Microscopic Model of Superconductivity in Carbon Nanotubes

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We propose the model of a manifold of one-dimensional interacting electron systems to account for the superconductivity observed in ropes of nanotubes. We rely on the strong suppression of single-particle hopping between neighboring nanotubes in a disordered rope and conclude that the tunneling takes place in pairs of electrons, which are formed within each nanotube due to the existence of large superconducting correlations. Our estimate of the transition temperature is consistent with the values that have been measured experimentally in ropes with about 100 metallic nanotubes.

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Carbon nanotubes have nowadays a great potential for technological applications in devices at the nanometer scale. This makes very important the precise knowledge of their electronic properties, taken as individual structures as well as when packed in the form of ropes. The first step of discerning their metallic or insulating behavior has been completed, as the results obtained from theoretical considerations [1] have been confirmed experimentally [2]. It turns out that the low-energy spectrum of a carbon nanotube may be gapless or not depending on the particular wrapping of the graphene sheet to form the tubular structure.

The electron interactions are also known to modify significantly the transport properties of the nanotubes [3,4]. In the case of metallic single-walled nanotubes, the one-dimensional (1D) character of the system leads to a strong correlation among the electrons, making the so-called Luttinger liquid [5–8] the most appropriate paradigm to describe the electronic properties [9–11]. Evidence of Luttinger liquid behavior has been found in measurements of the tunneling conductance in ropes [3] and in individual single-walled nanotubes [4].

Experiments have been also carried out to probe superconducting correlations in the carbon nanotubes [12,13]. By suspending them between superconducting contacts, large supercurrents have been measured in samples almost made of a single-walled nanotube and in ropes [12]. More recently, superconducting properties have been measured in ropes suspended between nonsuperconducting, good metallic contacts [14]. Evidence of superconducting fluctuations has been also obtained in individual single-walled nanotubes [15]. In the experiments presented in Ref. [14], a drop by 2 orders of magnitude in the resistance has been found, down to the minimum value consistent with the number of conducting channels in the rope. This feature, together with its suppression under a suitably high magnetic field, shows the existence of superconductivity inherent to the ropes of nanotubes [14]. The value of the transition temperature varies from one sample to another, being below 1 K in the two where the resistance drop has been measured.

In this Letter, we develop a model to account for the superconductivity intrinsic to the ropes of nanotubes. The problem that faces any model trying to describe such effect is twofold. In the first place, it is known that the single-particle hopping between neighboring nanotubes in a rope is strongly suppressed [16]. This is because, in general, the different helical structure of the nanotubes leads to the misalignment of their lattices and, therefore, to the difficulty of conserving momentum for an electron hopping from one nanotube to the other. On the other hand, the effect of superconductivity cannot rely exclusively on the properties of the individual nanotubes, since any correlation in a 1D system can only develop a divergence at zero temperature [8].

The experiments on the proximity effect of Ref. [12] show anyhow the existence of sensible superconducting fluctuations in carbon nanotubes. The precise value of the critical supercurrents found there can be explained only by the presence of a short-range attractive interaction coming from the coupling to the elastic modes of the nanotube [17]. The point is that, as long as Cooper pairs are formed locally with zero total momentum, they may overcome the special difficulty that single electrons find to tunnel between neighboring nanotubes.

According to the work of Ref. [16], the amplitude t_T for tunneling between nanotubes with the same chirality and orientation is of the order $t_T \sim 0.01$ eV. In a disordered rope, the misalignment of the lattices of neighboring nanotubes introduces in general an additional suppression of the hopping amplitude by a factor $\sim \exp[-Ra_0(\delta k)^2/4]$, where R is the radius of the tube, δk is related to the mismatch of the Fermi points, and a_0 is a parameter of the order $\sim$0.5 Å [16]. For a typical nanotube radius $R =$ 7 Å, this factor is $\sim$0.005.

The tunneling amplitudes have to be compared with the energy scale at which the metallic nanotubes behave as 1D objects. This is the scale E_c below which the gapless linear subbands dominate the physical properties, and it can be estimated as $E_c \sim 0.1$ eV. The probability λ_2 of tunneling of a Cooper pair, given by the square of t_T in units of E_c, has a relative weight of the order of $\sim$0.01. On the other

hand, the probability of tunneling of a single electron has a relative weight of the order of ~ 0.0005. This means that pair hopping is the dominant process for tunneling between neighboring nanotubes in a disordered rope.

Prior to considering pair hopping, the rope can be described at low energies by a model in which each nanotube is treated as a 1D system, whose charge can interact with the charge in the other nanotubes of the rope. The Hamiltonian for this model, including a collection of metallic nanotubes $a = 1, \ldots, n$ with linear branches of different chirality $i = +, -$, can be written in terms of the respective density operators $\rho_{ai\sigma}$ [18]:

$$H_1 = \frac{1}{2} v_F \int_{-k_c}^{k_c} dk \sum_{ai\sigma} :\rho_{ai\sigma}(k)\rho_{ai\sigma}(-k): + \frac{1}{2} \int_{-k_c}^{k_c} dk \sum_{ai\sigma} \rho_{ai\sigma}(k) \sum_{bj\sigma'} V_{ab}(k)\rho_{bj\sigma'}(-k), \quad (1)$$

where $k_c = E_c/v_F$.

For the potential between different nanotubes V_{ab} we take the Coulomb interaction $V_C(k) = (e^2/4\pi^2)\log|(k_c + k)/k|$ [19], which remains long ranged in one spatial dimension [20]. According to the results of Ref. [17], the interaction potential V_{aa} within each nanotube includes, moreover, the effective short-range attraction coming from the coupling to the elastic modes, so that $V_{aa}(k) = (e^2/4\pi^2)\log|(k_c + k)/k| - g/2\pi$. The strength g of the attractive interaction is inversely proportional to the mass of the atoms and directly proportional to $(t'/v_s)^2$, where t' is the modulation of the lattice hopping and v_s is the speed of sound [21]. A rough estimate for a carbon nanotube gives $g/v_F \sim 0.2$.

Terms which couple the spin densities have been neglected in writing the Hamiltonian (1). These are backscattering (BS) interactions, which arise as a remnant of the Coulomb interaction at short distances. Being local in the nanotube lattice, their couplings are reduced by a relative factor of the order of $\sim 0.1a/R$, where a is the nanotube lattice spacing [9–11]. These terms are marginally relevant in the renormalization group sense. This means that they have greater strength as the model is scaled to smaller energies, but the rate of increase starts being quadratic in their own couplings. Thus, the theory has to be scaled to extremely low energies, many orders of magnitude below E_c, to have the BS couplings comparable to the couplings in (1) [10].

The bundle of 1D electron systems coupled only by charge interactions resembles the system proposed in Ref. [22] for the description of the sliding Luttinger liquid. Here the Coulomb interaction couples each of the nanotubes to all the others in the bundle. We recall that, for the samples of the experiments reported in Ref. [14], the number of metallic nanotubes is very large, of the order of $n \sim 100$. Then, the coupling of the charge in the different nanotubes leads to a significant reduction of the effective repulsive interaction. On the other hand, the effect of the intratube attractive interaction does not depend on the number of nanotubes and, in a certain regime, it may dominate over the Coulomb interaction.

The above point can be checked by looking at the correlators of the model governed by H_1. These can be computed exactly by means of bosonization techniques. For instance, the propagator $D^{(0)}(x,t)$ for the Cooper pairs within each nanotube factorizes into the different interaction channels, taking the form

$$D^{(0)}(x,t) \equiv \langle \Psi^+_{a+\uparrow}(x,t)\Psi^+_{a-\downarrow}(x,t)\Psi_{a+\uparrow}(0,0)\Psi_{a-\downarrow}(0,0)\rangle = C(x,t) \prod_1^{n-1} N(x,t) \prod_1^{3n} F(x,t). \quad (2)$$

The first factor in Eq. (2) corresponds to the contribution of the total charge density, which is given at zero temperature by the expression

$$C(x,t) = \exp\left(-\frac{1}{2n} \int_0^{k_c} dk \, \frac{1}{\mu(k)k} \times [1 - \cos(kx)\cos(\tilde{v}_F k t)] \right), \quad (3)$$

where $\mu(k) = 1/\sqrt{1 + 8nV_C(k)/v_F - 4g/\pi v_F}$ and $\tilde{v}_F(k) = v_F/\mu(k)$. The factors $N(x,t)$ correspond to the rest of the charge channels, and they have a form similar to (3) but with $\mu = 1/\sqrt{1 - 4g/\pi v_F}$ instead of $\mu(k)$ and $\tilde{v}_F = v_F/\mu$ instead of $\tilde{v}_F(k)$. The factors $F(x,t)$ correspond to the noninteracting channels with $\mu = 1$. The computation can be extended to the case of temperature $T \neq 0$, just by inserting the factor $1 + 2/[\exp(\tilde{v}_F|k|/T) - 1]$ in the integrand of expressions such as (3) [5].

The couplings that produce the most accurate fit of the critical supercurrents reported in Ref. [12] are $2e^2/\pi^2 v_F \approx 1.0$ and $4g/\pi v_F \approx 0.6$ [17]. For $n \sim 100$, the strong reduction of the Coulomb interaction implies that the effect of the intratube attractive interaction prevails in the system. In the g-ology description [6], the model is in the regime with short-range attractive coupling $g_2 < 0$, where the singlet superconductor response is enhanced over the charge-density-wave response. The temperature dependence of the Fourier transform $\tilde{D}^{(0)}$ of the propagator at zero frequency and momentum is represented in Fig. 1. The enhancement of the propagator is the signal that large superconducting correlations exist in the individual nanotubes at low temperatures.

The above considerations are pertinent to the system at half filling, in which the linear subbands cross at the Fermi level. When the nanotubes are slightly doped, the shift of the Fermi level gives rise to four Fermi points. The Cooper pairs have then the possibility to resonate between the outer and the inner gapless subbands. Anyhow, as long as the repulsive interactions mediating these processes are reduced by a relative factor as small as that of the BS interactions [9,10], the s-wave pairing is favored over other channels with different symmetry.

The tunneling of Cooper pairs between the nanotubes can be taken into account by modifying the Hamiltonian (1) with the additional term

$$H_2 = \sum_{\langle a,b\rangle} (\lambda_2)_{ab} \int_{-k_c}^{k_c} dk \int_{-k_c}^{k_c} dp \int_{-k_c}^{k_c} dp' [\Psi^+_{ai\uparrow}(k+p)\Psi^+_{a-i\downarrow}(-p)\Psi_{bj\uparrow}(k+p')\Psi_{b-j\downarrow}(-p') + \text{H.c.}], \quad (4)$$

where $\Psi^+_{ai\sigma}$ is the electron operator and the sum runs over all pairs $\langle a, b\rangle$ of nearest-neighbor metallic nanotubes.

The term (4) is a relevant perturbation from the renormalization group point of view. However, the anomalous scaling dimensions of the relevant perturbations turn out to be in general rather small. They can be computed in the boson representation and, in the case of the term (4), the result is $\gamma_2 = 2[1/4n\mu(k_0) + (n-1)/4n\mu - 1/4]$. k_0 represents some effective value, which does not affect significantly the estimate. For the above mentioned couplings, we obtain $\gamma_2 \approx -0.07$. Thus, even 4 orders of magnitude below E_c, we observe that λ_2 is not enhanced by more than a factor $(10^{-4})^{\gamma_2} \sim 2$.

The proposed model has a superconducting instability at some finite temperature, provided that the Cooper pairs are able to percolate in the transverse directions of the rope. This is the case of the superconducting ropes of Ref. [14], although to meet such an experimental condition one has to find the appropriate sample out of a large number of them [23]. Assuming the coherence in the hopping of pairs in the transverse directions, we may write the propagator of the Cooper pair from a metallic nanotube a to another b as a function $D(l_a, l_b; x, t)$ of the distance x along the rope and the positions l_a and l_b of the nanotubes in the transverse section of the rope. This object can be related to the propagator $D^{(0)}$ along each nanotube through the self-consistent diagrammatic equation in Fig. 2, which takes into account the dominant terms in powers of λ_2.

By introducing the Fourier transform with respect to (x, t) as well as in the l_a variables [24], the equation in Fig. 2 can be written for the Fourier transformed propagator $\tilde{D}$ in the form

$$\tilde{D}(q; k, \omega_k) = \tilde{D}^{(0)}(k, \omega_k) + \tilde{D}^{(0)}(k, \omega_k)\lambda_2(q)\tilde{D}(q; k, \omega_k). \quad (5)$$

We are interested in the propagation of the Cooper pairs from a metallic nanotube to the rest in the rope, which is given by $\tilde{D}(0; 0, 0) = \sum_{l_b} \int dx \int dt D(l_a, l_b; x, t)$. By solving Eq. (5), we get the result

$$\tilde{D}(0; 0, 0) = \frac{\tilde{D}^{(0)}(0, 0)}{1 - \lambda_2(0)\tilde{D}^{(0)}(0, 0)}. \quad (6)$$

The relevant dependence of $\tilde{D}(0; 0, 0)$, as well as of $\tilde{D}^{(0)}(0, 0)$, is on the temperature. It becomes clear that, if the superconducting correlations are such that $\tilde{D}^{(0)}(0, 0)$ has a divergence at $T = 0$, then the effect of pair hopping gives rise to the appearance of a pole at a finite value of T in the propagator of the Cooper pairs in the rope. According to the conventional interpretation, this is the signal of the condensation of Cooper pairs and the onset of the superconducting transition in the system.

In practice, when dealing with a rope of finite length L, the divergence of $\tilde{D}^{(0)}(0, 0)$ is cut off at a temperature scale about 1 order of magnitude below v_F/L. The curves shown in Figs. 1 and 3, for instance, have been obtained for a system with $L = 1000/k_c$, which corresponds to $L \sim 1$ μm with an appropriate choice of the length scale.

Taking our estimate of the pair-hopping amplitude $\lambda_2 \sim 0.01$, we observe that the length $L = 1000/k_c$ may be in some samples at the limit below which a superconducting instability cannot arise in the system. This depends on the spatial distribution of metallic nanotubes, which should determine more precisely the effective value of λ_2 to be used. Quite remarkably, a superconducting transition has been found in samples whose length is 1 μm or greater, while a sample with low resistance and 0.3 μm long has shown no transition at all [14].

Relying also on our estimate for λ_2, we observe from Fig. 3 that the temperature of the transition to the superconducting phase in a disordered rope with about 100 metallic nanotubes can be in the range between 10^{-4} and

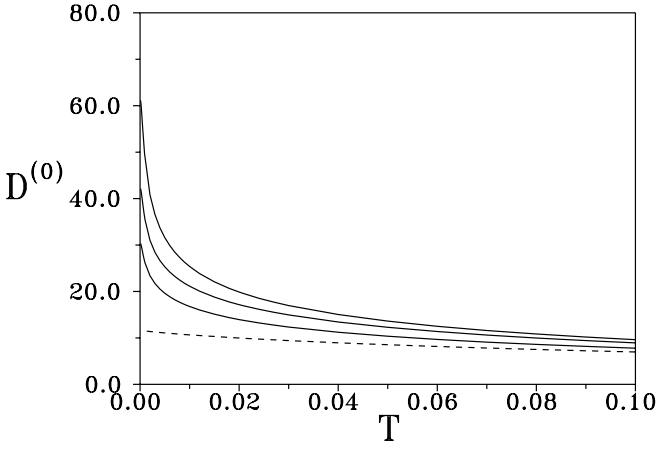

FIG. 1. Plot of the propagator $\tilde{D}^{(0)}$ at zero frequency and momentum versus T/E_c, for $2e^2/\pi^2 v_F = 1.0$. The dashed line corresponds to the case $n = 1$ and $g = 0$, and the solid lines to $n = 100$, and the respective values (from top to bottom) $4g/\pi v_F = 0.75, 0.5, 0$.

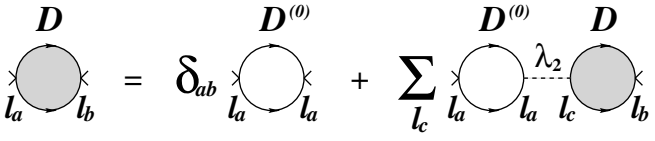

FIG. 2. Self-consistent diagrammatic equation for the propagator D of Cooper pairs along the rope.

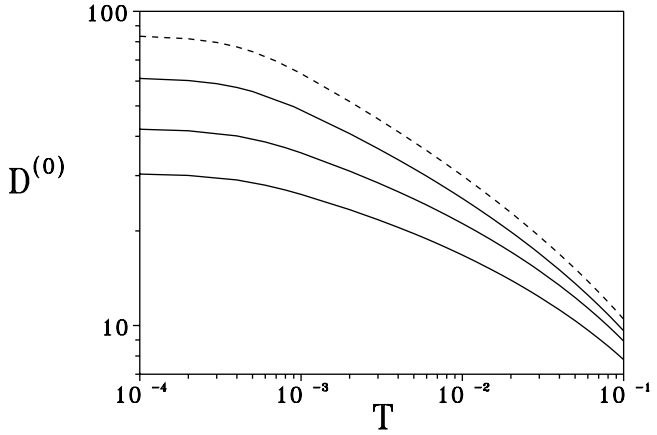

FIG. 3. Logarithmic plot of $\tilde{D}^{(0)}$ at zero frequency and momentum versus T/E_c. The solid lines are the transposition of the solid curves in Fig. 1 for $n = 100$ and the respective values $4g/\pi v_F = 0.75, 0.5, 0$. The dashed line corresponds to the case $n = 400$ and $4g/\pi v_F = 0.75$.

$10^{-3}E_c$. As the natural energy scale in our model is $E_c \sim 0.1$ eV, this sets the scale for typical transition temperatures in the range between 0.1 and 1 K. These values are consistent with the transition temperatures $T_c \approx 0.1$ K and $T_c \approx 0.4$ K measured experimentally in the two samples of Ref. [14].

The results of our analysis show that the superconductivity in the ropes of nanotubes is close in nature to that of the alkali-doped fullerenes [25]. We have seen that the tunneling of electrons between neighboring nanotubes in a rope takes place in pairs, which are formed within each nanotube due to the large superconducting correlations which develop at low temperatures.

The low values of T_c compared to those of the alkali-doped fullerenes can be understood on phenomenological grounds by the fact that the electron-phonon coupling is smaller in the nanotubes. This is consistent with a higher estimate of T_c obtained in Ref. [15] from measurements on small-diameter single-walled nanotubes, which have a larger electron-phonon coupling than the nanotubes in the ropes. As seen in Fig. 3, another way to obtain a higher T_c in the ropes may be to increase the number of nanotubes of the samples. Finally, the feasibility of controlling the rate of tunneling between the nanotubes should be studied since, as observed from Figs. 1 and 3, a slight change in that parameter may result in an increase of T_c by more than 1 order of magnitude.

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