Hopping Transport in Granular Superconductors

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We study the conductivity of granular superconductors in the weak coupling insulating regime. We show that it is governed by the hopping of either electrons or Cooper pairs depending on the relation between the superconducting gap and the charging energy of a single granule. Local superconducting pairing plays an important role in both cases. In particular, in the case of the transport via electron hopping the superconducting gap suppresses the inelastic cotunneling processes. We determine transport characteristics of an array in different regimes and construct the transport phase diagram.

Recent experiments posed the fundamental questions concerning mechanisms of conductivity in the insulating phase of superconductor granular arrays [1]. The origin of the Mott variable range hopping - like resistivity temperature behavior and the nature of strong enhancement of conductivity by the applied magnetic field in the weak coupling regime are far from being understood.

At the same time, significant progress has been recently achieved in understanding the electronic transport in the insulating phase of metallic granular arrays. A long standing puzzle of the low temperature resistivity $\rho(T)$ showing stretched exponential temperature dependence, $\ln \rho \sim T^{-1/2}$ [2], in the insulating phase was explained in Refs. [3, 4, 5] as the Mott-Efros-Shklovskii (ES) variable range hopping. The key ingredient of the model of Refs. [3, 4, 5] is the effect of the electrostatic disorder that lifts the Coulomb blockade on a part of sites of a granular array providing the necessary low energy electron and hole excitations carrying the current by hopping through the virtual states of intermediate grains. The specific hopping mechanism depends on the temperature range: at temperatures $T < T_1 \approx 0.1/\sqrt{\delta}$, with $E_c$ and $\delta$ being the charging energy and the mean energy level spacing in a single grain respectively, an electron hops via elastic cotunneling mechanism where the travelling electron creates or absorbs the electron-hole excitations dominates the transport. The multiple cotunneling as basic mechanism of hopping was recently confirmed in experiments on gold nanoparticle multilayers with controlled structure and size of the granules [6].

Building on these developments we address in this Letter the low temperature transport in the insulating phase of granular superconductors. We show that in this case the conductivity is also of the hopping nature but it is mediated by hopping of either electrons or Cooper pairs depending on the relation between the superconducting gap and the charging energy of a single granule. Electrostatic disorder plays a crucial role in our approach: models based on regular superconductor arrays studied extensively earlier [we refer to the book [3] for review] show activation transport behavior in the insulating phase.

The immediate effect of superconductivity on the properties of granules is two fold: first, the single particle gap, $\Delta$, forms within the each grain. Secondly, the so-called parity effect [10, 11] appears: grains that have an even number of electrons, $N$, have the lower energy than those that have an “unpaired” odd electron that carries extra energy $\Delta$ [12]. We demonstrate that these features affect strongly transport properties of granular superconductors when electrostatic disorder is taken into account. Depending on the relation between the local charging energy, $E_c$, and the local superconducting gap, $\Delta$, the low temperature transport goes either via hopping of electrons for $E_c > \Delta$ (we hereafter will be referring to this mechanism as to EH regime) or via hopping of the Cooper pairs for $E_c < \Delta$ (CPH regime). We show that this classification holds as long as the dispersion in grain sizes can be neglected; neither it is affected by the presence of the off-diagonal part of the Coulomb interaction. Derivation of the conductivity temperature behavior in a general case of an arbitrary relation between $E_c$ and $\Delta$ is, however, cumbersome and below we present the results only in the limiting cases corresponding to $E_c \gg \Delta$ in EH- and to $E_c \ll \Delta$ in CPH regimes.

In the EH regime the conductivity is determined either by the elastic or inelastic cotunneling mechanism depending on the temperature regime. In the low temperature elastic regime, the conductivity is almost unaffected by...
the gap at $E_c \gg \Delta$ and follows the ES law \[ \xi_{cl}^{EH} = 2/\ln(\tilde{E} \pi/\tilde{g} \delta), \]

where $\tilde{g}$ is of the order of the average tunneling conductance; more precisely it is the geometrical average of the tunneling conductances $g_{i,i+1}$ along the typical tunneling path $\ln g = (\ln g) = (1/N) \sum_{i=1}^{N} \ln g_{i,i+1}$. The energy $\tilde{E} \sim E_c$ is analogously defined as a geometrical average $\ln \tilde{E} = (\ln \tilde{E})$, where $\tilde{E}$ is the combination of single grain electron $E_i^+$ and hole $E_i^-$ excitation energies at $\Delta = 0$

$$\tilde{E}^i = 2/(1/E_i^+ + 1/E_i^-).$$

In the absence of the superconducting gap the elastic transport regime crosses over at $T \approx T_1$ to the regime dominated by inelastic cotunneling processes where the conductivity is given by ES law with weakly temperature dependent localization length

$$\xi_{es}^{EH} = 2/\ln(\tilde{E}^2/16\pi T^2 \tilde{g}).$$

In the presence of the gap and at $T \ll \Delta$ the inelastic cotunneling processes are suppressed. Thus the result holds only in the interval $T_2 \leq \max \{\Delta, T_1\}$. Considering the case $T_c > T_3$, we find the new transport regime at $T < T_3 \approx \xi_{es}^{EH} \Delta$, which is dominated by inelastic processes but has the activation form:

$$\sigma \sim \exp \left[-N(\ln(\tilde{E}/2\tilde{g}T\Delta) + 2\Delta/T)\right],$$

where the typical tunneling order $N = \sqrt{b e^2/16 a \kappa \Delta} \sim \sqrt{E_c/\Delta}$. Under temperature decease dependence remains applicable till it matches the elastic result at temperature $T_2 \approx \xi_{cl}^{EH} \Delta$.

Changing the gap $\Delta$ by varying magnetic field at fixed temperature one can drive the system between the elastic and inelastic ES regimes traversing the interval $T_2(H) < T < T_3(H)$, where conductivity follows the activation formula of Eq. (5) (see Fig.1). This manifests itself as a giant negative magnetoresistance in the temperature interval $(T_1, T_3)$ that exists provided $T_1 \ll T_c$. Such an effect in the weak coupling regime was indeed observed in Ref. [1].

In the CPH regime the conductivity follows the ES law with $T_0$ and the localization length given by

$$T_0 = b (2e)^2/\kappa a \xi^{CPH}, \quad \xi^{CPH} = 1/\ln(8\tilde{E}/\pi \tilde{g} \Delta).$$

![FIG. 2: Single particle (thin lines) and two particle (thick lines) excitation energies as functions of the applied potential in a single grain for the cases a) $E_c > \Delta$ and b) $E_c < \Delta$. Solid lines represent creation processes (addition of an extra electron or a pair) while dashed line represent annihilation processes. In both cases the dependencies are $4E_c$ periodic.](image)

We see that the localization length decreases with decrease of $\Delta$, which corresponds to the strong positive magnetoresistance. Note further that at $\tilde{g} \Delta \sim E_c$ the sample transforms into a superconducting state [14].

We begin our quantitative analysis with the discussion of the ground state charge configuration at $T \to 0$. First we consider an isolated superconducting grain in the presence of the random potential $V$ modelling electrostatic disorder. The energy of such a grain is

$$E = n^2 E_c - V n + P(n + p) \Delta,$$

where $P$ is the parity function defined as $P(2k + 1) = 1, P(2k) = 0$ for an integer $k$, and $n$ is the number of excessive electrons, counted with respect to the number of electrons, $N^0$, of a neutral state at $V = 0, \Delta = 0$. The discrete random variable $p = 0$ for even parity and $p = 1$ for odd parity of the charge neutral state $N^0$.

The effect of the applied potential $V$ on the ground state is qualitatively different for different relations between $E_c$ and $\Delta$ [10, 11]. If $E_c > \Delta$ (CPH), the dependence of the occupation number on $V$ also has a staircase form but electrons jump in pairs, $n \to n + 2$, at the equidistant values $V_n = E_c(2n + 1), V_n = \Delta \cos \pi (n + p)$. In the case $E_c < \Delta$ (CPH), the dependence of the occupation number on $V$ has a form of the Coulomb staircase with the charge jumps $n \to n + 1$ at $V_n = (2n + 1)E_c + \Delta \cos \pi (n + p)$.

Further, one can see that in the EH regime the Cooper pair excitations have a gap, in the weak coupling regime are gapless for certain values of $V$. In the contrary, in the CPH regime electron and hole excitations are gapped for all potential values while the pair excitations are gapless at certain values of $V$. Shown in Fig.1 are electron $\xi^{+}$ and hole $\xi^{-}$ excitation energies

$$\xi^{\pm} = (\pm 2n + 1)E_c \mp V + \Delta \cos \pi (n + p).$$
and pair creation $\mathcal{E}_{2+}$ and annihilation $\mathcal{E}_{2-}$ energies

$$\mathcal{E}_{2\pm} = 4(\pm n + 1)E_c \mp 2V,$$  \hspace{1cm} (9)

as functions of $V$: the minimal pair excitation energy in the EH regime is $2(E_c - \Delta) > 0$, and the minimal energy of an electron excitation in the CPH regime is $\Delta - E_c > 0$.

We assume that electrostatic disorder is strong taking characteristic dispersion of $V$ as $V_0 \gtrsim E_c$. Averaging over the potential $V$ results in the finite density of low energy electron-hole excitations in the EH regime while in the CPH regime only the pair gapless excitations appear.

The excitation spectrum we have discussed referred to noninteracting grains. Now we introduce interactions:

$$H^c = \sum_{ij} n_i E_{ij}^c n_j - V_i n_i + P(n_i + p_i) \Delta,$$ \hspace{1cm} (10)

where the matrix $E_{ij}^c$ represents the Coulomb interaction related to the capacitance matrix $C_{ij}$ as $E_{ij}^c = (\varepsilon^2/2)C_{ij}^{-1}$. Remarkably, the main conclusion concerning the nature of low energy excitations depending on the ratio of $E_c \equiv E_{ij}^c$ and $\Delta$ obtained for a single grain holds for model (10). Indeed, the energies of the single and two particle excitations on the site $i$ following from (10) are

$$\mathcal{E}_{i\pm}^1 = \pm \mu_i + E_c + \Delta \cos \pi(n_i + p_i),$$ \hspace{1cm} (11)

$$\mathcal{E}_{i\pm}^2 = \pm 2 \mu_i + 4E_c,$$ \hspace{1cm} (12)

where the local potential $\mu_i$ is $\mu_i = 2 \sum_j E_{ij}^c n_j - V_i$. The stability of the ground state charge configuration assumes that $\mathcal{E}_{i\pm}^1, \mathcal{E}_{i\pm}^2 > 0$ that limits possible values of $\mu_i$. Now suppose that $\mu_i$ is such that an electron excitation on the grain $i$ is gapless: $\mathcal{E}_{i}^1 = 0$. The ground state stability requires that $\mathcal{E}_{i\pm}^1, \mathcal{E}_{i\pm}^2 > 0$ giving immediately $E_c > \Delta$ and $\mathcal{E}_{i\pm}^2 > 2(\Delta - E_c)$. This means that gapless electron excitations exist only in the case $E_c > \Delta$ and that at the same time pair excitations have a minimal gap $2(\Delta - E_c)$.

Analysis of the case $\mathcal{E}_{i\pm}^2$ yields the same result.

Similarly, for a gapless pair excitation to appear at a certain grain $i$, it is required that $\mathcal{E}_{i\pm}^2 = 0$ and stability assumes $\mathcal{E}_{i\pm}^1, \mathcal{E}_{i\pm}^2 > 0$, meaning that $n_i + p_i$ has to be even and that $\Delta > E_c$, $\mathcal{E}_{i\pm}^2 > \Delta - E_c$. This in turn assumes that the gapless pair excitations exist only in the case $E_c < \Delta$ and that single particle excitations has the gap $\Delta - E_c > 0$.

To find the density of low energy excitations we follow the standard ES approach [2]. For the EH regime we require that the energy of the excitation consisting of replacing an electron from the site $i$ to the site $j$ were positive: $\mathcal{E}_{ij}^{1+} = \mathcal{E}_{i\pm}^1 + \mathcal{E}_{j\pm}^1 - 2E_{ij}^1 > 0$, resulting in the standard ES expression for the low energy single particle density of states (DOS)

$$\nu_1(\varepsilon) = a_d (\tilde{\kappa}/\varepsilon^2)^{d-1} \tilde{\varepsilon}^d, \hspace{1cm} (13)$$

where $a_d$ is the dimensionless factor [12]. In the CPH regime we find the density of two particles excitations by requiring the stability of the ground state with respect to a replacement of a pair from site $i$ to the site $j$: $\mathcal{E}_{ij}^{2+} = \mathcal{E}_{ij}^{1+} + 8E_{ij}^1 > 0$. We again arrive at the ES stability condition leading to the pair DOS as

$$\nu_2(\varepsilon) = \alpha_{d2} (\kappa/\varepsilon^2)^{d-1} \tilde{\varepsilon}^d. \hspace{1cm} (14)$$

The two regimes differ only in the doubled charge of the Cooper pair, and thus we expect that $\alpha_{d1} \approx \alpha_{d2}$.

Now we turn to the derivation of hopping probabilities. We work in the basis of exact eigenstates of noninteracting isolated grains. Electron tunneling processes between the states $k_i$ of the grain $i$ and $k_j$ of the grain $j$ are represented by the elements of the tunneling matrix $t_{ij}$. The Coulomb interaction within each grain is accounted for via the gauge transformation of the electron fields $c_k(\tau) \rightarrow c_k(\tau) e^{i\phi(\tau)}$, and the phase field $\phi$ appears as a renormalization of the hopping matrix elements $\tilde{t}_{ij}$.

$$t_{ij} \rightarrow t_{ij} e^{i\phi_i(\tau) - i\phi_j(\tau)}.$$ \hspace{1cm} (15)

The phase field $\phi$ is governed by the Coulomb action

$$S = -\frac{1}{2\varepsilon^2} \sum_{ij} \int d\tau (\dot{\phi}_i + iV_i) C_{ij} (\dot{\phi}_j + iV_j).$$ \hspace{1cm} (16)

Without the Coulomb interaction a grain is described by the standard Bardeen-Cooper-Schrieffer model.

The tunneling probability via the elastic process given by the diagram a) in Fig. 3 can be written as a product $P \sim \prod_i g_{i,i+1} P_i$ with $P_i$ representing an elementary contribution from the grain $i$

$$P_i = \frac{\delta}{2\pi} \int d\xi d\tau_1 d\tau_2 G_\xi(\tau_1) G_\xi(\tau_2) e^{-E_\xi^+|\tau_1| - E_\xi^-|\tau_2|}. \hspace{1cm} (17)$$

Here $E_\xi^+$ and $E_\xi^-$ are given by Eq. (11) with $\Delta = 0$ and $G_\xi(\tau)$ is the superconducting Green function

$$G_\xi(\tau) = \frac{1}{2} \left[ f(\mp E_\xi/\xi) (1 + \xi/|E_\xi|) e^{-E_\xi \tau} \right.
+f(|E_\xi|/\xi) (1 - \xi/|E_\xi|) e^{E_\xi \tau} \right], \hspace{1cm} (18)$$

where the upper(lower) sign stays for $\tau > 0$ ($\tau < 0$), $f(x) = 1/(1+e^x)$ and $E_\xi = \sqrt{\xi^2 + \Delta^2}$. Taking the integrals in (17) in the limit $T \ll \Delta$ we obtain

$$P_i = \frac{\delta}{\pi \varepsilon^i} \left( \tilde{E}_i + \pi \Delta/2 \right), \hspace{1cm} (19)$$

FIG. 3: The diagrams represent the tunneling probability via elastic (a) and inelastic (b) cotunneling processes. The crossed circles stay for the tunneling matrix elements $t_{ijn} e^{\mp i\phi_j(\tau)}$ where phase factors appear due to the gauge transformation. Wavy lines represent the average of the phase factors $\langle e^{i\phi(\tau_1)} e^{-i\phi(\tau_2)} \rangle$ with respect to the Coulomb action.
that leads to the localization length of the dependence

\[ N \] . Neglecting the term \( \pi \Delta /4 \) in the expression for \( \tilde{E}^i \) we arrive at the expression \( \tilde{\Delta} \) for the localization length.

We would like to note that this correction though being small in the considered limit \( (E_c \gg \Delta) \) can still lead to a noticeable negative contribution to the magnetoresistance in the regime of elastic cotunneling.

The tunneling probability via inelastic cotunneling processes is given by the diagram b) in Fig. 4 that in the limit \( T, \Delta \ll E_c \) gives

\[
P_{in} \sim \left( \frac{4\bar{g}}{\pi E^2} \right)^N \int_{-\infty}^{\infty} dt \left[ G(-it)G(it) \right]^N e^{-it},
\]

where \( N \) is the tunneling order, \( G(\tau) = \int d\xi G_{\xi}(\tau) \) and \( \varepsilon \) is the electron energy change. The expression \( \int \) has to be minimized with respect to \( N \) under constraint \( N \varepsilon \bar{g}/\varepsilon_c \ll 1 \), that follows from the Mott argument for finding the typical minimal distance to a site available for electron placement within the energy shell \( \varepsilon \) and from ES expression \( \int \) for DOS. In the limit \( N \gg 1 \) the integral in \( \int \) can be taken within the saddle point approximation leading to ES law \( \int \) for temperature \( T > T_3 \) and to the activation behavior \( \int \) at \( T < T_3 \).

Deriving the result \( \int \) we neglected the possibility of inelastic cotunneling through the unpaired states \( \int \) of "odd" grains that constitute about a half of all grains in the case \( E_c \gg \Delta \). One can show that such processes do not affect the results since the elementary probability of the inelastic cotunneling process via an unpaired state is smaller that for the elastic process by the factor of \( T/E_c \).

The tunneling in CPH regime can be described within the effective model acting on Cooper pairs

\[
\hat{H} = 4 \sum_{ij} \hat{n}_i \bar{E}_{ij} \hat{\varphi}_j - 2 \sum_i \hat{n}_i \bar{V}_i + (1/2) \sum_{<ij>} J_{ij} \hat{e}^{i\varphi_j - i\varphi_i},
\]

where \( \varphi \) and \( \hat{n} = -i\partial/\partial\varphi \) are the Cooper pair phase and number operator respectively and \( J_{ij} = g_{ij} \pi \Delta /2 \) is the Josephson coupling between the neighboring grains \( i \) and \( j \). Tunneling amplitude, \( A \), can be calculated within the straightforward perturbation theory in \( J \):

\[
A \sim \prod_{i=1}^{N} J_{i, i+1}/\tilde{E}_i, \quad \tilde{E}_i = 2/[1/\tilde{E}_{2_+} + 1/\tilde{E}_{2_-}],
\]

where pair excitation energies \( \tilde{E}_{2_+}, \tilde{E}_{2_-} \) are defined by Eq. \( \int \). The tunneling probability, \( P = A^*A \), decays with the tunneling order \( N \) as \( e^{-2N/\xi_{CPH}} \) with the localization length \( \xi_{CPH} = 1/\ln(2\tilde{E}_2/\pi \bar{g} \Delta) \), where \( \tilde{E}_2 \) is the geometrical average of effective pair excitation energies \( \tilde{E}_i \) along a typical tunneling path. Since the density of states in EH and CPH regimes differ only by the effective charge, \( \tilde{E}_2 \approx 4\tilde{E} \) leading to Eq. \( \int \).

In conclusion, we have described the hopping transport in granular superconductors and found that if the single grain charging energy exceeds the superconducting gap, \( E_c > \Delta \), the transport goes via hopping of electrons, while in the opposite case, \( E_c < \Delta \), hopping of Cooper pairs dominates the transport. In the former case we predict the negative magnetoresistance, while the latter regime exhibits the positive magnetoresistance. We relate the giant negative magnetoresistance observed in the insulating phase of the granular superconductors in [1] to the suppression of the inelastic cotunneling in the electron hopping dominated regime. Transport via Cooper pair hopping can be observed in samples with low enough grain charging energy, i.e. large enough grains. Such regime can also appear as a result of the renormalization of the Coulomb energy due to intergranular coupling in samples with intermediate coupling strength \( g \sim 1 \), in particular close to the insulator to superconductor transition one expects CP dominated transport. The regime \( g \sim 1 \) is a subject of our future investigation.

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