Density of electron levels of small metal particles and thin films with defects

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The density of electron levels in small metal particles with defects is analyzed in the case in which the defectiveness of the particles in terms of shape and structure is too slight for the application of the Dyson level statistics. Surface or bulk impurity atoms or vacancies play the role of small-scale irregularities in the particles, while fluctuations in the sizes of the particles play the role of large-scale fluctuations. Defects give rise to an "ensemble width" of the levels of identical particles of an ensemble with different distributions of these defects. This width is nonzero even in the first approximation in the defect potential, but it fades away with increasing particle size. This ensemble width also determines the correlation function of the levels. As different levels merge with each other, this correlation function vanishes in a manner which is generally different from that in Dyson statistics. The large-scale fluctuations wipe out the correlations in the arrangement of levels which are far apart. A smooth density of levels is found for small particles and thin films and is used to determine how the defects affect the size dependence of the Fermi level.

INTRODUCTION

The distribution of discrete electron levels is a question of fundamental importance to the low-temperature thermodynamics and kinetics of small metal particles. This distribution is extremely complex even for particles of regular shape without bulk defects. For spherical particles, for example, the energy of an electron level is determined directly by two quantum numbers, n and l, so at large values of n and l the sequence of levels appears to be random. These levels have a high degree of degeneracy, $2(2l + 1)$, where the typical orbital quantum number l is on the order of $k_F R$, where k_F is the Fermi momentum, and R is the radius of the particle.

Very often, the shape of small particles is far from regular, and the distribution of energy levels in them is even more complex, since the degeneracy in terms of the orbital angular momentum is lifted. Since there is obviously no hope for success in solving the problem of the distribution of levels for an arbitrary shape of the particles, an ansatz approach has been taken: The most important features of this distribution in an ensemble of particles with arbitrary shapes have essentially been guessed. Of primary interest for the low-temperature properties is a two-level distribution function $P(\omega)$ which describes the probability that two levels will be separated from each other by ω. It was assumed in Ref. 1 that there are no correlations in the arrangement of levels. It was suggested in Ref. 2 that the distribution of levels in particles is similar to that predicted by Dyson's theory of random matrices,[3] i.e., that at small values of ω the probability $P(\omega)$ vanishes, while at large distances it oscillates and falls off according to a power law.

The postulates of Refs. 1 and 2 of course require a foundation at the microscopic level, especially since doubt has been expressed regarding the universal validity of the Dyson distribution.[4] Unfortunately, microscopic calculations have yet to provide the unambiguous resolution of this question. A rigorous solution of the one-dimensional problem has shown that the Dyson level statistics is not valid in the one-dimensional case.[5] An ensemble of two-dimensional rectangular potential wells was studied in Ref. 6; the length of one side of the rectangle was varied. It was found that the distribution of levels in this ensemble again is not described by Dyson statistics: There is no repulsion between levels. This result essentially confirms that Dyson statistics is indeed not of universal applicability, so the range in which it actually is applicable must be determined.

Serious progress in this direction was made in Ref. 7, where it was shown that if the number of Fourier harmonics describing a surface irregularity is small then the level distribution is very different from a Dyson distribution, but as this number of harmonics increases it approaches a Dyson distribution. The results of a numerical simulation[8] provide further evidence for this tendency. The electron spectrum of a particle of regular shape but with a random internal potential $U(\mathbf{r})$ was studied in Ref. 9. Under conditions such that the potential U causes a shift of the levels in the spectrum which is large in comparison with the average distance between the quantum-size levels but small in comparison with the Fermi energy, it was found possible to analytically derive a correlation function of the levels which was independent of the amplitude U and which was the same as the Dyson correlation function for all three ensembles (unitary, symplectic, and orthogonal). Although the calculations of Ref. 9 directly confirm that there is a range of applicability for Dyson statistics, it is difficult to directly compare the results of those calculations with real physical systems because the calculations were based on a model.

If we look at real small particles, on the other hand, we find that their shape is fairly regular for many of the technological procedures used to produce them. For example, crystalline indium particles with a nearly ideal spherical shape were produced in Ref. 10. Nevertheless, the presence of surface defects (vacancies or impurity atoms) and the scatter in the sizes of the particles make the spectrum of particles random, although this random nature is definitely not described by the Dyson theory, because of the relatively small number of defects. Our purpose in the present study was to learn about the distribution of levels in small particles with a shape which is not very irregular.

Consider the following model. The particles making up

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the ensemble are rectangular parallelepipeds with a simple cubic lattice structure. At the surface or in the interior of a particle there are point defects. There is the further possibility that there are large-scale irregularities, which are modeled here, as in Ref. 6, by a scatter in the length of the edges of the rectangular parallelepipeds. The calculations are carried out in first order in the relative defect concentration v, but without any restriction on the magnitude of the defect potential U (the limit $U \to \infty$ corresponds to vacancies).

Strictly speaking, in this model the spectrum remains discrete (in contrast with Dyson's theory) after an average is taken over the distribution of defects over a particle. The average distance between levels is $\propto N^{-2}$, where $N \gg 1$ is the number of atoms in the particle (if the particle size is greater than 50 Å, the value of N will definitely be greater than 10^3–10^4). Since the typical distance between the levels in an ideal particle is $\propto N^{-1/3}$, however, the average spectrum can still be regarded as continuous. This continuous nature has nothing in common with the level broadening caused in an infinite sample by the scattering of electrons by defects. The width of a line, depending on U, will be nonzero even in first order in U. Since it is proportional to $N^{-1/2}$, however, it vanishes for bulk samples. Physically, an ensemble width of levels of this type describes a scatter in the positions of the levels in particles which are identical in shape but in which the distributions of defects are different. This scatter leads in particular to a scatter in the positions of the Fermi level of these particles, which in turn leads to differences in emission and other properties.

Repulsion between levels should naturally occur again in this case. The width of the distribution of distances between two levels is on the order of the ensemble width of these levels. If the level in the ideal crystal is degenerate, it is split by an impurity. A two-level distribution function vanishes with decreasing distance between the components of the level, in the same manner as in an orthogonal Dyson ensemble. If the levels in the ideal crystal are instead nondegenerate, then the decay of their two-level distribution function as the levels move closer together follows an exponential rather than a power law.

In addition to the correlations between nearest levels, the correlations between levels which are very far apart are also of interest. If we restrict the discussion to small-scale irregularities, we conclude that this correlation should persist, at least for small values of U, since the impurity which smears the levels has essentially no effect on the positions of their centers of gravity. Taking an average over the large-scale irregularities erases this "long-range order" in the arrangement of levels, while small-scale irregularities intensify the effect of the large-scale irregularities. The disappearance of correlations, however, occurs in a manner different from that described by Dyson statistics.

At high temperatures the actual density of levels g can be replaced by a smooth density $\tilde{g}(E)$ found by taking an average of g over energy intervals ΔE which are small in comparison with T but large in comparison with the average distance between levels. In contrast with $g(E)$, the quantity $\tilde{g}(E)$ is a continuous function of the energy E, and a "memory" of the level quantization is manifested by a surface increment $\tilde{g}_S(E)$ in the ordinary density of levels $\tilde{g}_V(E)$. If the irregularities are of large scale, this increment will depend on only the surface area, according to Ref. 11. There has been

no previous study of how large-scale irregularities affect $\tilde{g}(E)$. It is shown below that when $g(E)$ is averaged over the intervals ΔE the dependence of $\tilde{g}(E)$ on the nature of the impurity distribution disappears in first order in v. Since the impurity part of the surface density of levels $\tilde{g}_S$ depends on the energy more strongly than the ideal part of this density does, the relative contribution of surface defects to such characteristics as the Fermi energy may be far greater than the relative concentration of such defects.

DENSITY OF LEVELS OF A CRYSTAL OF FINITE DIMENSIONS WITH DEFECTS

We consider a crystal with a simple cubic lattice. The sample is a right parallelepiped with sides whose lengths are equal to L_i lattice constants ($i = x,y,z$). It is bounded by (100) planes. In the nearest-neighbor approximation, the electron Hamiltonian is

$$H = H_0 + H_d,$$
$$H_0 = U_0 \sum_s a_s^* a_s + B \sum' a_g^* a_{g'},$$
$$H_d = U \sum_n a_n^* a_n.$$

(1)

Here the operators a_g^*, a_g create and annihilate a conduction electron at site g (we are omitting the spin index); the subscript S specifies atoms in the first surface layer; and the prime on the summation sign for the summations over g and g' in the expression for H_0 means that the summation is to be carried out over nearest neighbors. The subscript n represents the coordinates of the defect, which has a δ-function potential U.

We perform a canonical transformation of the electron operators which diagonalizes the Hamiltonian H_0:

$$a_g = \sum_p F_{pg} a_p, \quad p = p_s \quad \text{or} \quad p_c,$$
$$F_{pg} = f(p_{xt_x} g_x) f(p_{yt_y} g_y) f(p_{zt_z} g_z),$$

(2)

where $f(p_t g)$ ($t = s$ or c) represents trigonometric functions:

$$f(p_{si} g_i) = N_{p_{si}}^{-1/2} \sin(p_{si} g_i), \quad N_{p_{si}} = \frac{L_i}{2}(1 - \chi_{p_{si}}),$$

(3)

$$f(p_{ci} g_i) = N_{p_{ci}}^{-1/2} \cos(p_{ci} g_i), \quad N_{p_{ci}} = \frac{L_i}{2}(1 + \chi_{p_{ci}}),$$

(4)

$$\chi_{p_i} = \sin(L_i p_i) / L_i \sin p_i.$$

The allowed values of the momentum components p_{ti} are determined by relations which follow from (1)–(3):

$$l_i p_{si} = \pi n_{si} + \text{arcctg}\, Q(p_{si}),$$
$$l_i p_{ci} = \pi n_{ci} - \text{arctg}\, Q(p_{ci}),$$

(5)

where

$$Q(p) = (v - \cos p)/\sin p, \quad v = U_0/B, \quad l_i = (L_i - 1)/2.$$

The integers n_{ti} in (5) are found from the condition that the momenta p_{ti} belong to the interval $[0, \pi]$. Relations (5) are based on the assumption that the surface potential U_0 is not strong enough to give rise to surface bands in the spectrum of

an ideal crystal. According to Ref. 12, the inequality $|v| \leqslant 1$ must therefore hold.

As a result of the transformation (2)–(5), the Hamiltonian (1) becomes

$$H = \sum_{\mathbf{p}} E_{\mathbf{p}} a_{\mathbf{p}}^{*} a_{\mathbf{p}} + U \sum_{\mathbf{p},\mathbf{p}',n} F_{\mathbf{p}n} F_{\mathbf{p}'n} a_{\mathbf{p}}^{*} a_{\mathbf{p}'}, \qquad (6)$$

$$E_{\mathbf{p}} = 2\dot{B}(\cos p_x + \cos p_y + \cos p_z). \qquad (7)$$

The density of electron levels is found from the imaginary part of the retarded one-electron Green's function:

$$\langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle_{\tau} = -i\langle [a_{\mathbf{p}}(\tau) a_{\mathbf{p}'}^{*} + a_{\mathbf{p}'}^{*} a_{\mathbf{p}}(\tau)]\rangle \theta(\tau),$$

$$a_{\mathbf{p}}(\tau) = \exp(iH\tau) a_{\mathbf{p}} \exp(-iH\tau),$$

where $\theta(\tau) = 1$ for $\tau \geqslant 0$ and $\theta(\tau) = 0$ for $\tau < 0$, and the angle brackets imply temperature averaging with the Hamiltonian (6). Constructing equations of motion for the Green's functions, and transforming to their Fourier time transforms,

$$\langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle_{\tau} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle_{E} \exp(-iE\tau),$$

we find

$$(E - E_{\mathbf{p}}) \langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle = \delta_{\mathbf{p}\mathbf{p}'} + U \sum_{n} F_{\mathbf{p}n} X_{n}, \qquad (8)$$

where

$$X_{n} = \sum_{\mathbf{p}''} F_{\mathbf{p}''n} \langle\langle a_{\mathbf{p}''} | a_{\mathbf{p}'}\rangle\rangle.$$

From (8) we find an equation for the quantities X_{n}:

$$X_{m} = F_{\mathbf{p}'m}(E - E_{\mathbf{p}'})^{-1} + U \sum_{n} R_{mn} X_{n},$$

$$R_{mn} = \sum_{\mathbf{p}} F_{\mathbf{p}n} F_{\mathbf{p}m}(E - E_{\mathbf{p}})^{-1}. \qquad (9)$$

Equations (8) and (9) can be solved by expanding in the relative impurity concentration v as in Ref. 13. To first order in v we should set $R_{nm} \sim \delta_{nm}$ on the right side of (9):

$$\langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle = (E - E_{\mathbf{p}})^{-1}\left\{ \delta_{\mathbf{p}\mathbf{p}'} + U(E - E_{\mathbf{p}'})^{-1} \sum_{n} F_{\mathbf{p}n} F_{\mathbf{p}'n} Z_{n}^{-1} \right\}, \qquad (10)$$

$$Z_{n} = 1 - U G_{n}(E), \quad G_{n} = \sum_{\mathbf{p}} F_{\mathbf{p}n}^{2}(E - E_{\mathbf{p}})^{-1} \equiv G_{nc} + G_{ns}, \qquad (11)$$

$$\frac{1}{x} = \frac{1}{x - i0} = \frac{P}{x} + i\pi\delta(x). \qquad (12)$$

From (10) we directly find an expression for the density of electron levels which is exact if there is only a single defect in the crystal:

$$g(E) = \frac{1}{\pi} \operatorname{Im} \sum_{\mathbf{p}} \langle\langle a_{\mathbf{p}} | a_{\mathbf{p}'}^{*}\rangle\rangle = g_0(E) + g_d(E), \qquad (13)$$

$$g_0(E) = \sum_{\mathbf{p}} \delta(E - E_{\mathbf{p}}), \qquad (14)$$

$$g_d(E) = \frac{1}{\pi} \operatorname{Im} \sum_{n} \frac{d}{dE} \ln Z_{n}(E). \qquad (15)$$

Obviously, g_0 is the density of levels of an ideal crystal, and g_d is the correction to it for defects. Expression (15) can be interpreted in any order in U with the help of (12) and the relations

$$x\delta(x) = 0, \quad \frac{d^n}{dx^n}\delta(x) = (-1)^n n! \delta(x) x^{-n}.$$

In the Born approximation we find, for $(E_{\mathbf{p}} - E_{\mathbf{p}'})^2 \gg |(H_d)_{\mathbf{p}\mathbf{p}'}|^2 \sim U^2 v/N$ [see expression (25) below],

$$g(E) = \sum_{\mathbf{p}} \delta(E - \tilde{E}_{\mathbf{p}}), \qquad (16)$$

$$\tilde{E}_{\mathbf{p}} = E_{\mathbf{p}} + U \sum_{n} F_{\mathbf{p}n}^{2}\left[1 + U \sum_{\mathbf{p}' \neq \mathbf{p}} F_{\mathbf{p}'n}^{2}(E_{\mathbf{p}} - E_{\mathbf{p}'})^{-1} \right]. \qquad (17)$$

In the limit $U \to \infty$, which corresponds to vacancies, on the other hand, we find from (15)

$$g_d = \frac{1}{\pi} \sum_{n} \frac{d}{dE} \operatorname{arctg}(\operatorname{Im} G_n / \operatorname{Re} G_n). \qquad (18)$$

According to (18), near the bottom of the conduction band the density of levels can be written as in (16) with

$$\tilde{E}_{\mathbf{p}} = E_{\mathbf{p}} + \sum_{n}\left[\sum_{\mathbf{p}' \neq \mathbf{p}} F_{\mathbf{p}'n}(E_{\mathbf{p}} - E_{\mathbf{p}'})^{-1} \right]^{-1} F_{\mathbf{p}n}^{2}. \qquad (19)$$

AVERAGING THE DENSITY OF LEVELS OVER THE IMPURITY DISTRIBUTION

The spectrum of a crystal of finite dimensions differs from that of an infinite crystal in that it depends on the impurity distribution even in first order in v [because the number of terms in the sum over n in (15) is finite]. The impurity does not by itself convert the discrete spectrum of an individual particle into a continuous spectrum, but in an ensemble of particles the arrangement of levels is random, so the spectrum of the entire set of particles in the ensemble can be assumed continuous. A change of g′ in the defect coordinate g changes the electron energy by an amount $\propto (F_{\mathbf{p}g}^2 - F_{\mathbf{p}g'}^2)$. Since $F_{\mathbf{p}g'}^2 \propto 1/N$ takes on N values as g is varied, the distance between neighboring possible positions of the level $\tilde{E}_{\mathbf{p}}$ is on the order of N^{-2}. In other words, according to (5) and (7) this distance is on the order of $N^{5/3}$ of the typical distance between levels in an ideal crystal with $p \sim 1$. The set of possible level positions in the particles of an ensemble can be interpreted as the spectrum of a particle averaged over the ensemble.

We will now average the density of levels over an ensemble of identical particles with different numbers of defects. The calculation below is valid both for impurities in the Born approximation and for vacancies, regardless of whether the defects are in the interior of the sample or at its surface. We first consider an ensemble of particles which are asymmetric parallelepipeds ($L_x \neq L_y \neq L_z$). In this case the spectrum of an ideal crystal is nondegenerate, since different energies, (5) and (7), correspond to states with sinusoidal and cosinusoidal wave functions (3) and (4), in contrast

with the case in an infinite crystal. Since the summation over $\mathbf{p'}$ in (17) and (19) actually leads to an averaging over the coordinates of the defects, the density of levels averaged over the distribution of the defects can be written

$$\langle g(E)\rangle_d=\sum_{\mathbf{p}}\left\langle \delta\left(E-E_{\mathbf{p}}-\widetilde{U}_{\mathbf{p}}\sum_k F^2_{\mathbf{p}g_k}\right)\right\rangle_d. \tag{20}$$

Here k is the defect index, and the quantity $\widetilde{U}_{\mathbf{p}}$, whose meaning is obvious from (17) and (19), is assumed to be independent of the defect distribution. It is possible to calculate (20) explicitly because there is no correlation in the positions of the defects. Using $F^2\propto 1/N$, we find from (20)

$$\langle g(E)\rangle_d=\frac{1}{2\pi}\sum_{\mathbf{p}}\sum_{g_1}w(g_1)\ldots\sum_{g_M}w(g_M)$$

$$\times\int_{-\infty}^{\infty}d\lambda\exp\left[i\left(E-E_{\mathbf{p}}-\widetilde{U}_{\mathbf{p}}\sum_k F^2_{\mathbf{p}g_k}\right)\lambda\right]$$

$$=\frac{1}{2\pi}\sum_{\mathbf{p}}\int_{-\infty}^{\infty}d\lambda\exp[i\lambda(E-E_{\mathbf{p}})]$$

$$\times\left(1-i\lambda\widetilde{U}_{\mathbf{p}}\langle F_{\mathbf{p}}^2\rangle_d-\frac{\lambda^2\widetilde{U}_{\mathbf{p}}^2}{2}\langle F_{\mathbf{p}}^4\rangle_d\right)^M$$

$$=\frac{1}{(2\pi M)^{1/2}}\sum_{\mathbf{p}}[D_d(F_{\mathbf{p}}^2)\widetilde{U}_{\mathbf{p}}^2]^{-1/2}$$

$$\times\exp\left[-\frac{(E-E_{\mathbf{p}}-\widetilde{U}_{\mathbf{p}}M\langle F_{\mathbf{p}}^2\rangle_d)^2}{2\widetilde{U}_{\mathbf{p}}^2 D_d(F_{\mathbf{p}}^2)M}\right], \tag{21}$$

where the distribution function $w(g)$ describes the distribution of defects over the crystal, and $M=\nu N$ is the total number of defects in a particle consisting of N atoms ($N=L_1L_2L_3$). We also have

$$D_d(F_{\mathbf{p}}^2)=\langle F_{\mathbf{p}}^4\rangle_d-\langle F_{\mathbf{p}}^2\rangle_d^2.$$

If the impurity is distributed uniformly over the entire crystal, we have

$$\langle F_{\mathbf{p}}^2\rangle_d=\frac{1}{N}, \quad D_d(F_{\mathbf{p}}^2)=\frac{19}{8N^2}.$$

If the impurity is instead distributed uniformly over the surface, we have

$$\langle F_{\mathbf{p}}^2\rangle_d=2\sum_i f^2(p_iL_i), \quad \langle F_{\mathbf{p}}^4\rangle=\frac{9}{4N}\sum_i L_if^4(p_iL_i).$$

The result (21) is equivalent to that found by the usual method of steepest descent. This result can be used after the summation over $g_1\ldots g_M$ is replaced by an integration. As a result of this integration, we are left with an integral over λ whose integrand contains the large parameter M in an exponential function. Since the calculation of (21) is approximate, we find an expression which is smoothed in energy and thus a continuous function of the energy. Mathematically, this smoothing arises as a consequence of the truncation of the series expansion of the exponential function on the right side of the first equation in (21) in terms of $1/N$. It is not difficult to verify, by direct calculation, for example, that this truncation causes a smoothing of a rectangular pulse into a Gaussian curve which has the same characteristic parameters as those of the rectangular pulse. The *physical* justification for the switch to a continuous spectrum is given below.

It follows from (21) that each of the lines has finite width $\sim\widetilde{U}\nu^{1/2}N^{-1/2}$. Although this width is small in comparison with the average level shift $\widetilde{U}\nu$, it is definitely large in comparison with the average distance between levels, $\sim B/N$, because of the obvious condition $M\gg 1$. For infinitely large samples, this ensemble broadening of the levels does not occur. We should stress that this ensemble broadening, which is nonzero even in the first approximation in U, has nothing in common with the level broadening in an individual large particle. In that case the broadening stems from the decay in the continuous spectrum, i.e., is proportional to U^2.

Although the results derived above apply to particles which are parallelepipeds, they are also valid qualitatively for particles of arbitrary shape. The estimate of the ensemble width of a level found above depends only on the bulk characteristics of the crystal, not its surface characteristics. An attempt to find a more rigorous solution of this problem runs into serious mathematical difficulties. For a spherical particle, for example, one would have to deal with the circumstance that the particle can be regarded as spherical only in the long-wave approximation, but that approximation is inadequate for a correct description of point defects. At the atomic level, on the other hand, the surface of such a particle is a set of microscopic steps, so a quantitative description of the surface becomes extraordinarily difficult.

Ensemble broadening may be manifested as scattering in the Fermi energies of particles which are identical in size and shape; with $\nu=0.1$, $\widetilde{U}=5$ eV, and $N=10^4$, this scatter could reach 0.05 eV. Because of this, the threshold for the external photoelectric effect would be smeared, etc. Another possible manifestation of this broadening is mutual charging of small particles with different Fermi energies, as a result of the tendency for their electrochemical potentials to equalize (in the estimates above, this charging could actually occur if the small particles were in a medium with a dielectric constant $\gtrsim 10$). Because of this charging, forces would arise between the particles; these forces would fall off with distance in a Coulomb fashion, i.e., far more slowly than the van der Waals forces do.[14,15]

It should also be noted that if there is a spread in the size of the particles in the ensemble and if there is a spread in the impurity concentration in the particles, these spreads will also contribute to the level broadening (more on this below), promoting the manifestation of the effects described above. However, the effect of a spread in size on the Fermi energy of the particles has already been discussed, in Refs. 14 and 15; the corresponding effect of a spread in concentration is not specific to small particles. For this reason, one can also ignore the fluctuations in the density of conduction electrons which stem from fluctuations in the impurity concentration.

Although the mutual charging of small particles differing in size has been observed experimentally,[16] there appear to be no corresponding results on identical particles with an impurity or with shape defects. The same comment applies to the smearing of the threshold for the photoelectric effect in such particles.

CORRELATION FUNCTION OF THE LEVELS

The same method has been used to calculate the level correlation function $P(\omega)$, which determines the probability

that two levels will be separated from each other by a distance ω:

$$P(\omega) = \frac{1}{N^2} \sum_{pp'} P_{pp'}(\omega),$$

$$P_{pp'} = \langle \delta(\omega - \tilde{E}_p + \tilde{E}_{p'}) \rangle_d = [2\pi M (\tilde{U}_p^2 + \tilde{U}_{p'}^2) D_{pp'}]^{-\frac{1}{2}}$$

$$\times \exp\left\{ -\frac{[\omega - E_p + E_{p'} - (\tilde{U}_p - \tilde{U}_{p'}) M \langle F^2 \rangle_d]}{2M D_{pp'} \cdot (\tilde{U}_p^2 + \tilde{U}_{p'}^2)} \right\} \quad (22)$$

where

$$D_{pp'} = D_d - \frac{2\tilde{U}_p \tilde{U}_{p'}}{\tilde{U}_p^2 + \tilde{U}_{p'}^2} (\langle F_p^2 F_{p'}^2 \rangle_d - \langle F^2 \rangle_d^2)$$

(if none of the three components of p coincides with a component of p', we have $D_{pp'} = D_d$).

It follows from (22) that the two-level probability reaches a maximum at $\omega = \tilde{E}_p - \tilde{E}_{p'}$ and vanishes over a length scale which is on the same order of magnitude as that in the ensemble width of a level, i.e., $\tilde{U}v^{1/2}N^{-1/2}$. Because of the imprecision of the method of steepest descent, which we mentioned in the preceding section of this paper, $P_{pp'}(0)$ formally does not vanish and is instead merely exponentially small. In any case, it can be seen from (22) that $P_{pp'}$ vanishes in the limit $\omega \to 0$ not according to a power law but exponentially (one should recall that the typical distance between nondegenerate levels in an ideal crystal, having the behavior $\propto N^{-1/3}$, is large in comparison with the ensemble width of the levels).

It is not difficult to see that a characteristic energy on the order of the ensemble level width is determined by the two-level probability even when the particle is symmetric in shape and has degenerate unperturbed levels. The presence of an impurity lifts the degeneracy, and the components of a split level repel each other. Below we will discuss the case of a parallelepiped with a square base (x,y). We will find the quantity $P_{+,-}(\omega)$ for the components of the split level, $\tilde{E}_p^+$ and $\tilde{E}_p^-$. For a doubly degenerate level with wave functions $f(pg_x)f(p_1g_y)f(qg_z)$ and $f(p_1g_x)f(pg_y)f(qg_z)$, the energies of its components are given by the following expressions in first order in U, according to (3), (4), and (6):

$$E^\pm(p, p_1, q) = E(p, p_1, q) + \frac{U}{2}(V_{11} + V_{22} \pm R^{\frac{1}{2}}) \sum_{n_z} f^2(qn_z),$$

$$R = (V_{11} - V_{22})^2 + 4V_{12}^2, \quad (23)$$

$$V_{11} = \sum_{n_x, n_y} f^2(pn_x) f^2(p_1 n_y), \quad V_{22} = \sum_{n_x, n_y} f^2(p_1 n_x) f^2(pn_y),$$

$$V_{12} = \sum_{n_x, n_y} f(pn_x) f(p_1 n_x) f(p_1 n_y) f(pn_y).$$

According to (23), the level splitting is determined not only by the random off-diagonal matrix elements but also by the random difference between diagonal matrix elements. This result is at odds with the standard hypothesis. This random difference between diagonal matrix elements increases the level splitting even further.

One can determine the manner in which $P_{+,-}(\omega)$ vanishes in the limit $\omega \to 0$ by assuming, as in Ref. 6, that the distribution function of the quantity R is

$$w(R) = \Gamma^{-1}(n+1)\gamma^{n+1} R^n e^{-\gamma R}, \quad (24)$$

where $\Gamma(n)$ is the gamma function. To find the parameters $w(R)$ it is sufficient to know the first two moments of R. Under the assumption of a random distribution of the impurity over the volume, we find the following values for these moments:

$$\langle R \rangle = 13U^2 M / 32N^2, \quad \langle R^2 \rangle = 0,34U^4 M^2 / N^4. \quad (25)$$

It follows from (24) and (25) that the two-level probability $P(\omega)$ is proportional to $\omega^{0.9}$ in the limit $\omega \to 0$, i.e., that its ω dependence is very nearly linear and valid for an orthogonal ensemble. The relatively slow vanishing of $P_{+,-}(\omega)$ in the limit $\omega \to 0$ confirms that it vanishes according to a power law nature as suggested above. In addition, and in contrast with Dyson theory, the length scale for $P(\omega)$ is not W/N but $Uv^{1/2}N^{-1/2}$, i.e., the ensemble level width (W is the width of the conduction band).

Up to this point, the number of defects in a particle, M, has been assumed fixed. In the case of alloys (an impurity in the interior) one can deal with the fluctuations in these numbers from particle to particle by assuming that only the total number of impurity atoms in the ensemble is given. If there is no correlation between defects, then the distribution of the number of defects, M, in the particles is described by a Gaussian function for which the mean value $\bar{M}$ of the number of defects is equal to the standard deviation (a Poisson distribution reduces to a distribution function of this type in the case $M \gg 1$). Averaging expressions (21) and (22) over M with a distribution function of this sort increases the ensemble width of a line but does not change the order of magnitude of the broadening.

Lines of course acquire an ensemble width as the result of an averaging not only over small-scale irregularities but also over large-scale irregularities. An important difference between the averaging procedures in these two cases is that the small-scale irregularities do not by themselves wipe out the correlations in the positions of well-separated levels, while large-scale irregularities do precisely that. That the former part of this assertion is true can be seen from (22): The value of $P_{pp'}(\omega)$ at the maximum is essentially independent of the difference $E_p - E_{p'}$. To verify the second part of the assertion, we consider the class of irregularities consisting of fluctuations in the dimensions L_1, L_2, L_3 of asymmetric right parallelepipeds, i.e., essentially, fluctuations in their shape. These fluctuations are assumed to be small enough that we can ignore the level degeneracy due to a coincidence of side lengths.

For the calculation below it is sufficient to assume $p_i = 2\pi n_i / L_i$ [see (5)]. In the absence of defects, and if the dimensions are distributed in an equiprobable fashion over intervals of width $2\kappa \bar{L}_i$ centered at $\bar{L}_i$, the average two-level probability is given by

$$\langle P_{pp'}(\omega) \rangle_l = \frac{1}{8\kappa^3} \int_{-\kappa}^{\kappa} dr_1 \int_{-\kappa}^{\kappa} dr_2 \int_{-\kappa}^{\kappa} dr_3 \, \delta\left(\omega_0 - \sum_i \omega_i r_i\right)$$

$$= \frac{1}{2\pi\kappa^3 |\omega_1 \omega_2 \omega_3|} \int_{-\infty}^{\infty} \frac{e^{i\omega_0 t}}{t^3 - i0} \prod_i \sin(\omega_i \kappa t) \, dt, \quad (26)$$

$$\omega_i = 2B(\bar{p}_i \sin \bar{p}_i - \bar{p}_i' \sin \bar{p}_i'), \quad \omega_0 = \omega - E_{\bar{p}} + E_{\bar{p}'},$$

$$\bar{p}_i = 2\pi n_i / \bar{L}_i, \quad \{1, 2, 3\} = \{x, y, z\}.$$

Although the integral in (26) can be calculated in terms of the residue in an elementary manner, we will not reproduce the general expression for it, since this expression changes, depending on the relations between ω_0, on the one hand, and ω_1, ω_2, and ω_3, on the other. In all cases, $\langle P_{pp'}\rangle$ vanishes at $|\omega_0| > \varkappa\Sigma_i|\omega_i|$. If $\omega_2 = \omega_3 = 0$, then at $|\omega_0| < \varkappa|\omega_1|$ the quantity $\langle P_{pp'}\rangle$ is equal to $|\varkappa\omega_1|^{-1}$. In general, $\langle P_{pp'}\rangle$ is proportional to $|\omega_1\omega_2\omega_3|^{-1}$. Under the conditions $|\omega_1| + |\omega_2| + |\omega_3| > |\omega_0|\varkappa^{-1} > |\omega_1| + |\omega_2| - |\omega_3|$, for example, we have

$$\langle P_{pp'}(\omega)\rangle_f = \varkappa^{-3}|\omega_1\omega_2\omega_3|^{-1}[\omega_0 - \varkappa(|\omega_1| + |\omega_2| + |\omega_3|)]^2. \quad (27)$$

It follows from (26) that the decay of the amplitude $\langle P_{pp'}\rangle$ with increasing separation of levels p and p' depends directly on this separation only in the one-dimensional case and with a quadratic dispersion law. In general, $\langle P_{pp'}(\omega)\rangle_f$ is a far more complex function of p and p'.

SMOOTHED LEVEL DENSITY AND FERMI ENERGY

In many problems it is sufficient to know, instead of the actual level density, a smoothed level density of an individual particle, which can be found by taking an average of the actual density over energy intervals $\Delta\varepsilon$ which are small in comparison with the characteristic energies but large in comparison with the mean distance between levels, δ. At this point, a smoothed density $\tilde{g}(E)$ of this type has been constructed for ideal crystals. It has been shown that this density can be represented as a sum $\tilde{g}(E) = \tilde{g}_V + \tilde{g}_S$, where $\tilde{g}_V$ and $\tilde{g}_S$ are proportional to the volume V and the surface area S, respectively, of the crystal (provided that the surface is sufficiently smooth; see the review in Ref. 11). Although $\tilde{g}$ is a continuous function of the energy, a memory of the discrete spectrum is retained through the surface increment $\tilde{g}_S$ in $\tilde{g}_V$. The inequality $pL \gg 1$ is a necessary condition for the splitting of $\tilde{g}$ into $\tilde{g}_V$ and $\tilde{g}_S$.

To simplify the equations, we will discuss the particular case of a film with surface or bulk defects. We find a smoothed level density for the film by making use of the fact, established in Ref. 12, that the procedure of taking an average is equivalent to the use of the Euler–Maclaurin formula in the summation over the quantized momentum projection. According to Ref. 12, for any function $f(p)$ the following relations hold in first order in L^{-1}:

$$\sum_{p_s} f(p_s) = \frac{L}{2\pi}\int_0^\pi f(p)\,dp + \left[\frac{1}{\pi}\int_0^\pi \frac{Q'(p)f(p)}{1+Q^2(p)}\,dp\right.$$
$$\left. - \frac{1}{2}f(0) - \frac{1}{2}f(\pi) - \frac{1}{2\pi}\int_0^\pi f(p)\,dp\right],$$

$$\sum_{p_c} f(p_c) = \frac{L}{2\pi}\int_0^\pi f(p)\,dp$$
$$+ \left[\frac{1}{\pi}\int_0^\pi \frac{Q'(p)f(p)\,dp}{1+Q^2(p)} - \frac{1}{2\pi}\int_0^\pi f(p)\,dp\right], \quad (28)$$

where p_s and p_c are given by (5).

In a calculation of $\tilde{g}$, relations (28) must be applied to

expressions (13)–(15). It is first necessary to find smoothed values $\tilde{G}_{cn}$ and $\tilde{G}_{sn}$ of the Green's functions G_{cn} and G_{sn} in (11). For this purpose we should transform the expression for χ_p in (4), which enters G_n through F^2_{pn}, in such a way that the large parameter pL can be eliminated from it with the help of (5). We then find

$$\tilde{G}_n \equiv \tilde{G}_{cn} + \tilde{G}_{sn} = G_0, \qquad G_0 = \frac{1}{(2\pi)^3}\int_{-\pi}^{\pi} d^3p\,[E - E(p)]^{-1}, \quad (29)$$

where G_0 is the Green's function of an infinitely large ideal crystal. The contribution of defects to the smoothed level density is correspondingly given by the same expression as for a crystal of unbounded dimensions:

$$\tilde{g}_d = -UMR/\pi|Z_0|^2,$$
$$R = (1 - U\,\mathrm{Re}\,G_0)\,\mathrm{Im}\,G_0' + U\,\mathrm{Im}\,G_0\,\mathrm{Re}\,G_0', \qquad G_0' = \frac{d}{dE}G_0,$$
$$|Z_0|^2 = (1 - U\,\mathrm{Re}\,G_0)^2 + U^2(\mathrm{Im}\,G_0)^2. \quad (30)$$

The smoothing in energy thus erases the dependence of the level density on the defect distribution. Nevertheless, $\tilde{g}_d$ can be incorporated in the bulk or surface parts of the smoothed level density, depending on whether the impurity is distributed over the volume or over the surface.

Both surface and bulk defects can strongly influence the size dependence of the Fermi energy μ, which can be written in the form $\mu = \mu_0 + \mu_S$ for samples of finite dimensions, where μ_0 is the Fermi energy of an infinite sample, and $\mu_S \propto S/V$. Surface defects act directly on μ_S, contributing to this part of μ a quantity

$$\mu_{Sd} = -[\tilde{g}_{0i}(\mu_{0i})]^{-1}\int_{-\infty}^{\mu_{0i}} \tilde{g}_d(E)\,dE, \quad (31)$$

where $\tilde{g}_{0i}$ and μ_{0i} are the level density and Fermi energy in an ideal crystal.

Bulk defects, in contrast, act on μ_S indirectly, through a change in the density of levels at the Fermi surface of an infinite sample upon the appearance of defects in the sample. In this case we have

$$\mu_S = -[\tilde{g}_0(\mu_0)]^{-1}\int_{-\infty}^{\mu_0} \tilde{g}_{Si}\,dE, \quad (32)$$

where $\tilde{g}_{Si}$ is the surface density of levels of an ideal crystal. An expansion of $\tilde{g}_0$ and μ_0 in ν makes it a simple matter to distinguish the defect component of μ_S.

As an example, we can estimate the shift of the Fermi level due to surface defects. According to (30) and (31), the Fermi level is given by the following expression near the bottom of the conduction band:

$$\mu_{Sd} \approx U\nu/Z_0(0),$$

where the relative defect concentration ν is related to the surface coverage by defects, σ, by $\nu = 6\sigma/L$ in the case of a cube-shaped sample. Consequently, even in the absence of virtual impurity levels [$Z_0(0) \approx 1$], with $U \sim 1$–5 eV, $\sigma = 0.1$, and $L = 20$ the value of μ_{Sd} may be extremely large, possibly greater than 0.1 eV. It becomes even larger if there are virtual levels.

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