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Superconductivity in armchair carbon nanotubes

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We use the momentum space renormalization group to study the influence of phonons and the Coulomb interaction on the superconducting response function of armchair single-walled nanotubes. We do not find superconductivity in undoped single nanotubes. When doped, superconducting fluctuations can develop because of the phonons but remain small and are easily destroyed by the Coulomb interaction. The origin of superconductivity in ropes of nanotobes is most likely an intertube effect. Projections to zigzag nanotubes indicate a more favorable disposition to superconducting fluctuations.

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Since 1991,[1] carbon nanotubes have attracted a lot of interest due to their unusual geometry and their structural and electronic properties.[2] Band calculations[3] (confirmed by experiments[4,5]) have stressed the one-dimensional (1D) character of single-wall carbon nanotubes (SWCNT).

Recently Kociak *et al.*[6] reported measurements on ropes of SWCNT making low-resistance contacts to nonsuperconducting (normal) metallic pads, at low voltage and at temperatures down to 70 mK. The preparation technique they have used yields armchair nanotubes.[7] Their results show signs of superconductivity below 0.55 K. The authors predict a purely electronic mechanism. The question we address here is whether or not 1D superconducting fluctuations can exist in a single single-walled nanotube (SWNT) and if phonons can play any role.

To achieve this, we perform perturbative renormalization-group (RG) calculations[8,9] to analyze the low-energy behavior of a (n,n) armchair nanotube. The electronic and phonon parts H_0 and the electron-phonon contribution $H_{e\text{-}ph}$ of the Hamiltonian were described in a previous publication.[10] We added the Coulomb interaction $H_{e\text{-}e}$. The electron wave functions come from a nearest-neighbor tight-binding model using a π_z orbital on each carbon atom of a sheet of graphene which is rolled up in the proper way to generate an armchair nanotube.[11] In order to build an effective Hamiltonian $(H=H_0+H_{e\text{-}e}+H_{e\text{-}ph})$ for low temperatures, we discard all bands that do not intersect the Fermi level. We then linearize the band energies around the Fermi level, $\varepsilon_{\gamma,p}(k')=(-1)^{\gamma+1}pv_Fk'$, where $k'=(k-pk_F)$, $\gamma=1,2$ is the band index, v_F is the Fermi velocity, k_F is the Fermi momentum, and $p=\pm$ is the sign of k. This is shown in Fig. 1. The Fermi level lies exactly at the crossing point for a half-filled band. This is the situation we shall first examine. In the g-ology approach to the RG, both the direct electron-electron and the phonon-mediated interactions give rise to twelve independent scattering amplitudes $g^{(j)}_{i,e\text{-}e}$ and $g^{(j)}_{i,ph}$ $(i=1,2,4$ and $j=1,\ldots,4)$. Here we have adopted the notation of Krotov *et al.*[12] The index i refers to the momentum branches (p) and j to the velocity branches [sign of the electron velocity $=(-1)^{\gamma+1}p$] such that $1=$ interbranch backscattering, $2=$ interbranch forward scattering, $3=$ umklapp scattering, and $4=$ intrabranch forward scattering. There are no momentum branch umklapp processes since $4k_F=8\pi/3a$ is not equal to a reciprocal-lattice vector, where a is the tube's unit-cell length. The coupling constants $g^{(j)}_{i,e\text{-}e}$ were calculated by summing over all tube sites using a Coulomb interaction of the form used by Egger and Gogolin.[13]

$$g^{(1)}_{1,e\text{-}e}=g^{(3)}_{1,e\text{-}e}=b,\quad g^{(2)}_{1,e\text{-}e}=g^{(4)}_{1,e\text{-}e}=b',$$

$$g^{(1)}_{2,e\text{-}e}=g^{(3)}_{2,e\text{-}e}=g^{(1)}_{4,e\text{-}e}=g^{(3)}_{4,e\text{-}e}=u',$$

$$g^{(2)}_{2,e\text{-}e}=g^{(4)}_{2,e\text{-}e}=g^{(2)}_{4,e\text{-}e}=g^{(4)}_{4,e\text{-}e}=u, \tag{1}$$

where u (u') and b (b') are related to the strength of the bare Coulomb interaction. The ratios $(u/b,b'/b,u'/u)$ vary between (2,0.005,0.01) and (20,0.01,0.002) when going from a strongly screened to an unscreened interaction. The phonon-mediated electron-electron coupling constants in the nonadiabatic regime,[14] $g^{(j)}_{i,ph}$, are given by[10]

$$g^{(j)}_{i,ph}\equiv-\frac{2}{\omega_q}g_{e\text{-}ph,\gamma}(q)g_{e\text{-}ph,\gamma'}(-q), \tag{2}$$

where $g_{e\text{-}ph,n}(q)$ is the electron-phonon interaction with each of the two electrons involved and ω_q is the phonon frequency. One has $q\approx 2k_F$ for backward scattering and $q\approx 0$ for forward scattering. These parameters are valid for temperatures $(k_B=1)$ smaller than the phonon energy.

The symmetry of the electronic functions[11] leads to the following sign constraints for the $g^{(j)}_{i,ph}$:

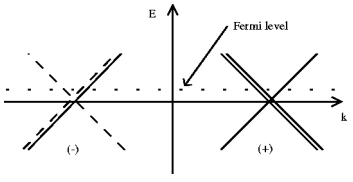

FIG. 1. Energy bands of an armchair nanotube near the Fermi energy. The double and single lines refer to each of the overlapping bands. The Fermi level is at the crossing point in the undoped tube and shifts when doped.

$$g^{(1)}_{1,ph}=-g^{(3)}_{1,ph}=g_1<0,\quad g^{(2)}_{1,ph}=0,\quad g^{(4)}_{1,ph}<0,$$

$$g^{(1)}_{2,ph}=-g^{(3)}_{2,ph}=g^{(1)}_{4,ph}=-g^{(3)}_{4,ph}=g_2<0,$$

$$g^{(2)}_{2,ph}=-g^{(4)}_{2,ph}=-g^{(2)}_{4,ph}=g^{(4)}_{4,ph}=g_4<0. \tag{3}$$

We then perform a one-loop RG calculation, which is a generalization of the one band calculation,[8,9] by considering only the diagrams presenting a logarithmic divergence with temperature, that is, with electrons on different velocity branches. The result of this procedure yields the same flow equations for the coupling constants that were found by Krotov *et al.*[12] Note that this approach is quite different from the one of Egger and Gogolin.[13] At half-filling, we use a two-cutoff approach[14] with $W>\hbar\omega_{ph}$ where W is the bandwidth and the renormalization starting energy scale while $\hbar\omega_{ph}$ is the phonon energy. For energy (or temperature) scales $E_0=We^{-l}>\hbar\omega_{ph}$, the phonons are adiabatic and the $g_{e\text{-}ph,\gamma}$ renormalize only in the random-phase approximation. When E_0 reaches $\hbar\omega_{ph}$, the phonons become nonadiabatic, and the $g^{(j)}_{i,ph}$ become active and are added to the $g^{(j)}_{i,e\text{-}e}$. Contrary to the usual case of a single band crossing the Fermi level, the coupling constants in our case scale towards the strong-coupling sector. An analytical solution of the renormalization equations seems to be impossible in the general case, which forces us to resort to a numerical solution.

The important physical properties of the system can be probed through its various response functions. These have the coupling constants as input and measure the relative importance of the underlying fluctuations. It is important to realize that, because of the interband interaction terms $(g^{(2)}_1,g^{(1)}_2,g^{(3)}_i,g^{(j)}_4)$, the particle-hole pairs in the Peierls channel and the particle-particle pairs in the Cooper channel will be evolving in both bands. It is thus necessary to define the following response functions in Matsubara-Fourier space:

$$\chi^{\kappa,M}_{\mu}(\tilde{q})=-\int_0^{\beta}\int d\tau dx e^{iqx-i\omega_m\tau}\times\langle O^{\kappa,M}_{\mu}(x,\tau)^{\dagger}O^{\kappa,M}_{\mu}(0,0)\rangle, \tag{4}$$

with $\kappa=\pm$, $M=\pm$, and $\tilde{q}=(q,\omega_m)$. The Fourier transforms $O^{\kappa,M}_{\mu}(\tilde{q})$ are defined by

$$O^{\kappa,M}_{\mu}(\tilde{q})=\frac{1}{\sqrt{2}}[O^{\kappa}_{\mu}(\tilde{q})+MO^{\kappa}_{\mu}(\tilde{q})^{\dagger}]. \tag{5}$$

In the Peierls channel, one defines

$$O^{\kappa}_{\mu}(q\approx 2k_F)=\frac{1}{\sqrt{L}}\sum_{k,\alpha,\beta}[\psi^{\dagger}_{1,-,\alpha}(k-q)\sigma^{\alpha\beta}_{\mu}\psi_{1,+,\beta}(k)+\kappa\psi^{*}_{2,-,\alpha}(k-q)\sigma^{\alpha\beta}_{\mu}\psi_{2,+,\beta}(k)]/2, \tag{6}$$

$$O^{\kappa}_{\mu}(q\approx 0)=\frac{1}{\sqrt{L}}\sum_{k,\alpha,\beta}[\psi^{\dagger}_{1,-,\alpha}(k-q)\sigma^{\alpha\beta}_{\mu}\psi_{2,-,\beta}(k)+\kappa\psi^{\dagger}_{2,+,\alpha}(k)\sigma^{\alpha\beta}_{\mu}\psi_{1,+,\beta}(k-q)]/2, \tag{7}$$

in which $\mu=0$ stands for charge-density (CDW) operators and $\mu=1,2,3$, for spin-density (SDW) ones. Here σ_0 and $\sigma_{1,2,3}$ are the identity and the x,y,z Pauli matrices, respectively, and $\psi_{\gamma,p,\alpha}(k)$ annihilates an electron of spin α in band γ having momentum k in branch p. In the Cooper channel, one has

$$O^{\kappa}_{\mu}(q\approx 0)=\frac{1}{\sqrt{L}}\sum_{k,\alpha,\beta}\alpha[\psi_{1,-,\alpha}(-k+q)\sigma^{-\alpha,\beta}_{\mu}\psi_{1,+,\beta}(k)+\kappa\psi_{2,-,\alpha}(-k+q)\sigma^{-\alpha,\beta}_{\mu}\psi_{2,+,\beta}(k)]/2, \tag{8}$$

$$O^{\kappa}_{\mu}(q\approx 2k_F)=\frac{1}{\sqrt{L}}\sum_{k,\alpha,\beta}\alpha[\psi_{1,-,\alpha}(-k+q)\sigma^{-\alpha,\beta}_{\mu}\psi_{2,-,\beta}(k)+\kappa\psi_{1,+,\alpha}(-k+q)\sigma^{-\alpha,\beta}_{\mu}\psi_{2,+,\beta}(k)]/2, \tag{9}$$

where $\mu=0$ are singlet superconducting (SS) operators and $\mu=1,2,3$ are triplet superconducting (TS) ones. It is through these band-entangled operators that our response functions are different from the ones of Krotov *et al.*[12] who only used the untangled $(O^{+}_{\mu}\pm O^{-}_{\mu})$ operators. Our definition of the response functions leads to a fundamentally different behavior with temperature.

In order to calculate the evolution of the response functions with the energy scale E_0 (or temperature), we introduce the auxiliary response functions $\overline{\chi}^{\kappa,M}_{\mu}$ defined through

$$\chi^{\kappa,M}_{\mu}(l,\tilde{q})=-\frac{1}{\pi v_F}\int_0^{l}\overline{\chi}^{\kappa,M}_{\mu}(l',\tilde{q})dl', \tag{10}$$

where $l=\ln(W/E_0)$. We deduce the following renormalization equations:

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa,M}_{CDW}=\overline{g}^{(2)}_2(l)-2\overline{g}^{(1)}_1(l)+\kappa[\overline{g}^{(3)}_2(l)-2\overline{g}^{(3)}_1(l)],$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa,M}_{SDW}=\overline{g}^{(2)}_2(l)+\kappa\overline{g}^{(3)}_2(l), \tag{11}$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa,M}_{CDW'}=\overline{g}^{(2)}_4(l)-2\overline{g}^{(1)}_4(l)+\kappa[\overline{g}^{(2)}_1(l)-2\overline{g}^{(1)}_2(l)]+M\{-\overline{g}^{(3)}_4(l)+\kappa[\overline{g}^{(3)}_1(l)-2\overline{g}^{(3)}_2(l)]\},$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa,M}_{SDW'}=\overline{g}^{(2)}_4(l)+\kappa\overline{g}^{(2)}_1(l)+M[\overline{g}^{(3)}_4(l)+\kappa\overline{g}^{(3)}_1(l)],$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa}_{SS}=-\overline{g}^{(2)}_2(l)-\overline{g}^{(1)}_1(l)+\kappa[\overline{g}^{(1)}_2(l)+\overline{g}^{(2)}_1(l)],$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa}_{TS}=-\overline{g}^{(2)}_2(l)+\overline{g}^{(1)}_1(l)-\kappa[\overline{g}^{(1)}_2(l)-\overline{g}^{(2)}_1(l)],$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa}_{SS'}=-\overline{g}^{(2)}_4(l)-\overline{g}^{(1)}_4(l),$$

$$\frac{d}{dl}\ln\overline{\chi}^{\kappa}_{TS'}=-\overline{g}^{(2)}_4(l)+\overline{g}^{(1)}_4(l),$$

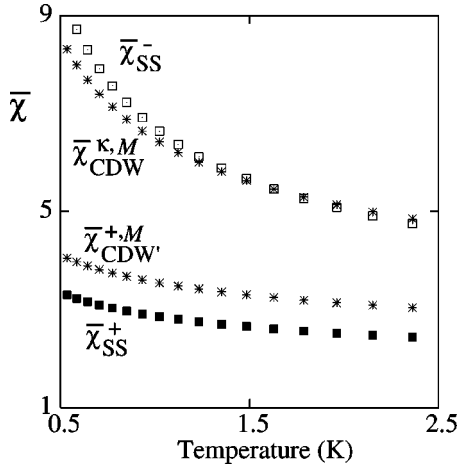

FIG. 2. Typical flow diagram for the response functions of a doped armchair nanotube.

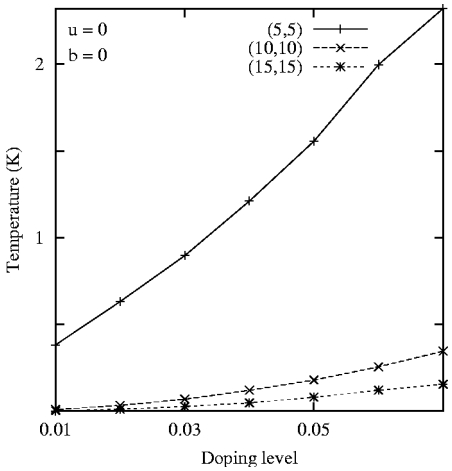

FIG. 3. Temperature at which the superconducting fluctuations dominate as a function of the doping level for three (n,n) armchair tubes. Only phonon-mediated interactions are considered.

with $\overline{g_i^{(j)}}=g_i^{(j)}/\pi v_F$. CDW' and SDW' refer to the anomalous $q\approx 0$ interband situations while SS' and TS' refer to the $q\approx 2k_F$ ones.

We first report on the calculations without the Coulomb interaction, that is, solely with the phonon-mediated effective electron-electron interactions (at temperatures below the Debye temperature for nonadiabatic interactions[14]). This was done for arbitrary amplitudes but with the sign constraints given in Eq. (3). We find no sign of a dominant superconducting response in a single-walled armchair carbon nanotube. Charge correlations ($\overline{\chi}^{-,M}_{CDW}$ and $\overline{\chi}^{-,-}_{CDW'}$) are in all cases the most divergent and open a pseudogap which subdues the superconducting fluctuations. The introduction of Coulomb interactions, through u and b, reinforces this tendency even more. Kociak *et al.*,[6] however, mention the possibility that the band occupancy might not be exactly $\frac{1}{2}$. If this were the case, as far as we can estimate from a tight-binding calculation, the sign constraints mentioned in Eq. (3) still hold. However, the Fermi level would shift by $\Delta E=dv_Fk_F/2$ (d is the doping level) and the two bands would have different Fermi momenta. As a consequence, for energy scales below ΔE the $\overline{g_i^{(3)}}$ would vanish because of longitudinal momentum conservation. Moreover, the interband backward scattering $g^{(2)}_{1,ph}$, which was previously zero [see Eq. (3)], now is $\sim d^2g_1$. We now use a three-cutoff procedure $W>\hbar\omega_{ph}>\Delta E$. The crossing of ΔE and $\hbar\omega_{ph}$ occurs at an 8% doping level. In the case where only the phonon-mediated interactions are considered we have estimated[10] $\overline{g_1}=-0.3/n$ and $\overline{g_2}=\overline{g_4}=-0.1/n$. Superconducting correlations $\overline{\chi}^{-,M}_{SS'}$ are found to dominate for l greater than a critical l_s. This is shown for a typical run in Fig. 2. Figure 3 shows the crossover temperatures T_s below which this occurs for various doping levels and different diameter SWCNT. The turning on of the Coulomb interaction lowers T_s and eventually destroys the superconducting fluctuations dominance for $u\gtrsim|g_1|$. At this point, we can conclude that superconducting fluctuations in single armchair nanotubes originating from a phonon mechanism are possible at an appreciable doping level provided the Coulomb interaction is very small. This last condition seems restrictive in view of our own evaluation $u\gg|g_1|$ and the evidence of strong electronic correlations in SWCNT.[15] Moreover, the finite length of the nanotubes results in a discretization of the energy levels.[16] Consequently, the energy scale in the renormalization-group procedure cannot be smaller than this spacing. We estimate this would occur at best at 1 K which is still larger than the temperatures at which the work of Kociak *et al.*[6] shows any indication of superconductivity. It thus seems likely that the superconductivity seen in ropes takes place by a coupling effect between the nanotubes. At the dimensionality crossover temperature $T_x\sim t_\perp/\pi$, where $t_\perp$ is the net intertube hopping amplitude, intertube hopping becomes coherent.[17] Any fluctuating superconducting pair that might exist will thereafter be able to coherently tunnel between tubes. This surely occurs much before the SWCNT discrete spectrum is felt. The single tube superconducting fluctuations need not be dominant for this to take place. The existence of frustration in ropes of close-packed SWCNT would prevent the further development of bond-order wave deformations (associated with a Kekule CDW modulation[10]) or magnetic order and allow superconductivity to develop. Moreover, the interchain particle-hole interactions that might exist at T_x could also play a role in enhancing superconductivity through a mechanism similar to the one proposed for organic materials.[18] All of this is consistent with the small temperatures observed for superconductivity in ropes of armchair nanotubes.

The recent discovery of superconducting fluctuations at 15 K in a single (5,0) zigzag single-walled carbon nanotube[19] thus seems puzzling in view of the above analysis of armchair nanotubes. In this specific instance, the very strong σ-π hybridization due to the very small diameter of the SWCNT changes the band structure in a dramatic way and makes the tubes metallic instead of being the expected insulating state.[2] The band structure might share similarities with the one in a conducting (6,0) zigzag SWNT.[20] The band structure in the vicinity of the Fermi level would then show the crossing between a nondegenerate band (1) and doubly

degenerate bands (2,3) of opposite curvature and would have a different transverse angular momentum. Because of the twofold degeneracy, the Fermi level no longer lies at the crossing point but is offset so that the bands (1) and (2,3) have different Fermi momenta. Moreover, the tight symmetry relationship of the armchair bands exists no longer between (1) and (2,3). There are also many different phonons contributing to effective phonon-mediated electron-electron interactions. Finally, all $\bar{g}_i^{(3)}$ will vanish because of longitudinal momentum conservation. This, we believe, is quite sufficient to allow for important superconducting fluctuations in the zigzag tubes. Purely as an illustration and only for crude order of magnitude estimates, we used the model developed above with only two cutoffs $W=\Delta E\sim 0.3$ eV,[20] $\hbar\omega_{ph}\sim 0.166$ eV, and $n=3$ to account for the smaller tube diameter such that $\bar{g}_1=-0.1, \bar{g}_2=-0.03$. We find a dominance of the superconducting response below room temperature with just the phonons. This is much larger than for the armchair tubes and might explain the origin of the superconducting fluctuations observed by Tang *et al.*[19] But again adding a Coulomb interaction quickly reduces this temperature. Superconductivity disappears again for $u\gtrsim|g_1|$. The results of Tang *et el.* would thus indicate an unexpectedly small Coulomb interaction in zigzag nanotube.

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