Superconductivity in bundles of a mixture of doped carbon nanotubes

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Using inhomogeneous Bogoliubov-de Gennes formalism we study superconducting properties of bundles of single wall carbon nanotubes, consisting of a mixture of metallic and semiconducting nanotubes, having different critical transition temperatures. We investigate how the averaged superconducting order parameter and the critical transition temperature depend on the fraction of semiconducting carbon nanotubes in the bundle.

Single wall carbon nanotubes (SWCNT) represent a unique class of quasi-one dimensional nanoscale systems, exhibiting various interesting phenomena. Among other exciting features, it was demonstrated that individual single wall carbon nanotubes may have intrinsic superconducting properties. However, because of their extremely small diameter (just few nanometers), and thus strongly one dimensional character, the superconducting order parameter may have significant “phase slips” due to thermal and quantum fluctuations, leading to a finite conductivity in the system below the critical temperature. Carbon nanotubes can form bundles and ropes, with tens and hundreds of individual SWCNTs in the bundle, coupled to each other by dispersive Van der Waals forces. Such kind of system may exhibit reduced “phase slips” effects, due to three-dimensional coupling of the nanotubes in the bundle and as a result, much stronger conductivity drop below the critical temperature. The overall length of a SWCNT in the bundle also plays a significant role. For example, reducing the bundle’s length to 300 nm destroys the superconductivity in the system due to increasingly high quantum fluctuations. Generally speaking, for nanoscale systems with the quantum level spacing approaching the superconducting gap energy $\Delta$, the superconductivity vanishes.

It is expected that doping of SWCNTs in a bundle by, for example, boron, may significantly improve their superconducting properties. It is believed that a proper level of doping may result in the Fermi level at a one dimensional singularity of the energy spectrum and thus in a higher density of states (DOS), that will lead to a higher critical temperature $T_c$. In particular, we suggest that such kind of mechanism of doping enhanced $T_c$ may be much better pronounced in the case of semiconducting SWCNTs, which may have higher DOS due to lower in energy van Hove singularities. This is in contrast to metallic SWCNTs, where singularities in the DOS are much higher in energy, and start being filled much later during the doping process (according to the famous Kataura plot). Therefore, a bundle consisting of doped semiconducting nanotubes could be a much better superconductor, compared to a bundle made of metallic SWCNTs.

However, synthesis of SWCNTs by all currently known methods results in a mixture of semiconducting and metallic nanotubes. Since the nanotubes after the synthesis initially are not doped (or unintentionally slightly p-type doped, e.g. by oxygen of atmosphere), those are only metallic tubes, which may have superconducting transition, while semiconducting tubes will be “diluting” superconductivity in the bundle by the inverse proximity effect. Upon doping (i.e. by electrochemical charging), the semiconducting tubes can become superconducting with a higher superconducting gap and thus a higher $T_c$ than in metallic nanotubes.

Therefore, one should be able to estimate spatially averaged order parameter and the corresponding effective critical temperature for a bundle consisting of a mixture of SWCNTs of these two model types. From an experimentalist’s point of view it is even more important to solve the inverse problem: for a given fraction $a$ of semiconductor SWCNT in the bundle and the experimentally determined critical temperature $T_c(a)$, to estimate the critical temperature for a bundle, consisting only of semiconductor SWCNTs $T_c(a = 1)$? It will be also interesting to know, can one obtain $T_c$ much higher than in other carbon based nanostructures, and particularly higher than in alkali metal doped fullerenes.

Spatial variations of the superconducting order parameter are significant for nanoscale systems, including nanotubes. In this work we use a microscopic theory based on inhomogeneous Bogoliubov-de Gennes equations to establish how the superconducting properties of a bundle depend on the fraction of doped semiconductor nanotubes, with a higher SC order parameter. We assume that the nanotubes in the bundle are approximately of the same radii and tightly packed making a triangular lattice in the bundle’s transverse section, with the primitive vectors $\vec{a}_1 = R\vec{x}, \vec{a}_2 = R\vec{x}/2 + \sqrt{3}/2\vec{y}$. Here $\vec{x}, \vec{y}$ are the unit basis vectors, and $R$ is the intertube distance. The lattice can be enumerated by indexes $(i,j)$, which correspond to the position of a nanotube $R_{i,j} = \vec{a}_1 i + \vec{a}_2 j$, but in this work we prefer to enumerate nanotubes in a $N \times N$ bundle using a single index through the mapping $k = i+jN$, where $N$ is the number of nanotubes in a raw.
In the bundle semiconductor nanotubes are assumed to occupy the fraction \( a \) of the sites, and metallic nanotubes 1 \(- a\), accordingly. In our model the conduction electrons can freely travel along the nanotubes, and in this picture it corresponds for an electron staying at the same lattice site. However, electrons can also hop to the neighboring nanotubes (sites). In principle, there may be three different hopping constants, with the hopping matrix elements \( t^{kk'} \) equal to either \( t_{nnn}, t_{nnm}, t_{nmm} \), corresponding to the hopping between metallic-metallic (mm), metallic-semiconducting (ms), or semiconducting-semiconducting (ss) nanotubes. Moreover, these parameters may significantly fluctuate from one site to another, due to mismatch between SWCNTs of different chirality. In the superconducting regime Cooper pairs can be formed and can freely move along the nanotubes, and can also hop from one tube to another.

For the description of the system we utilized a tight-binding Hubbard Hamiltonian of the form:

\[
H_0 = \sum_{\langle i, j \rangle, \sigma} t^{ij} c^\dagger_{i, \sigma} c_{j, \sigma} - \mu \sum_{i, \sigma} c^\dagger_{i, \sigma} c_{i, \sigma} + \sum_{i, \sigma} U_{int} n_{\downarrow}(i)n_{\uparrow}(i) + \sum_{\langle i, j \rangle, \sigma} V^{ij}_{int} n_{\downarrow}(i)n_{\uparrow}(j),
\]

where a quantum-mechanical operator \( c^\dagger_{i, \sigma} \) creates an electron on site \( i \) (using single indexing), the operator \( c_{i, \sigma} \) eliminates an electron from the site \( i \), and \( n_{\sigma}(i) = c^\dagger_{i, \sigma} c_{i, \sigma} \) represents the electron density on site \( i \) with the spin polarization \( \sigma \). The electron spin, \( \sigma \), can point up or down. \( U_{int} \) is on site interaction potential. This term in a case of attractive interaction \( U_{int} < 0 \) may lead to pairing in the nanotube \( i \). \( V^{ij}_{int} \) is a strength of the coupling between electrons localized at neighboring tubes \( i \) and \( j \).

Using the Bogoliubov transformation, which diagonalizes the Hamiltonian Eq. (1), we arrive to inhomogeneous Bogoliubov-de Gennes equations for the quasiparticle amplitudes on the lattice \( i \) sites \( (u_n(i), v_n(i)) \):

\[
\begin{pmatrix}
\xi & \Delta \\
\Delta^* & -\xi^*
\end{pmatrix}
\begin{pmatrix}
u_n(i) \\
v_n(i)
\end{pmatrix}
= E_n
\begin{pmatrix}
u_n(i) \\
v_n(i)
\end{pmatrix},
\]

where the kinetic operator \( \xi \) and the superconducting order parameter \( \Delta \) can be represented as:

\[
\xi = -\sum_\delta t^{ij} u_n(i + \delta) + (V^s(i) - \mu) u_n(i),
\]

\[
\Delta = \sum_\delta \Delta_\delta(i) v_n(i + \delta) + \Delta_s(i) v_n(i),
\]

where \( \delta \) are the nearest neighbor vectors for a triangular lattice, \( V^s(i) \) is the mean-field (Hartree) potential, \( \mu \) is the chemical potential. \( \Delta_\delta \) is the conventional, s-type order parameter. One should solve Eq. (2) together with the self-consistency conditions:

\[
\Delta_\delta(i) = \sum_n \frac{V^{ij}_{int}}{2} (u_n(i + \delta) v_n^*(i) + u_n(i) v_n^*(i + \delta)) \tanh(\frac{E_n}{2k_B T}),
\]

where the pairing strength \( V^{ij}_{int} \) may depend on the type of CN at sites \( i \) and \( j \). The s-type order parameter (within a given nanotube \( i \)) is simply

\[
\Delta_s(i) = \sum_n \frac{U_{int}}{2} (u_n(i) v_n^*(i) + u_n(i) v_n^*(i)) \tanh(\frac{E_n}{2k_B T}).
\]

Note, the summation in Eqs. (4) is over the positive eigenvalues \( E_n \) only.

Here we adopted a simplified picture assuming the same constant hopping parameter \( t \) between any type of nanotubes. In this work we considered for simplicity that the pairing may happen between electrons in the same nanotube, therefore neglecting much weaker pairing mechanism between neighboring nanotubes. In principle, a weak attraction mechanism may stimulate the formation of a Cooper pair with one electron in one nanotube, and the second electron in one of its nearest neighbors. This may result in co-existing order parameters in the system, one of the order parameters with the conventional (s-type) symmetry, and another with unusual symmetry. The co-existence of order parameters with different symmetries, was studied, for example, for Uranium-based superconducting materials. The possibility of such pairing on a triangular lattice may result in unconventional superconducting properties. For example, a 2D triangular lattice was recently considered as a test-bed for a possibility of f-wave spin-triplet superconductivity.

The amplitudes \( u_n(i), v_n(i) \) obey the constraints \( \int dr (|u_n(i)|^2 + |v_n(i)|^2) = 1 \) for any \( n \) (normalization) and \( \sum_n (|u_n(i)|^2 + |v_n(i)|^2) = 1 \) for any \( i \), \( i \) being the site index of the triangular lattice.

![FIG. 1. Spacially averaged superconducting order parameter \( \langle \Delta > \) (in units of \( t \)) as a function of fraction of semiconductor nanotubes \( a \) for different temperatures.](image-url)
fraction of semiconductor SWCNTs \(a\) in a \(N \times N\) bundle at different temperatures. For this purpose we generated \(P = 50\) realizations for a given number of randomly placed semiconductor nanotubes in the bundle. The rest of nanotubes in the bundle are assumed to be metallic. To model different superconducting pairing strength for different types of nanotubes we set \(U_{int}^m = 2t\) for semiconducting nanotubes and \(U_{int}^m = 0.68t\) for metallic ones, and assumed \(\mu = 0\) (half filled band). In our simulations we considered \(16 \times 16\) nanotubes in the bundle, forming a triangular lattice.

The results of calculations are shown in Fig. 1. At \(T = 0\) the order parameter scales approximately as a square root of the fraction of the semiconducting SWCNTs in the bundle \(T_c \propto (T_c^m - T_c^s) \sqrt{a} + T_c^s\). Note the convexity of the dependence. However, at finite temperatures, which are between the critical temperature of a pure metallic \(T_c^m\) and pure semiconducting \(T_c^s\) bundles, the averaged order parameter vanishes much faster with the decreasing of \(a\). For example, at \(T = 0.32t\), which is close to the critical temperature of a pure semiconducting SWCNT bundle \(T_c^s \approx 0.35t\), the order parameter decreases in the exponential fashion with the decreasing of \(a\), and almost vanishes at \(a \approx 0.5\).

In Fig. 2 we also plot \(\langle \Delta \rangle\) as a function of temperature for several values of \(a\). One can clearly see how the order parameter vanishes above the critical temperature. Note that with the lowering of the fraction of semiconducting nanotubes \(a\), the temperature dependence of the order parameter shows less pronounced phase transition because of the “dirty” nature of inhomogeneous spatial distribution of the pairing properties, similar to dirty superconducting transition in case of large concentration of impurities and in alloys.

Using the data plotted in Fig. 2, we calculated how the critical temperature \(T_c\) depends on the concentration of semiconducting SWCNT. We used \(t = 4.8 \times 10^{-4} eV\) to fit the data in [22-23], so \(a = 0.6\) will correspond to \(T_c \approx 15K\). In Figure 3 one can see that the critical temperature decreases for \(a < 0.5\) with a steeper slope, where \(a = 0.5\) corresponds to the percolation threshold in 2D triangular lattices (please see Fig. 4). For \(a < 0.5\) weaker superconducting metallic CN are arranged in bigger size islands. If one would take into account the phase fluctuations of the order parameter, this decrease of critical temperature would be even steeper, because of enhanced phase slips in relatively well isolated semiconducting nanotubes.

It should be noted that our model has general applicability to any system in which there are two types of nanotubes, (or very thin nanowires) with different superconducting pairing strength are coupled in bundles. So it also describes the most common case of undoped pristine SWCNT bundles, which contain 30-40% of metallic SWCNT and the rest are non-doped semiconducting

![FIG. 2. Spatially averaged superconducting order parameter \(\langle \Delta \rangle\) (in units of \(t\)) as a function of temperature for different values of \(a\) (fraction of semiconductor CN).](image)

![FIG. 3. Critical temperature \(T_c\) as a function of the fraction of semiconducting CN. Note a steeper slope for \(a < 0.5\) (the percolation limit in two dimensions on the triangular lattice).](image)

FIG. 4. Spatial distribution of the superconducting order parameter (in units of \(t\)) at the percolation regime (\(a = 0.5\)) and zero temperature. Red dots mark the triangular lattice.

![FIG. 4. Spatial distribution of the superconducting order parameter (in units of \(t\)) at the percolation regime (\(a = 0.5\)) and zero temperature. Red dots mark the triangular lattice.](image)
SWCNTs, which usually do not have carriers. As has been shown this bundles have typical $T_c$ of 0.55 K [20-21], which according to our model is suppressed by the inverse proximity effect from non-superconducting undoped semiconducting tubes. According to our model if 100% separated only metallic tubes are in the bundles, then the gap and $T_c$ should be significantly higher and we expect that without fluctuations account it can be around $T_c \approx 1.3K$. Similarly for optimally doped 100% semiconducting SWCNTs the $T_c$ should increase from observed in [22-23] $T_c \approx 15$ K to the unsuppressed (by the inverse proximity effect of low $T_c$ metallic tubes) $T_c$ of 19-20 K. The effect of $T_c$ suppression similar to discussed here has been observed in alkali metal fulleride molecular alloys of $A_x(C_{60})_x(C_{70})_{1-x}$ (24) and adding non-superconducting component, i.e. $C_{70}$ molecules, which do not show any superconducting pairing due to symmetry reasons and probably due to weaker electron-phonon coupling, strongly suppressed $T_c$ from 19 K in 100% $C_{60}$, i.e. in $K_yC_{60}$ to $T_c=10$ K in 20% substituted $C_{70}$ alloy. The experiments with selectively separated metallic and semiconducting SWCNTs, which now become available by new methods of effective separation will allow to check the validity of presented here simple model and to clarify the role of quantum fluctuations, which has not been accounted here.

We introduced a microscopic model of superconductivity in a bundle of a mixture of carbon nanotubes. We have studied the dependence of a spatially averaged superconducting gap $< \Delta >$ on the fraction of semiconducting SWCNT (having higher pairing strength) in the bundle at different temperatures. Note that for inhomogeneous nanoscale systems the dependence $T_c(< \Delta(T=0) >)$ for different concentration $a$ may be non-linear, as a manifestation of the breakdown of the BCS theory for bulk materials. Indeed, our calculations of $T_c(< \Delta(T=0) >)$ show a kink at $a = 0.5$. The reason is that the bundle is a highly inhomogeneous system. At $a < 0.5$, below the percolation threshold for a 2D triangular lattice, the bundle can be seen as a collection of finite islands of “good” superconductors (doped semiconducting nanotubes), diluted by normally conducting material (metallic nanotubes). Such islands demonstrate significantly suppressed superconductivity, even in the mean field description, due to the enhanced inverse proximity effect. Note that our mean-field BdG model is unable to predict and properly describe quantum phase fluctuations of the order parameter in quasi one dimensional systems, where the superconductivity will be suppressed even stronger. Future research using, for example, Ginzburg-Landau inhomogeneous equations is necessary to describe such kind of effects. Because the dynamics of Cooper pairs in doped carbon nanotubes can be more close to the diffusive regime, the Usadel equations can be applied to calculate the finite conductivity at $T << T_c$.

1. Z. K. Tang, L. Zhang, N. Wang, X. X. Zhang, G. H. Wen, D. Li, J. N. Wang, C. T. Chan, P. Sheng, Science 292, 2462 (2001).
2. G. V. Pai, E. Shimshoni, and N. Andrei, Phys. Rev. B 77, 104528 (2008).
3. D. S. Golubev and A. D. Zaikin, Phys Rev B 78, 144502 (2008).
4. M. Kociak, A. Yu. Kasumov, S. Guaron, B. Reulet, I. I. Khodos, Yu. B. Gorbatov, V. T. Volkov, L. Vaccarini, and H. Bouchiat, Phys. Rev. Lett. 86, 2416 (2001).
5. D.C. Ralph, C.T. Black, and M. Tinkham, Phys. Rev. Lett. 74, 3241 (1995).
6. H. Kataura et al., Synth. Met. 103, 2555 (1999).
7. S. Gueron, H. Pothier, Norman O. Birge, D. Esteve, and M. H. Devoret, Phys Rev. Lett. 77, 3025 (1996).
8. J. E. Han and V. H. Crespi, Phys. Rev. B 69, 214526 (2004).
9. A.A. Shanenko, M.D. Croitoru, F.M. Peeters, Physica C 468 593 (2008).
10. M. Ma and P. A. Lee, , Phys. Rev. B 32, 5658 (1985).
11. H. Ikeda, Y. N. Isikawa and K. Yamadai, Jour. of Phys. Soc. Jap. 73, 17 (2004).
12. A. Bezryadin, J. Phys.: Condens. Matter 20 043202 (2008).
13. A. Zharov, A. Lopatin, A. E. Koshelev, and V. M. Vinokur, Phys. Rev. Lett. 98, 197005 (2007).
14. A. V. Semenova, P. A. Krutitskii, and I. A. Devyatov, JETP Letters, 92, 762 (2010).
15. S. V. Nikolaev, I K. N. Yugay, J. U. Kim, and Y. Huh, Jour. Supercond: Incorp. Nov. Magn., 18, (2005).
16. D. S. Golubev and A. D. Zaikin, Phys. Rev. B, 64, 014504 (2001).
17. R. Moradian, A. Fathalian, Jour. of Phys. and Chem. of Sol. 69, 2589 (2008).
18. P. Kumar and P. Wölfle, Phys. Rev. Lett. 59, 1954 (1987).