Paraconductivity in Carbon Nanotubes

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Abstract

We report the calculation of paraconductivity in carbon nanotubes above the superconducting transition temperature. The complex behavior of paraconductivity depending upon the tube radius, temperature and magnetic field strength is analyzed. The results are qualitatively compared with recent experimental observations in carbon nanotubes of an inherent transition to the superconducting state and pronounced thermodynamic fluctuations above \(T_c\). The application of our results to single-wall and multi-wall carbon nanotubes as well as ropes of nanotubes is discussed.

Carbon nanotubes are mesoscopic systems with a remarkable interplay between dimensionality, interaction and disorder [1]. Recent experiments found that the electron transport in single-wall nanotubes (SWNT) has a one-dimensional ballistic behavior [2]. Therefore it may be theoretically described within the model of one-dimensional interacting electron systems known as Luttinger liquid [3, 4, 5]. At the same time, the multiwall nanotubes (MWNT), which are composed of several concentrically arranged graphite shells, show properties which are consistent with the weak-localization features of the diffusive transport in magnetoconductivity and zero-bias anomaly in the tunneling density of states [6]. Similar properties have been observed in ropes of SWNTs [2, 7].

Very recent experimental works [8, 9] have addressed the problem of superconductivity in carbon nanotubes. In the article by Tang et al. [8] a superconducting behavior was detected in SWNT at a mean-field critical temperature evaluated as \(T_c=15\) K. At the same time a pure superconducting state with zero resistance was not found and the authors attribute this fact to the presence of strong fluctuations which alter severely the superconducting order parameter both below and above \(T_c\). In Ref. [9] ropes of SWNT were studied and a truly superconducting transition was discovered at \(T_c=0.55\) K. The suppression of \(T_c\) by a magnetic field applied along the tube was also measured.

In the present communication we study the paraconductivity and corresponding magnetoconductivity of a carbon nanotube, i.e. the contribution to the conductivity induced by the fluctuations of the superconducting order parameter above \(T_c\). In what follows we assume the validity of the Ginzburg-Landau (GL) formalism for the description of the fluctuation superconductivity. In order to describe the one-electron spectrum of carbon nanotubes one has to take into consideration that the electron wavelength around the circumference of a nanotube is quantized due to the periodic boundary conditions and only a discrete number of wavelengths can fit around the tube. Along the tube, however, electronic states are not confined and electrons can move ballistically. Because of the circumferential modes quantization, the electron states in the tube do not form...
Ψ can be presented as a Fourier series in different order parameter modes. These critical temperatures are:

\[ \Phi = H R \]

\[ \tau = \frac{4 m \pi}{n} \]

\[ \kappa = \frac{4 m \pi}{R} \]

where \( n = -N, ..., N \), \( N = \left[ \frac{p_F R}{\pi} \right] \), \( p_F \) is the Fermi momentum and \( R \) is the nanotube radius. The number \( N \) is determined by the value of the chemical potential \( \epsilon \) and the distance between the levels. It defines the number of electrons filling the \( 2N + 1 \) electron sub-bands of the nanotube electron spectrum. A typical value for a realistic nanotube is \( N \sim 5 \).

The longitudinal coordinate \( z \) and the angular variable \( \varphi \) are chosen as the natural coordinate system for the problem under discussion. The linearized time-dependent GL equation (TDGL) for the fluctuation order parameter \( \Psi(z, \varphi, t) \) takes the form:

\[
- \gamma \frac{\partial \Psi(z, \varphi, t)}{\partial t} = \hat{H} \Psi(z, \varphi, t) = \alpha T_c \left[ \epsilon - \xi^2 \frac{\partial^2}{\partial z^2} - \xi^2 \left( \frac{1}{R} \frac{\partial}{\partial \varphi} - 2i e A_\perp \right)^2 \right],
\]

where \( \hat{H} \) is the GL Hamiltonian written for the nanotube geometry, \( \gamma = \pi \alpha / 8 \), \( \epsilon = (T - T_c) / T_c \), \( A_\perp = H R = \frac{\Phi}{e R} \) is the tangent component of the vector potential, \( \Phi_0 = \pi / e \) is the magnetic flux quantum, \( \xi = (4m_\alpha T_c)^{-1/2} \) and \( \xi_\perp = (4m_\perp T_c)^{-1/2} \) are the longitudinal and the transversal GL coherence lengths. The latter is supposed to be comparable with the nanotube radius: \( \xi_\perp \sim R \). The fluctuation order parameter \( \Psi \) can be presented as a Fourier series

\[
\Psi(z, \varphi, t) = \sum_{n = -\infty}^{\infty} \int_{-\pi/a}^{\pi/a} \frac{dq_i}{2\pi} \psi_n(q_i, t) \exp(-i n \varphi) \exp(-i q_i z),
\]

and the TDGL equation for the Fourier component \( \psi_n(t) \) is read as:

\[
- \gamma \frac{\partial \psi_n(q_i, t)}{\partial t} = \varepsilon_n(q_i, \Phi) \psi_n(q_i, t) = \alpha T_c \left[ \epsilon + \xi_\parallel^2 q_i^2 + \frac{\xi_\perp^2}{R^2} \left( n - \frac{2\Phi}{\Phi_0} \right)^2 \right] \psi_n(q_i, t).
\]

Here \( \varepsilon_n(q_i, \Phi) \) are the eigenvalues of \( \hat{H} \).

The angular quantization gives rise to rather distinctive critical temperatures corresponding to the different order parameter modes. These critical temperatures are: \( T_c^{(n)}(\Phi = 0) = T_c^{(0)} \left[ 1 - \left( \frac{\xi_\perp^2}{R^2} \right) n^2 \right] \) and the characteristic dimensionless temperature difference is \( \Delta \varepsilon_0 \sim \xi_\perp^2 / R^2 \). As expected, when the temperature decreases the system tends to the mode with \( n = 0 \). In nonzero magnetic fields, when the magnetic flux is \( \Phi \in (-\Phi_0 / 2, \Phi_0 / 2) \), the superconducting transition occurs at the \( \psi_0 \) state.

Let us move to the study of the paraconductivity in a small superconducting cylinder at temperatures above the critical one. The fluctuation-induced current can be expressed by its general quantum mechanical form averaged over all possible values of the fluctuation order parameter \( \Psi(z, \varphi, t) \). The latter can be defined as the solution of the TDGL equation \( (2) \) when the Langevin forces are introduced in the right hand side. After some algebra the general expression for the paraconductivity tensor can be obtained (see details in [1]) in the form of a convolution product of the velocity matrix elements \( \hat{V}_\parallel(i, l) \) and the kernel containing the eigenvalues of the GL Hamiltonian of Eq. \( (3) \). We will only need its longitudinal diagonal component:

\[
\sigma^\parallel(\epsilon, H) = \frac{\pi \alpha e^2}{2} T \sum_{(i, l) = 0} \frac{\hat{V}_\parallel(i, l) \hat{V}_\parallel(i, l)}{\varepsilon(g, l) \varepsilon(g, l) + \varepsilon(g, l)}. \quad (5)
\]
The appropriate matrix elements of the velocity operator are

$$v^2_{i/pq} = v_p \delta_{pq} \delta_{il}, \quad v^z_p = \frac{\partial \epsilon_p}{\partial p} = 2\alpha T \xi^2_{\epsilon, p}. \quad (6)$$

The summation over subscript \{i\} is carried out over the levels of the angular quantization up to the maximal number $N$ and includes the integration over the $z$-axis momentum. As a result the general formula (6) for the longitudinal paraconductivity of a nanotube is read as

$$\sigma^{\|}(\epsilon, H) = \frac{\pi \alpha e^2}{2S} T \int \frac{dp_n}{2\pi} \int \frac{dq}{2\pi} \sum_{i,l=-N}^{N} \frac{v^z_{il,pq} \hat{v}^i_{il,qp}}{\epsilon_i (p_n) \epsilon_l (q_i) [\epsilon_i (p_n) + \epsilon_l (q_i)]} = \quad (7)$$

(here $S = \pi R^2$ is the cross-section area of the nanotube). This formula can be numerically evaluated to obtain the magnetoconductivity. Nevertheless, in order to get a qualitative understanding of the paraconductivity temperature dependence in zero field and its behavior in the presence of a magnetic field at fixed temperature, let us assume $N \gg 1$ and try to proceed analytically.

1. Zero magnetic field. The most convenient way to analyze Eq. (6) is to isolate the term with $n = 0$ and treat the first term and the remaining sum separately. Relatively far from the critical temperature, where $\xi_{\perp} (\epsilon) = \xi_{\perp} / \sqrt{\epsilon} \ll R$, (but still $\epsilon \ll 1$), one can replace the sum in Eq. (6) with an integral to get

$$\sigma^{\|}(\epsilon, 0) = \frac{\pi e^2}{16S} \xi_{\perp} \frac{1}{\epsilon^{1/2}} + \frac{\pi e^2}{8S} \xi_{\perp} \left(\frac{R}{\xi_{\perp}}\right)^3 \left\{ \frac{1}{\sqrt{1 + \frac{R^2}{\xi_{\perp}^2 (\epsilon)}}} \left[1 + \frac{1}{\sqrt{1 + \frac{R^2}{\xi_{\perp}^2 (\epsilon)}}}\right] - \frac{1}{\sqrt{N^2 + \frac{R^2}{\xi_{\perp}^2 (\epsilon)}}} \left[ N + \sqrt{N^2 + \frac{R^2}{\xi_{\perp}^2 (\epsilon)}} \right] \right\}. \quad (8)$$

One can see that for temperatures far enough from $T_c$, such that $\xi_{\perp} (\epsilon) \ll R/N$, the 1D limit is reached while in the interval where $R/N \ll \xi_{\perp} (\epsilon) \ll R$ the Eq. (6) reproduces the 2D result for paraconductivity. In the immediate vicinity of the critical temperature, where $\xi_{\perp} (\epsilon) \gg R$, only the first term in Eq. (6) contributes to the paraconductivity and the system is again in the 1D limit.

All the asymptotics of Eq. (6) can be presented in a more compact form as:

$$\sigma^{\|}(\epsilon, 0) = \frac{e^2 \xi_{\perp}}{16R^2} \begin{cases} \frac{1}{\sqrt{\epsilon}}, & \epsilon \ll \left(\frac{\xi_{\perp} N}{R}\right)^2 \\ \left(\frac{R}{\xi_{\perp}}\right)^2 \frac{1}{\epsilon^{1/2}}, & \left(\frac{\xi_{\perp} N}{R}\right)^2 \ll \epsilon \ll \left(\frac{\xi_{\perp} N}{R}\right)^2 \\ \left(\frac{2N+1}{e^{1/2}}\right)^2 \frac{1}{\epsilon^{1/2}}, & \left(\frac{\xi_{\perp} N}{R}\right)^2 \ll \epsilon \end{cases}. \quad (9)$$

The physics of these crossovers is the following. The first one has a geometrical nature: very near to $T_c$ the fluctuation Cooper pairs are so large that they have only one degree of freedom to slide along the tube axis. The first line of Eq. (6) exactly reproduces the paraconductivity of a wire with cross-section $S \ll \xi_{\perp}^2$. In the intermediate regime rotations over the tube surface become possible and the paraconductivity temperature dependence transforms into the 2D one. Finally, relatively far from $T_c$, where $\xi_{\perp} (\epsilon) \sim R/N$, the last, most nontrivial, crossover $2D \rightarrow 1D$ in the fluctuations dimensionality takes place. Let us stress the longitudinal paraconductivity in this range of temperatures acquires a degeneracy factor $2N + 1$ equal to the number of electron sub-bands.
2. Non-zero magnetic field. We now move to the study of paraconductivity in the presence of a magnetic field applied. Due to the Little-Parks effect \([2]\), the critical temperatures \(T_{c}^{(n)}(\Phi)\) are periodic functions of the flux through the tube with period \(\Phi_{0}\). Therefore we can restrict ourselves to the flux range \(-\Phi_{0}/2 < \Phi < \Phi_{0}/2\), where \(T_{c}(\Phi) = T_{c}^{(0)}[1 - \frac{\xi_{\perp}^{2}}{R^{4}}]\left(\frac{2\Phi_{0}}{\Phi}\right)\). Evidently, two different regimes can take place: a weak-field one when \(\Phi \lesssim \Phi_{0}\) (which is equivalent to \(H \lesssim H_{c2}\left(\frac{R}{\xi_{\perp}}\right)\sqrt{\epsilon}\)) and a strong-field regime when \(\Phi_{0}\) \(\frac{R}{\xi_{\perp}}\sqrt{\epsilon} \ll \Phi \ll \Phi_{0}/2\). The general formula \([7]\) may be rewritten as

\[
\sigma''(\epsilon, \Phi) = \frac{\pi e^{2} \xi_{\parallel}}{16 S_{\perp}} \left(\frac{R}{\epsilon_{\perp}}\right)^{3} \frac{1}{\left[2\Phi_{0}^{2} + \frac{R^{2}}{\epsilon_{\perp}}\right]^{3/2}} + \frac{\pi e^{2} \xi_{\parallel}}{16 S_{\perp}^{2}} \left(\frac{R}{\epsilon_{\perp}}\right)^{3} \sum_{n=1}^{N} \frac{1}{\left[\left(n + \frac{2\Phi_{0}}{\Phi}\right)^{2} + \frac{R^{2}}{\epsilon_{\perp}}\right]^{3/2}}. \tag{10}
\]

In the case of the weak-field regime one can easily see that the main magnetic field dependence comes from the renormalization of the critical temperature, so

\[
\delta \sigma''(\epsilon, \Phi) = \sigma''(\epsilon, \Phi) - \sigma''(\epsilon, 0) = -\frac{e^{2} \xi_{\parallel}}{8} \left(\frac{\Phi}{\Phi_{0}}\right)^{2} \left\{ \begin{array}{l}
\frac{1}{\epsilon_{\perp}}, \epsilon \ll \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \\
4 \left(\frac{R}{\epsilon_{\perp}}\right)^{2} \frac{1}{\epsilon_{\perp}}, \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \ll \epsilon \ll \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \\
3(2N+1) \frac{1}{e^{3/2}}, \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \ll \epsilon
\end{array} \right. \tag{11}
\]

The strong-field regime \(\Phi_{0}\) \(\frac{R}{\xi_{\perp}}\sqrt{\epsilon} \ll \Phi \ll \Phi_{0}/2\) can be reached (without passing to the next foil of the Little-Parks effect) in the case \(R \ll \xi_{\perp} (\epsilon)\) only. In this case one finds that the main contribution originates from the first term in Eq. \([10]\):

\[
\sigma''(\Phi) = \frac{e^{2} R \xi_{\parallel}}{27} \left(\frac{\Phi}{\Phi_{0}}\right)^{3}. \tag{12}
\]

This result is valid for temperatures \(\epsilon \ll \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2}\). In the temperature range \(\left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \ll \epsilon \ll \left(\frac{\Phi}{\epsilon_{\perp}}\right)^{2} \ll 1\) (if such interval exists), where in the absence of the magnetic field the fluctuations have a 2D character, the effect of the magnetic field is relevant only for fields so high as \(\Phi_{0} N \frac{R}{\xi_{\perp}}\sqrt{\epsilon} \ll \Phi \ll \Phi_{0}/2\), but it still is described by the formula \([12]\). One can recognize in the effect of the magnetic field on paraconductivity the usual suppression of the effective fluctuation dimensionality, as it happens even in the 3D case. Nevertheless we would like to attract the reader’s attention to the unusually strong suppression of the nanotube paraconductivity in strong magnetic fields. Its comparison with the corresponding paraconductivity of a layered superconductor shows a remarkable difference in the critical exponent: 3 against 1 (see Ref. \([13]\)). This follows from the channel separation in the Cooper pairs motion and hence the effective decrease of their density in the momentum space. A similar effect is observed in superconducting rings. In its 0D regime \(\sigma^{(0)}_{\text{ring}}(H) \sim H^{-4}\) (see Refs. \([14]\)) instead of \(\sigma^{(0)}_{\text{gran}}(H) \sim H^{-2}\) as for superconducting granules (see Refs. \([1, 15]\)).

Let us discuss the results obtained. In Fig. 1 we have plotted the resistivity of carbon nanotubes calculated from Eq. \([10]\), choosing \(N = 5\) for different magnetic field strengths. It can be seen that the simulated behavior is similar to the experimental one reported in Ref. \([7]\) for metallic ropes of nanotubes. Discussing the application of our results to recent experimental data concerning realistic nanotubes \([2, 16, 17, 18]\), it is important to remember that the physics of superconductivity in these systems is still controversial and
it is very likely to be qualitatively different for systems like MWNT, the ropes of SWNTs or individual SWNT. Namely, the effect of interactions within multiwall tubes or hopping between neighboring tubes in a rope drives the system away from the one-dimensionality characterizing an individual nanotube. Therefore the physical properties are substantially altered in both the normal and superconducting states depending on whether hopping is effective or not. Nevertheless our considerations are quite general because the model proposed is based on the GL phenomenology which is independent of the specific pairing mechanism leading to the superconductivity. It is clear that an individual nanotube is rather within the one-dimensional limit of Eq. (8), \( \xi_\perp(\epsilon) \gg R \), while for multiwall tubes or ropes the other regimes may be observed.

As it was demonstrated above, the nontrivial geometry of tube leads to a number of possible crossovers in the temperature dependence of the paraconductivity. The crossover closest to the critical temperature has a clear geometric nature and is analogous to the one occurring in thin films of layered superconductors [16]. As the system moves away from the transition point, the coherence length decreases, thus rotations over the tube surface become possible and the system goes into the 2D regime. The last 2D \( \rightarrow \) 1D crossover has an intrinsic origin, it occurs when \( \xi_\perp(\epsilon) \lesssim R/N \).

The alternative interpretation of different regimes of paraconductivity behavior can be given on the basis of comparison of the characteristic fluctuation Cooper pair "binding energy", \( T - T_c \), with the angular quantization energy level structure. Here it is necessary to remind that the fluctuation Cooper pairs above the critical temperature are not condensed with the zero energy, like it happens below \( T_c \), but they are distributed over energy with the rapid decay at \( \epsilon \gtrsim T - T_c \). When \( \xi_\perp(\epsilon) \gg R \left( T - T_c \ll 1/2m_\perp R^2 \right) \) the binding energy is so small that the electrons occupying only the \( n = 0 \) level can be involved in fluctuation pairing. In result the 1D behavior takes place. As \( T - T_c \) grows (\( R/N \ll \xi_\perp(\epsilon) \ll R \) the electrons from more and more subbands can be involved in pairing (within the same subband) and due to this additional degree of freedom (subband number \( n \)) the fluctuation behavior becomes 2D. Finally, when \( T - T_c \) exceeds the energy of the last filled level of angular quantization \( \epsilon_N = N^2/2m_\perp R^2 \) what means \( \xi_\perp(\epsilon) \lesssim R/N \) all \( 2N + 1 \) subbands are involved in pairing and each one presents the independent one-dimensional channel. Indeed, the corresponding formula differs from the one near \( T_c \) by a factor \( 2N + 1 \) (see Eqs. (9) and (10)).

The experimental observation of such crossovers, side by side with the strong suppression of the paraconductivity by magnetic fields would be good "pro" or "contra" arguments in the discussion of the validity of the GL phenomenological approach to the study of superconductivity in such nontrivial objects as nanotubes.

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Figure caption

Theoretical prediction for the temperature dependence of the resistivity of carbon nanotube. Plotted is the resistivity calculated as a sum of normal-state temperature-independent contribution and paraconductivity versus the reduced temperature \((T - T_c(0))/T_c(0)\). The field strengths are \(\Phi/\Phi_0 = 0, 0.25\) and 0.5.