Ground State of Granular Metals

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We argue that for granular metals a sizable fraction of the grains becomes charged because the energy fluctuation of the highest-occupied level of each grain, as predicted by random matrix theory, is larger than the charging energy. We have computed the ground state density of states and the degree of ionization of granular metals. The density of states shows a Coulomb gap around the Fermi energy, produced by the long-range part of the Coulomb interactions, which should dominate transport properties at low temperatures.

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The effects of intragrain and intergrain electron-electron Coulomb interactions are bound to be very important in granular metals (GM), mainly in the dielectric regime [1]. Intragrain Coulomb interactions are responsible for the charging energy of the grains and for the possible formation of a Hubbard-type gap. On the other hand, in the dielectric regime the long-range intergrain Coulomb interaction could produce a Coulomb gap, a decrease around the Fermi level in the single-particle density of states (DOS) [2].

The $T^{1/2}$ law of variable range hopping conductivity has been extensively found in GM and has been interpreted as a manifestation of the Coulomb gap [3]. Photoemission experiments and tunnel conductivity measurements of GM in the dielectric regime have also been interpreted in terms of the Coulomb gap [4–6]. Sheng [7] has given an alternative explanation of both this type of behavior for the dc conductivity and of the DOS in terms of the distribution of charging energies. Pollak and Adkins [8] have argued against this explanation and claimed that the Coulomb model rather than the Hubbard model best represents GM.

For the Coulomb gap to exist in GM in the dielectric regime a significant portion of the grains must be charged in the ground state. Whether this is the case and, if so, what the ionization-producing mechanism is remains to be clarified, and it is this problem we wish to address in this Letter.

The accepted belief, at least until recently, is that the only two relevant energies are the charging energy of the grains and the interlevel spacing δ near the highest-occupied level, both due to the microscopic size of the grains. If this were so, the vast majority of the grains would be neutral, since the charging energy is much bigger than this interlevel spacing, and no Coulomb gap could exist.

Shklovskii and Efros [1] and more recently Pollak and Adkins [8] have proposed that variations in the "work function" associated with the different crystallographic faces of the grains could be of the same order of magnitude as the charging energies and thus be responsible for their ionization. Chui [9] has claimed that a great variety in grains size is responsible for overcoming the charging energies.

In this Letter, we argue that the large variation in energy of the highest-occupied level of neutral grains, due to their random surfaces and small sizes, is the most important disorder energy of the problem which ionizes a large portion of the grains. We also calculate numerically the DOS of GM, taking into account both Coulomb and Hubbard effects.

In order to study the DOS and the degree of ionization of GM in the ground state, we consider the following extreme tight-binding Hamiltonian

$$H=\sum_i \phi_i a_i^\dagger a_i + U\sum_i a_i^\dagger a_i a_i^\dagger a_i + \sum_{i>j} V_{ij} a_i^\dagger a_i a_j^\dagger a_j \,. \tag{1}$$

$a_i^\dagger$ (a_i) is the creation (annihilation) operator of a particle in grain i; in our approximation, we do not have to label this operator with either spin or intragrain indices. As the one-particle energy spacing is much smaller than the charging energy, the repulsion between electrons due to the exclusion principle is much less important than that due to Hubbard effects. ϕ_i is the energy of the highest-occupied electronic level in grain i, which strongly fluctuates as we will show. U is the charging energy, defined as the energy needed to take an electron from a neutral grain to another neutral distant grain, and equal to

$$U=2e^2/\kappa d \,, \tag{2}$$

where d is the average diameter of a grain and κ the effective dielectric constant of the medium. We calculate this within a mean field approximation and obtain the value $\kappa=32$ for typical Al grains in an Al_2O_3 matrix whose dielectric constant is equal to 8, with a metal fraction $x=0.5$, which produces an increase in the dielectric constant by a factor of 4 [10]. The charging energy is $U=30$ meV for typical 30 Å grains. V_{ij} is the Coulomb interaction energy between a single charge in grain i and another in j. For this, we consider the expression $V_{ij}=e^2/\kappa r_{ij}$, where r_{ij} is the distance between the centers of grains i and j, and the effective dielectric constant κ is the same as for the charging energy. This expression of V_{ij} does not adequately incorporate the screening effects between grains at short distances, although this should

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not change the DOS near the Fermi level E_F for the following reason. At low energies, only the long-range part of the interaction is relevant; the grains with energies close to E_F are very far apart and their mutual interaction is well described by V_{ij}. The typical Coulomb interaction is $E_c = e^2/\kappa a = 13$ meV, where a is the average separation between grains.

Let us analyze the amount of disorder in the energy ϕ_i of the grains. The energy fluctuation of ϕ_i of different grains, due to their irregular shapes and sizes, is usually ascribed as the source of this diagonal disorder in GM. This fluctuation is supposed to be of the order of the level spacing δ near the highest-occupied level [6], which is too small, of the order of 3 meV for a grain of 30 Å in diameter, compared with the charging energy. However, we believe that the last assumption is wrong and that the fluctuations in ϕ_i, before any charge transfer has taken place, are substantially larger than δ.

Let us study the fluctuations in ϕ_i, considering that the grains are metallic spheres with slightly different diameters, whose energy spectrum can be calculated exactly [11]. A small change in diameter results in a large and pseudorandom change in ϕ_i The standard deviation σ of ϕ_i corresponding to diameters between 27 and 33 Å, taken every 0.5 Å, is equal to 140 meV. This large value of σ could be partly due to the degeneracy of the energy levels, which is clearly not present in real metallic grains. To avoid this possible degeneracy effect, we have studied the fluctuations in ϕ_i for parallelepids with different edges, but with the same volume as a sphere of 30 Å diameter. We choose irrational ratios between the edges to suppress spectrum degeneracies. We found that the fluctuations in ϕ_i are of the order of 70 meV, while those in the energy of the first level are approximately 40 meV. The large fluctuations in ϕ_i are due to the fact that we are adding many uncorrelated energy spacings and that the low-energy spacings are large and fluctuate widely. The energy spacings are uncorrelated for classically integrable systems, such as the spheres and parallelepids considered, while for classically chaotic systems they present so-called spectral rigidity, which reduces the fluctuations in the energy difference of levels far apart.

Thus, the surface randomness of real metallic grains could, in principle, reduce the large fluctuations previously found. To estimate the importance of this reduction, we calculate the fluctuations in ϕ_i for chaotic systems, which can be adequately described by means of random matrix theory [12,13]. In the absence of a magnetic field, so that time-reversal symmetry is preserved, quantum level spectra of metallic particles are closely simulated by the Gaussian orthogonal ensemble of random matrices [13,14]. The variance of the probability distribution of the energy of the Nth level, using normalized energy spacings, is equal to [13]

$$\sigma^2(N) = \frac{2}{\pi^2} \ln\left[\frac{\pi}{2}(N+1)\right]. \tag{3}$$

To obtain the disorder energy of our grains we have to "fold" back this expression into absolute (not normalized) units. In order to do so, we take into account that the average energy spacing for three dimensional systems goes as $i^{-1/3}$, where i is the number of the state. We have numerically calculated the standard deviation σ of ϕ_i for Al grains of different sizes. For a typical 30 Å grain (that has 2×1280 electrons), we obtain $\sigma(1280) = 35$ meV, which is of the order of the charging energy. For diameters $d = 20$, 40, 50, and 80 Å, the corresponding standard deviations are $\sigma = 76$, 20, 13, and 5 meV.

The spectral rigidity, characteristic of random systems, basically reduces the fluctuations in ϕ_i to those of the low energy levels, which are still large when compared with δ. As a rule of thumb, we can say that the disorder energy of metallic grains is of the order of the average energy difference between the first and the second electronic levels.

To our knowledge there seems to be no calculation in the literature supporting the standard belief that δ is the parameter that sets the scale of the fluctuations. On the other hand, all our calculations and estimates indicate that the relevant parameter is the first interlevel spacing and that the fluctuations are much larger than previously expected.

Other types of disorder, such as impurities, surface states at grain boundaries, and the variation of the "work function" associated with different faces, are also possible. Furthermore, in impure grains, or clusters of grains, the spectral rigidity would be lost for energies greater than the Thouless critical energy [14]. All these effects would add to the disorder predicted above, and our conclusion that the disorder energy is greater than the charging energy would be even more strongly supported.

In our model, we will assume that the energies ϕ_i are Gaussian random variables with a variance equal to that predicted by random matrix theory, and with no correlations between different grains. In order to simplify the calculations, we suppose that the grains are never doubly charged. Thus, we have three possible charge states per grain: neutral, positively charged, and negatively charged. This differs from the standard Coulomb gap model where there are only two possible charge states per site. We can concentrate only on the highest-occupied electron of each (neutral) grain. A grain can lose this electron or can gain a similar electron from another grain. In this renormalized model, a neutral grain has one electron, a positively charged grain has no electrons, and a negatively charged grain has two electrons.

For each grain i, let us define E_i^0 as the sum of its disorder energy ϕ_i and the Coulomb interaction with all other grains

$$E_i^0 = \phi_i + \sum_{j\neq i} V_{ij} q_j , \tag{4}$$

where q_j is the charge (in units of e) of grain j. The single-particle energy of an occupied state is defined as

the energy required to take the electron to infinity, and the energy of an empty state as that required to bring an electron from infinity to this state. A grain with no electrons has two degenerate empty states with a single-particle energy E_i^0; a singly occupied grain contributes one hole and one electron state to the DOS with energies E_i^0 and E_i^0+U, respectively; a doubly occupied grain contributes two degenerate electron states with energies E_i^0+U.

If an electron is transferred from a grain i to another grain j, the change in energy of the system is

$$\Delta_{ji}=E_j^0-E_i^0+\Delta U-V_{ij}\,. \tag{5}$$

The last term is due to the electron-hole interaction between different grains and causes a Coulomb-like gap. ΔU is the change in Hubbard energy of the system, which depends on the type of transition. There are four possible one-electron transitions: from a singly occupied to an empty grain ($\Delta U=0$), from a singly occupied to another singly occupied grain ($\Delta U=U$), from a doubly occupied to an empty grain ($\Delta U=-U$), and from a doubly occupied to a singly occupied grain ($\Delta U=0$). Δ_{ji}, in Eq. (5), must be positive for the ground state to be stable. Our numerical algorithm ensures that this condition is verified by all pairs of grains.

In our computer simulation, we start from an initial state with grains placed at random locations with the constraint that they do not overlap. In most of the calculations, we have considered samples with grains of the same diameter d. We have also used samples with Gaussian and log-normal distributions of grain sizes and the results for the DOS at low energies are fairly similar in all cases. A set of uncorrelated disorder energies is chosen at random from a Gaussian distribution, with the variance previously obtained from random matrix theory. We assume that all the grains are initially neutral, which, translated into our model, implies that every site starts with one electron. Thus, an algorithm performs in a systematic way transitions that lower the total energy of the system. At first, we change the occupancy of single grains until all the occupied states have negative energies and all the empty states have positive energies. In this step, there is no constraint in the total number of particles, but there is a well-defined Fermi level. In a second step, the algorithm checks all the electron-hole excitations which lower the total energy of the system. The procedure is similar to that described by Baranovskii *et al.* [15] and Davies [16]. The result is generally a metastable pseudoground state rather than the true ground state, because stability against many electron transitions is not ensured, although earlier studies showed that there is very little difference in the DOS [15,16]. Most of the calculations have been performed on samples with 1000 grains and we have averaged over 1000 runs.

The results for the DOS of Al-Al_2O_3 are shown in Fig. 1 for $d=30$ Å and a metal fraction $x=0.5$. The open

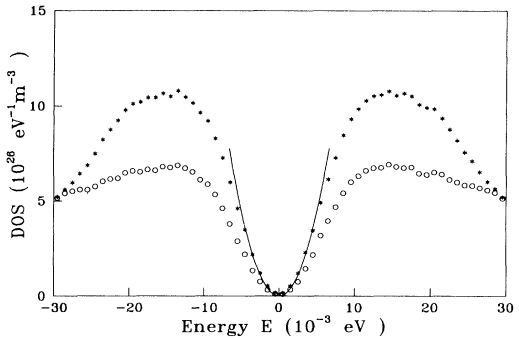

FIG. 1. Density of states for a typical granular metal. The open circles correspond to ionized grains and the stars to neutral grains. The coefficient of the parabola shown is 1.7 times the value predicted by Efros and Shklovskii.

circles correspond to doubly occupied grains (for $E<0$) and to empty grains (for $E>0$). The stars correspond to the DOS of singly occupied grains (represented on top of the previous density of doubly occupied and empty states). There is electron-hole symmetry with respect to the Fermi level. Beside this, the density of singly occupied holes is the same as that of singly occupied electrons, but shifted upwards by the charging energy U.

The total DOS is roughly parabolic, in agreement with Efros and Shklovskii's predictions for the standard Coulomb gap, but the curvature of the parabola differs with respect to these predictions. The coefficient of the parabola shown in Fig. 1 is 1.7 times the value $c_3=(3/\pi)(\kappa/e^2)^3$ obtained for the standard Coulomb gap. This coefficient should go from $0.25c_3$ when $U=0$ to $2c_3$ when U is very large [16]. We found that the curvature of the parabola is independent of the diameter of the grains for constant x. When x is varied, the curvature should change because the ratio U/E_c varies, but this change is hardly noticeable in the range $0.2\leq x\leq 0.6$. In GM, U is always greater than twice E_c and the curvature is close to its limiting value, $2c_3$, for all realistic values of x. The parabolic shape for the DOS and the order of magnitude of the gap are in agreement with photoemission experiments [4] and tunneling conductance measurements [5,6] on GM.

From the DOS we can obtain the degree of sample ionization. The ratio between the integrated DOS corresponding to the lower curve and the total DOS gives the fraction of ionized grains. In Fig. 2 we have represented this fraction as a function of grain diameter. We have kept the metal fraction constant and equal to $x=0.5$. Thus, the dielectric constant does not depend on d, while the charging and Coulomb energy scale is inversely proportional to d, and the standard deviation of the site energies goes as $\sigma\propto d^{-2}$. The degree of ionization goes to zero as the diameter of the grains tends to infinity.

The proposed ionization mechanism does not require any distribution of grain size, unlike Chui's model, for

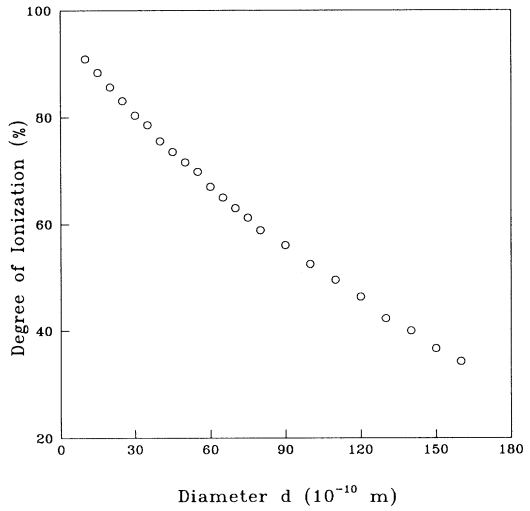

FIG. 2. Degree of ionization as a function of the diameter of the grains for a typical granular metal. The metal volume fraction is kept constant at 0.5.

overcoming the Coulomb charging energy [9].

To summarize, the DOS of GM presents a Coulomb gap around the Fermi level, with a curvature which differs from that predicted by Efros and Shklovskii's model. This is in agreement with the parabolic DOS seen in photoemission and conductance tunneling experiments. It also implies that, at low temperatures, transport properties should be dominated by the long-range Coulomb interactions rather than by charging effects.

The $T^{1/2}$ law, so extensively found in GM, could be interpreted as a manifestation of this type of Coulomb gap. On the other hand, the overall width of the gap is determined by the Hubbard energy. Thus, charging energy effects [7] should be a manifestation of this dependence on the overall width of the gap.

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