6 that ω has no size dependence; in other words, ω is a function of R but not N. Now let us consider the R dependence of ω in more detail. Figure 7 shows that the relation between $\log(1-\omega)$ and $\log R$ is almost linear. We get the value of slope $-\eta$ as $\eta \simeq 1.7$. Then, ω is written as follows:

$$\omega=\omega_0\left[1-\frac{c}{R^{\eta}}\right] \quad \text{for } R \gtrsim 0.1 , \tag{3.4}$$

where $\omega_0=1$, $\eta=1.7\pm0.1$, and c is a constant relating to the dimensionality of clusters and the lattice symmetry, but independent of irregularity R and particles size N. The solid curve shown in Fig. 6 is drawn by using Eq. (3.4). A high degree of surface irregularity seems to guarantee the applicability of RMT in spite of the disagreement in the ensemble-averaged density of states.

We have studied the level-spacing distributions at the bottom of the energy band as well as at the middle of the band. As an example, we show the distribution at the band bottom for ensemble (300, 0.210) in Fig. 8. The solid curve, which is given by Brody distribution with $\omega=21.38$, agrees well with the histogram. It is mysterious that we obtain a good agreement of the results of simulations with Brody distribution for $\omega \gg 1$.

As mentioned in the preceding section, we have also carried out computer simulations for the three-dimensional clusters of $N=200$, which are grown on the simple-cubic lattice sites. By using the irregularity parameter defined in Eq. (2.5), the R dependence of ω is calculated as shown in Fig. 9. It appears that ω reaches a value $\omega_0<1$ if R increases. If we assume $\omega_0=0.96$, we obtain the linear relation between $\log(\omega_0-\omega)$ and $\log R$ as shown in Fig. 10. The value of slope $-\eta$ is given by $\eta \simeq 2.2$. Therefore, we get a relation similar to that in Eq. (3.4). In the present case, $\omega_0=0.96\pm0.02$, $\eta=2.2\pm0.2$,

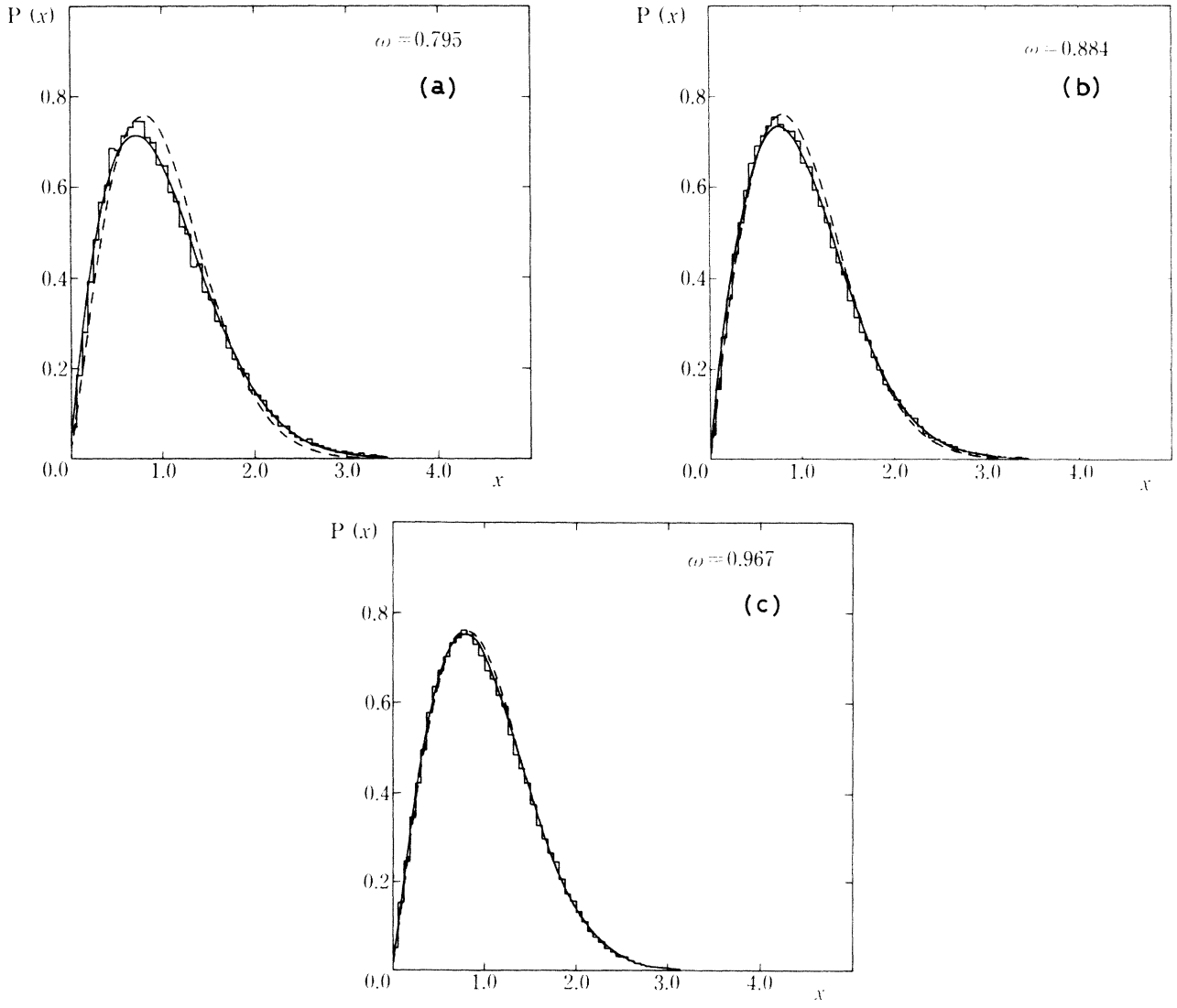

FIG. 5. Level-spacing distributions $P(x)$ of the ensemble of two-dimensional clusters (300, 0.068), (300, 0.102), and (300, 0.210) in (a), (b), and (c), respectively. Each ω value is also shown. Solid curves are Brody distributions $P_B(x;\omega)$ given by Eq. (3.1). For comparison, Wigner distributions $P_W(x)=(\pi/2)x\exp[-(\pi/4)x^2]$ are shown by dashed curves. A good agreement of $P_B(x;\omega)$ with $P(x)$ is found in each case when an appropriate value of ω is used.

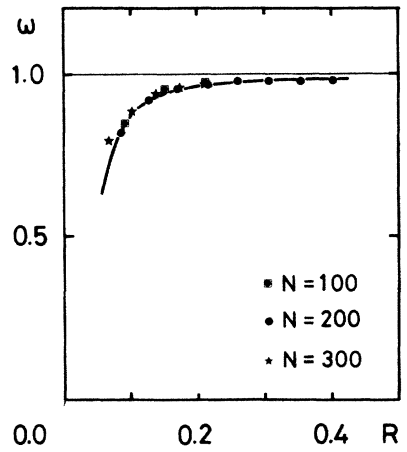

FIG. 6. Level-repulsion exponent ω against surface irregularity R for $N=100$, 200, 300 in the two-dimensional case. The thin solid line is $\omega=1$, and the solid curve is $\omega=1-c/R^{\eta}$, where $\eta=1.7$ and $c=2.6\times10^{-3}$.

and c is a constant different from that of the two-dimensional case. Note that η is nearly 2 in both the cases of two and three dimensions.

IV. DISCUSSION AND CONCLUSION

First we consider the physical meaning of the surface irregularity R. We define n_{irreg} as the sum of the number of sites protruding out and caving in from the regular cluster with a given size N (see Fig. 11). The irregularity R may be defined as the ratio of the number of irregular sites n_{irreg} to cluster size N, that is,

$$R\simeq\frac{n_{\text{irreg}}}{N}\ , \tag{4.1}$$

as is explained in the following way. Let us denote by L_0 ($N=L_0^2/48$) the perimeter of a regular hexagon containing N atoms. This perimeter is increased to $L=L_0+\Delta L$ due to the protruding out and the caving in of the surface sites causing the microscopic irregularities. As far as $(\Delta L/L_0)\ll1$, one can show that n_{irreg} is given as

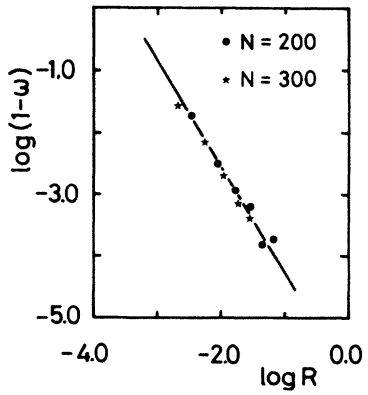

FIG. 7. $\log(1-\omega)$ vs $\log R$ in the two-dimensional case. A linear relation is found in this figure.

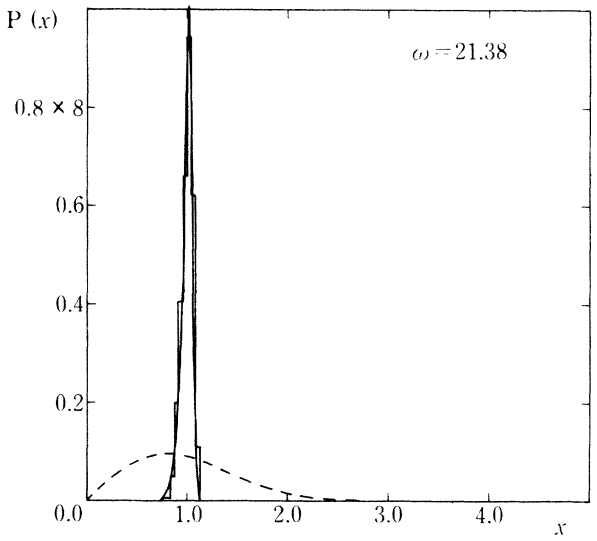

FIG. 8. Distribution $P(x)$ of spacing x between the first and second energy levels at the band bottom for ensemble (300, 0.210). The solid curve is the Brody distribution $P_B(x;\omega)$ with $\omega=21.38$ and the dashed curve the Wigner distribution.

$$n_{\text{irreg}}=\frac{L_0^2}{48}\left[2\frac{\Delta L}{L_0}\right]\simeq\frac{L^2}{48}-N\ , \tag{4.2}$$

in agreement with Eq. (2.2). In the general cases, including the three-dimensional ones, the relation (4.1) can be shown to be also valid in a similar manner.

It is likely that the irregularities of actual fine particles are confined to one or two atomic layers at the surface. Therefore, n_{irreg} is approximately limited by n_{surf}, the number of atoms at the surface of the regular cluster. Then, we find that R is limited by $R_{\max}$ given by

$$R_{\max}\simeq\frac{n_{\text{surf}}}{N}\ , \tag{4.3}$$

which is inversely proportional to the diameter of fine

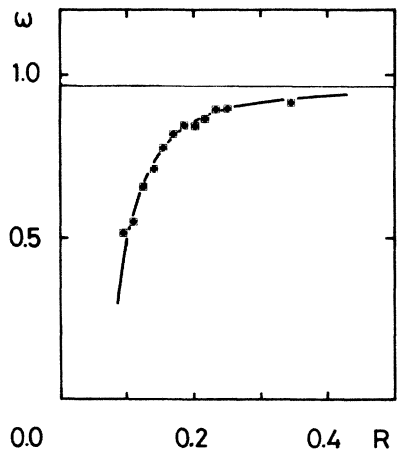

FIG. 9. Level-repulsion exponent ω versus surface irregularity R for $N=200$ in the three-dimensional case. The thin solid line is $\omega=\omega_0$ and the solid curve $\omega=\omega_0(1-c/R^{\eta})$, where $\eta=2.2$, $\omega_0=0.96$, and $c=3.1\times10^{-3}$.

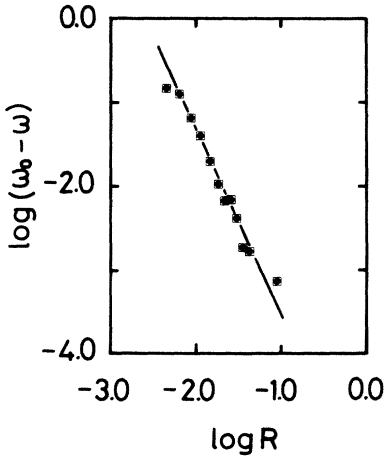

FIG. 10. $\log(\omega_0-\omega)$ vs $\log R$ in the three-dimensional case.

particles. Then, the level-repulsion exponent has a maximum value $\omega_{\max}$ when $R=R_{\max}$, where $\omega_{\max}=\omega_0(1-c/R_{\max}^{\eta})$. $\omega_{\max}$ decreases as the particle size increases. As already pointed out, the level statistics break down for very small particles due to the shortage of the members of ensemble. From these two limitations, there may be appropriate sizes neither too large nor too small where the results of RMT approximately hold. These sizes may depend upon the dimensionality and the lattice symmetry.

For three-dimensional fine particles with simple-cubic lattice symmetry, the value of ω is at most 0.7, if the size N is about 5×10^4 (the diameter $d\simeq100$ Å). On the other hand, the large ω value at the band bottom means rigidity of the first two energy levels. This is due to the fact that the wave functions, which have very small amplitudes near the surface region, are insensitive to the surface irregularity.

In conclusion, investigating the level-spacing distribution of clusters with the same size and the same degree of surface irregularity, we have seen that the Brody distribution with fitting parameter ω is a good approximate function for the distributions not only around the middle of the energy band ($\omega\simeq1$) but also at the band bottom ($\omega\gg1$). We also have found that, as the surface irregularity R increases, the level-repulsion exponent ω increases up to a certain constant $\omega_0(\simeq1)$ in such a manner as $\omega\sim\omega_0(1-c/R^{\eta})$, where η is almost equal to 2 and c is a constant which depends upon the dimensionality and the lattice symmetry of the clusters. We have pointed out that there may be a maximum surface irregularity $R_{\max}$ which is inversely proportional to the diameter of fine particles in real cases. Then, it is probable that ω becomes much smaller than the value expected from RMT as the particle size increases. Level statistics evidently break down for small enough particles due to the shortage of the members of ensemble. Therefore, there should be an approximate particle size neither too large nor too small for the particles to which RMT may be applied. In a future publication we intend to discuss the relation between ω and R for the symplectic ensemble as well as the orthogonal one by the use of an analytical method which is developed on the basis of the Brownian motion theory of random matrices.[5]

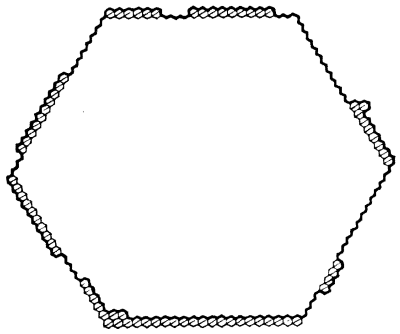

FIG. 11. Picture of a cluster for $N=1200$. n_{irreg} is given as the number of sites inside the hatched region.

ACKNOWLEDGMENT

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