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EXTENSION OF PERCOLATION THEORY TO DETERMINE THE THREE-DIMENSIONAL VARIABLE-RANGE HOPPING CONDUCTIVITY IN GLASSY CHALCOGENIDES

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In this paper, we explore the three-dimensional conductivity within the variable-range hopping regime for glassy chalcogenides via the Coulomb glass model. We first develop a theoretical approach based on an extension of the two-dimensional percolation theory and then we perform numerical simulations to confirm the validity of the theory. From the theoretical results we obtain a prefactor of the type T^{γ} for the 3D Efros-Shklovskii law, where T is the temperature of the system and γ is a characteristic exponent different from 1, which is found for the two-dimensional problem. From the numerical simulations we verify the theoretical results and find that characteristic parameters for the 3D Efros-Shklovskii law are consistent with those found in the literature.

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1. Introduction

Coulomb glasses (CG) are strongly localized systems in which the blend of disorder and long-range Coulomb interaction plays a key role [1]. CG exhibit glassy behavior, showing slow relaxation, loss of ergodicity and aging, among other phenomena, and present a gap in the single-particle density of states near the Fermi level, which expression at zero temperature is [2]:

$$g(\epsilon) \propto |\epsilon - \epsilon_F|^{d-1}. \quad (1)$$

In this expression, d is the dimension of the problem, ϵ is the site energy and ϵ_F is the energy corresponding to the Fermi level. For non-zero temperature, the bottom of the Coulomb gap is rounded near the Fermi level.

The standard tight-binding Hamiltonian describing the system in presence of an external electric field is [1]:

$$H = \sum_i \phi_i n_i + \sum_{i<j} \frac{(n_i - K)(n_j - K)}{r_{ij}} + \sum_i \mathcal{E}\, x_i, \quad (2)$$

where ϕ_i a random site potential, chosen from an uniform distribution of amplitude W, n_i is the occupancy number of site i (which can equal 0 or 1), r_{ij} is the distance between sites i and j and K is the compensation, to guarantee the electrical neutrality of the system. The electric field is denoted as $\mathcal{E}$, being x_i the horizontal component of the position vector of the i-th impurity.

The CG model describes a broad spectrum of materials and systems, for instance, lightly doped and amorphous semiconductors, high temperature semiconductors, disordered and granular metals, vortex in superconducting films, and conducting polymers, modeling interesting

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phenomena such as hopping conductivity in λ-ADN chains [3]. The connection between glassy chalcogenides and Coulomb glasses has been revealed in some recent publications [4-7].

Conductivity in CG lies into the so-called *variable-range hopping regime*, following the Efros-Shklovskii law (ES law) [1]:

$$\sigma T^{\gamma} = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]; \quad T_0 = \frac{\beta_0 e^2}{\kappa\xi}, \tag{3}$$

where σ is the conductivity, σ_0 is a constant, T is the temperature, e is the electron charge, κ is the dielectric constant and. Parameters γ and β_0 depend on the dimension of the system.

In two-dimensions, percolation theory demonstrates that $\gamma = 1$, and numerical simulations show compatible results with theory [1]. The calculus starts from the theory of Miller and Abrahams, who associated a resistance to each pair of sites of the CG model, provided that its current, I_{ij} is proportional to the electric field $\mathcal{E}$ and inversely proportional to T. The original expression for the resistance between sites i and j is [8]:

$$R_{ij} = R_{ij}^0 \exp\left(\frac{2r_{ij}}{\xi} + \frac{\epsilon_{ij}}{k_{\mathrm{B}}T}\right), \tag{4}$$

where ξ is the localization length, k_{B} is Boltzmann's constant, R_{ij}^0 is a constant and ϵ_{ij} is an energy factor that depends on the site energy.

In three dimensions, numerical studies for determining γ are still scarce and, in general, β_0 in Eq. (3) does not match with theory by choosing $\gamma = 1$, as occurs for the 2D situation. One problem arising in the three-dimensional case is that Ohm's law should be recovered when the system is large enough [3]:

$$R \propto \rho \frac{l^{d-2}}{L^{d-2}}, \tag{5}$$

where ρ is the resistivity of the system, d is the dimension, L is the length of the sample and l is a particular length from which the system is approximately uniform.

In this paper, we investigate both theoretically and numerically the dependence of conductivity in three-dimensional CG on prefactor T^{γ}, by extending the two-dimensional approach to the three-dimensional case, taking into account Eq. (5) for large systems. We report numerical simulations of the 3D ES law in order to compare parameter β_0 with literature, finding a good agreement between them. The results model the 3D conductivity of glassy chalcogenides at very low temperatures within the variable-range hopping regime.

2. Percolation theory applied to three-dimensional Coulomb glasses

The first application of Miller and Abrahams' theory was the determination of local conductivities. These calculations used to fail because some resistances of the set took values much smaller than the rest, thus affecting the value of the averaged quantities. That is why theoretical efforts derived towards the calculation of conductivity via percolation approaches [9,10], which has been invested as the most effective theory to obtain relevant results. From equation (4) we can define, for convenience:

$$\zeta_{ij} = \frac{2r_{ij}}{\xi} + \frac{\epsilon_{ij}}{k_{\mathrm{B}}T}. \tag{6}$$

It can be demonstrated that the distribution of these values for the whole sample is approximately uniform [11]. This fact leads to an exponential distribution of the resistances

associated to each pair of sites. It is possible to model the conductivity in CG as that of a network of interconnected resistors, where each of them takes the value given by Eq. (4). The basic procedure of the percolation method is to connect the resistors smaller than a given one. The calculation involves finding the critical value of ζ_{ij}, named ζ_c, for which an infinite network of interconnected sites exists. The resistance of the sample will be dominated by the links in which ζ_{ij} is close to the percolation threshold. Resistances obeying $\zeta_{ij} < \zeta_c$ are part of the critical set. If we consider a limiting value greater than ζ_c, the conductivity still takes place through the critical network, because the distribution of resistances is exponential. Therefore, the conductivity in the system is governed by the value of the largest resistances within the critical set:

$$\sigma \propto \exp(-\zeta_c). \tag{7}$$

The limitation of percolation theory for the calculation of σ comes from the crossover with Ohm's law, which should hold for sufficiently large sizes. This fact is equivalent to assume that new conducting paths emerge as a consequence of increasing the size of the system. In a qualitative way, in two dimensions and for an approximately square system, when considering larger sizes we find a much more complex percolation path, of almost fractal nature. The price paid for connecting more resistors in series is compensated with new paths arising in parallel. In this kind of systems it is found that percolation theory still remains valid for large sizes. On the other hand, Ohm's law is relatively easily verified for the three-dimensional case, where the resistance of the system, *R*, follows Eq. (5).

A suitable method to determine in 3D the parameter γ for Eq. (3) is to consider the system as a network of random resistances, as discussed above. From Eq. (3), ES law, it can be stated that conductivity is governed by resistances

$$R_i \propto \exp\left(\frac{a_i}{T}\right)^{1/2}, \tag{8}$$

where $\{a_i\}$ represents a certain set of variables. We can consider that the network of resistances contributing to the conductivity consists of a set of exponential random resistances

$$R_i = R_0 \exp\ (\omega x_i), \tag{9}$$

where $x_i \in [0,1]$. In this expression, ω is directly related to the factor $1/\sqrt{T}$. Since the distribution is exponential, for values $\omega \gg 1$ we can suppose that the largest resistors carry a negligible current, and can be removed from the set without the total resistance of the system being affected. An approximation to the total resistance could be obtained, as in the two-dimensional case, via percolation studies. Let us consider only resistances obeying $x_i < x_c$, where x_c is the percolation threshold. In this way, there will be a unique conductivity path and the total resistance of the system could approximated by the greatest of the series resistances of the path, the so-called *critical resistance*, which expression is

$$R_c = R_0 \exp\ (\omega x_c), \tag{10}$$

This approximation fails as said before because, for large sizes, Ohm's law must be verified, and the resistance of the system will be determined by Eq. (5). To improve the approximation for the 3D situation, let us increase the set of resistances above the percolation threshold. That is, resistances satisfying $x_i < x_1$, with $x_1 > x_c$ are now considered. Thus, the total set forms an interconnected network, where we call $\lambda(x_1)$ the typical length between two connections. The typical resistance of each branch, $r(x_1)$, will be greater than R_c. For x_1 not very far from x_c we perform a Taylor-series expansion:

$$r(x_1) = R_c[1 + \alpha_1(x_1 - x_c)^a + \cdots], \tag{11}$$

where a represents a certain exponent that does not depend on ω, although both R_c and the coefficient α_1 does. When the sample size is $L \gg \lambda$ the conduction becomes ohmic, and the value of the resistance of the system follows Eq. (5):

$$R(L) = r(x_1)\frac{\lambda(x_1)^{d-2}}{L^{d-2}}. \tag{12}$$

Near the percolation threshold, we can consider that

$$\lambda(x_1) = c(x_1 - x_c)^{-\nu}, \tag{13}$$

where c is a constant and ν is a certain exponent that comes from the percolation calculation, which is independent of the selected network. Now we are looking for value of x_1 which minimizes the resistance $R(L)$ and, therefore, optimizes the conduction. By taking $d = 3$, and substituting Eqs. (11) and (13) into Eq. (12):

$$\frac{\mathrm{d}R(L)}{\mathrm{d}x_1} \Rightarrow (x_1 - x_c)^a = \frac{\nu}{\alpha_1(a-\nu)}. \tag{14}$$

We substitute this value in Eq. (12) and obtain that the value of the minimum resistance, $R_{\min}$, is:

$$R_{\min}(L) \propto \frac{R_c}{L}\alpha_1{}^{\frac{\nu}{a}}. \tag{15}$$

As an example, we can perform the calculation for a simple cubic network in 3D with a link model. Here, the percolation threshold is $x_c = 0.2488$ [12]. We employ the units $R_0 = 1$ and $c = (a-\nu)/a$. In three dimensions, $\nu = 0.88$ [13]. Taking $a = 1$, from Eq. (15) we obtain the new expression:

$$R_{\min}(L) \approx \frac{\exp(\omega x_c)}{\omega^{\nu}}. \tag{16}$$

Since we have argued that $\omega \propto 1/\sqrt{T}$, the extra dependence on temperatures introduced by our approximation has the form $T^{-\nu/2}$. This fact, together with the dependence proportional to T, leads us to consider a prefactor $T^{\left(-\frac{\nu}{2}\right)+1}$ for the expression of the resistance, instead of T. Regarding the conductivity, the prefactor is $T^{\left(\frac{\nu}{2}\right)-1}$, and so $\gamma = \left(\frac{\nu}{2}\right) - 1$. Our system is equivalent to a tridimensional link model, so we can substitute the value $\nu = 0.88$ and find the following dependence on temperatures for the expression of conductivity:

$$\sigma T^{0.56} \propto \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{2}}\right]. \tag{17}$$

3. Numerical simulations of 3D conductivity. Results and discussions

Numerical simulations for the ES law in 3D constitute a field yet to be explored. In models with positional disorder it is difficult to reach large sizes, which leads to finite-size effects at low temperatures, since the dimensions of the system are comparable to the typical hopping length. In fact, in three dimensions, $L = N^{1/3}$, and for a size N = 2000, which is yet difficult to compute, we obtain $\frac{L}{2} = 6.3$. For this reason it is hard to obtain a wide range of temperatures. In network models, simulation sizes may be a little larger, but they have the limitation that the hopping

distance must be much greater than the network parameter. This fact shortens the range of study temperatures, in the same way.

We have employed the hybrid Monte Carlo algorithm of Tsigankov and Efros [14] to obtain data corresponding to the 3D conductivity in the linear regime for a system of variable size, within the temperature range $0.02 \leq T \leq 1.5$. Data for temperatures within the range $0.05 \leq T \leq 1.5$ have been calculated for a system of size 2000. Below this temperature, finite-size effects gain importance. So, for lower temperatures we have computed systems of size 8000, with special interest in reaching the steady state and avoiding finite-size effects at lowest temperatures. After exploring the data, the range for obtaining the ES law is restricted to the interval $0.02 \leq T \leq 0.08$, narrower than in 2D simulations. This is due to the filling of the Coulomb gap for temperatures greater than 0.08. Largest temperatures were employed to verify the crossover with Mott's law and the activated regime [2], but none of them properly appear within the range considered. Additional numerical details can be found in previous literature [5-7].

We investigate the behavior of conductivity for semiconductor samples doped with impurities randomly placed, within the regime of strong localization. Transitions between states are held by electron jumps between impurities in the regime of variable range hopping [3]. The position of the electron matches that of the impurity since the localization length is considered quite small. We study samples of dimensions $N = L^3$, where L is the lateral dimension. To show real experimental conditions, we build the system by implementing periodic boundary conditions, which simulates a more realistic experimental situation. The units employed are: $1/l_0$ is the energy and temperature unit, whereas $l_0 = L/\sqrt{N}$ is the length unit, provided that both the electron charge, e, and Boltzmann constant, k_B, are set equal to one. We consider systems with a minimum distance between sites equal to 0.2. The range of disorder is $W = 2$ and the localization length is $\xi = 1$. The characteristic electron-phonon time, τ_0, has been employed as the unit of time. We also choose compensation $K = 1/2$ and consider that each particle only interacts with its nearest image. Therefore, we do not perform Ewald summation.

In Fig. 1 it is plotted $\sigma T^{0.56}$ on logarithmic scale versus $T^{-1/2}$ for the range $0.02 \leq T \leq 0.08$. The data error is determined from the standard deviation of the conductivity of the samples, and is of the order of the point size. The linear dependence in the fitted region is very good, which confirms the validity of the the random resistor network approximation for determining ES law, Eq. (17). The straight line represents the linear fit of the data. From the slope we obtain a value $\beta_0 = 3.40 \pm 0.02$, close to that proposed by Shklovskii and Efros [2], equal to 2.8. The error in β_0 is, as in 2D, merely statistical.

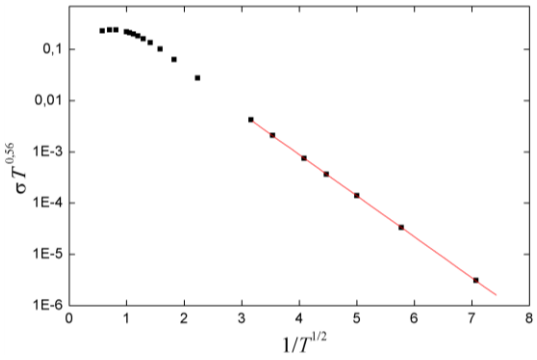

Fig. 1. Dependence of conductivity σ on temperature T within the range $0.02 \leq T \leq 1.5$. The linear fit corresponds to the range $0.02 \leq T \leq 0.08$, where the ES law is valid. The size of system is 2000 in the range $0.05 \leq T \leq 1.5$ and 8000 for lower temperatures.

Once obtained β_0, it is recommended to analyze the validity of the lowest temperature range considered. For a system of size 2000 we obtain $\frac{L}{2} = 6.3$. Employing our calculated value of β_0, the typical hopping length for $T = 0.05$ is 2.1 [2]. This value is close to the dimensions of the

system, so it is not convenient to compute lower temperatures for this size. However, for N = 8000 we obtain $\frac{L}{2} = 10$, dimensions that allow us to reach $T = 0.02$, where the typical hopping length is equal to 3.3. The simulation of even lower temperatures becomes a difficult task. From $T = 0.02$ it is necessary to consider sizes greater than 8000, along with the need to obtain longer times to reach the steady state.

4. Conclusions

In this paper we investigate the form of the 3D ES law for glassy chalcogenides via the Coulomb glass model. The two-dimensional case has been extensively study via percolation theory, finding a good agreement between theory, experiments and simulations. However, studies in the three dimensional case are still scarce. In our work, we extent the 2D percolation theory taking into account that for greater sizes of the system Ohm's law must be recovered. This fact leads to a temperature prefactor in 3D ES law with and exponent lesser than unity. Numerical simulations for this model depict a value for the characteristic parameter β_0 according to literature.

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