On the possible reason for superconductivity strengthening in multiwall carbon nanotubes

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Basing on the structural peculiarity of two-layer graphene which consists of translational and energetical nonequivalency of carbon atoms from different sublattices, it is shown that the density of long-wave electronic states at the Fermi level is finite (in contrast to the monolayer graphene). It is suggested that the same may be the reason why the critical temperature of superconducting transition in multiwall nanotubes more than ten times higher than in single-wall nanotubes.

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1. Introduction

Since the discovery of fullerene [1] (see also review papers [2–4]) there is an increasing interest in the investigation of fullerene-like structures which besides carbon nanotubes (CNT) [5] include also single- and multilayer graphene [6]. Carbon nanotubes are very perspective both from fundamental and applied view points. CNT may be used as the elements of different nanoelectronic devices, constant-force nanosprings [7], containers to hold in storage of light gases (in particular hydrogen), pressure transducers and so on. On the other hand, CNT are known as model systems for the study of one-dimensional electronic transport. Depending on their diameter and helicity, carbon nanotubes are either semiconducting or metallic [4]. It is well known that the usual Fermi liquid which is described by the Landau–Silin theory is expected to be unstable in one-dimensional (1D) metals with the formation of a correlated Tomonaga–Luttinger liquid state where the electron–electron repulsive interaction prevents the appearance of superconducting state to a greater extent than in conventional 3D metals.

Investigations of the magnetic and transport properties of ropes of single-walled small-diameter carbon nanotubes (SWNT) [8] and SWNT embedded in a zeolite matrix [9] revealed that a few angstrom tubes exhibit superconducting behavior manifest as an anisotropic Meissner effect, with a superconducting gap and fluctuation supercurrent. It turned out that the superconducting transition in SWNT occurs at very low temperature, less than 0.55 K [8]. It is quite natural to connect such a low critical temperature with the low-dimensional character of CNT*, with strong quantum and thermal fluctuations and with proximity to Peierls instabilities which drive the system to an insulating state. Therefore the report [10] that multiwalled carbon nanotubes (with up to 9 shells) exhibit superconductivity with an unexpectedly high transition temperature $T_c \approx 12$ K, which is approximately 30 times greater than $T_c$ reported for SWNT [8] has attracted considerable attention. The value of the superconducting gap $\Delta \approx 1.15$ meV which

* It is worth to emphasize that carbon nanotubes can not be considered as genuine one-dimensional objects. In 1D systems the processes of electron–electron, electron–phonon and electron–impurity scattering involve only one, «longitudinal» component of the electron wave vector while in nanotubes these processes include also the «transversal» or orbital component of the quasimomentum.
is in excellent agreement with the BCS canonical ratio \(2\Delta/k_B T_c \approx 3.5\), the observed behavior of the critical current as a function of the temperature and external magnetic field is also in good qualitative agreement with the Ginzburg–Landau critical current behavior. It can be therefore said with confidence that the observed superconductivity in multiwalled carbon nanotubes is of the BCS type and that the multinshell structure of the nanotubes plays a crucial role.

The aim of this work is to show that the big difference of the critical temperature of single- and multiwalled nanotubes may be due to a qualitatively different behavior of the density of states of low-energy charge carriers. As a model we consider mono- and bi-layer graphenes whose structure is similar to the structure of graphit sheets rolled-up in nanotubes.

It is a great honour and pleasure for us to devote this work to the 100 year jubilee of outstanding physicist-experimentalist and marvellous person, Antonina Fedorovna Prikhot’ko, who did so much for our formation as scientists. It is worth to note also that being a bright and leading figure in the low temperature physics, she always supported new lines of inquiry in this area and was one of devotees of the quest of new superconductors with unusual and un-expectable features.

2. Hamiltonian and electron spectrum

We employ the tight-binding model to describe the band structure of single- and bi-layer graphenes. Basing on the well developed theory of molecular crystals with several molecules per unit cell (see, e.g., [11]), the electronic Hamiltonian of bi-layer graphene can be represented in the form

\[
H = v_\pi \sum_{n_\alpha} (a_{n_\alpha}^+ a_{n_\alpha} + b_{n_\alpha}^+ b_{n_\alpha}) + \\
+ \frac{1}{2} \sum_{n_\alpha, m_\beta} t_{n_\alpha, m_\beta} (a_{n_\alpha}^+ a_{m_\beta} + b_{n_\alpha}^+ b_{m_\beta}) + \\
+ \frac{1}{2} \eta_{||} \sum_{n_\alpha} (a_{n_\alpha}^+ b_{n_\alpha} + b_{n_\alpha}^+ a_{n_\alpha}),
\]

where \(v_\pi\) is the on-site energy of \(\pi\)-electron at the site \(n_\alpha\) (the vector \(n\) gives the position of the elementary cell, the index \(\alpha (= 1, 2)\) characterizes the sublattices); the matrix element \(t_{n_\alpha, m_\beta}\) describes an intra-layer electron hopping (tunneling) between the sites \(n_\alpha\) and \(m_\beta\), and \(\eta_{||}\) characterizes an inter-layer electron transfer; the Fermi-operators \(a_{n_\alpha}^+\) and \(b_{n_\alpha}^+\) describe a creation of an electron at the site \(n_\alpha\) of the first and second layer, respectively (the index of the electron spin is omitted for brevity). It is worth noting that the last term of the Hamiltonian (1) is chosen in the form which takes into account that the sheets in the bi-layer graphene are shifted with respect to each other by the vector \((a_1 + a_2)/2\), where \(a_j\) are the primitive vectors of graphene sheet [12]. In consequence of such an unusual geometry the atoms in each sheet become energetically (as well as translationally) nonequivalent. *Note that the same phenomenon takes place in multi-wall carbon nanotubes consisting of several rolled-up graphit sheets in the cylindrical form. Here the atoms which belong to different cylindrical surfaces are energetically nonequivalent.

By applying the Fourier transform

\[
a_{\alpha}(k) = \frac{1}{\sqrt{N}} \sum_n a_{n\alpha} e^{i k n}, \\
b_{\alpha}(k) = \frac{1}{\sqrt{N}} \sum_n b_{n\alpha} e^{i k n},
\]

where \(k\) is the wave vector and \(N\) is the number of cells in the sheet, the Hamiltonian (1) can be presented in the form

\[
H = \sum_k \{ t_1(k) [a_{1\alpha}(k)a_{2\alpha}(k) + b_{1\alpha}(k)b_{2\alpha}(k)] + h. c. \} + \\
+ \sum_{k, \alpha=1,2} t_2(k) [a_{\alpha}(k)a_{\alpha}(k) + b_{\alpha}(k)b_{\alpha}(k)] + \\
+ \frac{1}{2} \sum_k [a_{1\alpha}(k)b_{2\alpha}(k) + b_{2\alpha}(k)a_{1\alpha}(k)],
\]

where

\[
t_1(k) = t_1 \gamma_1(k); \gamma_1(k) = 1 + e^{i k a_1} + e^{i k a_2};
\]

\[
t_2(k) = t_2 \gamma_2(k);
\]

\[
\gamma_2(k) = \cos k a_1 + \cos k a_2 + \cos k(a_1 - a_2)
\]

are the Fourier-components of so-called resonance interactions which form the dispersion of electronic bands. The functions \(t_1(k)\) and \(t_2(k)\) given by Eqs. (4) and (5) represent the intra- and intersublattice electron dispersion, respectively. The latter leads to a splitting which in the theory of molecular excitons is called the Davydov splitting (see, e.g., [11]). The parameters \(t_1\) and \(t_2\) in Eqs. (4) and (5) are the hopping integrals between nearest and next nearest neighbors, respectively; \(a_1 = (\sqrt{3}, 0), a_2 = (\sqrt{3}/3, 2, 2/3)\) are the primitive vectors of the rhombic lattice with the distance between the nearest neigh-
one can diagonalize the Hamiltonian (3) and obtain which can be obtained by rotations of the vectors Eqs. (9) and (10) by neglecting the interlayer hopp-
in integral:

$$E_{\text{int}} = \frac{1}{N} \sum_{k,q} V(k,q) \sigma_{-}^{+} (k) \sigma_{+}^{-} (-k) \sigma_{-}^{+} (-q) \sigma_{+}^{-} (q)$$, (11)

where the parameter $V(k,q)$ characterizes the strength of the electron—electron interaction; $\sigma_{\pm}^{+} (k)$ ($\sigma_{\pm}^{-} (k)$) is the creation (annihilation) operator of a carrier with the wave vector $k$ and the spin $\sigma = \uparrow, \downarrow$. By using the standard procedure [19,20] it is easy to obtain that the order parameter

$$\Delta(k) = N^{-1} \sum_{q} V(k,q) \langle \sigma_{-}^{+} (-k) \sigma_{+}^{-} (q) \rangle$$

(the gap in the electron spectrum) is determined by the equation

$$\Delta(k) = \frac{1}{2N} \sum_{q} V(k,q) \frac{\Delta(q)}{\sqrt{\varepsilon_{\text{F}}^{+}(q) - \varepsilon_{\text{F}} + |\Delta(q)|}}$$, (12)

where the symbol $\langle \cdots \rangle$ denotes a thermodynamic mean value and $\varepsilon_{\text{F}}$ is the Fermi energy which in our case is doping controlled.

In the simplest approximation when $V(k,q) \approx V$ the gap is $k$ independent $\Delta(k) \approx \Delta$, and Eq. (12) takes the form
\[
\frac{1}{8\pi^2} \int dk \frac{1}{\sqrt{|\varepsilon_{\text{cond}}(k) - \varepsilon_F|^2 + |\Delta|^2}} = \frac{1}{V}, \tag{13}
\]

where
\[
\varepsilon_{\text{cond}}(k) = \frac{9}{8} t_2 k^2 - \frac{1}{2} t_\parallel + \sqrt{\left(\frac{1}{2} t_\parallel\right)^2 + \left(\frac{3}{2} t_2 k\right)^2} \tag{14}
\]
is the energy of charge carriers in the vicinity of the node points \(k_j\) \cite{12,17}. By introducing the density of quasiparticle states \(\rho(\varepsilon)\) (see Appendix for details) Eq. (14) can be transformed to the form
\[
\int_{\varepsilon_F}^{\infty} \frac{d\varepsilon}{\sqrt{(\varepsilon - \varepsilon_F)^2 + |\Delta|^2}} = \frac{2}{V},
\]
which for a given \(\rho(\varepsilon)\) (see Eq. (A.2)) gives the expression
\[
\Delta = 2\Omega_D \exp \left\{ -\frac{9\pi t^2_2}{4V(t_\parallel + \varepsilon_F)} \right\}, \tag{15}
\]
for the superconducting gap in the one-electron spectrum. Here \(\Omega_D\) is the Debye frequency.

Comparing the superconducting gap \(\Delta = \Delta_{\text{bi}}\) in the bi-layer graphene which is given by Eq. (15) with the superconducting gap \(\Delta = \Delta_{\text{mono}}\) in the mono-layer graphene which can be also obtained from Eq. (15) by putting \(t = 0\) one can see that the ratio
\[
\frac{\Delta_{\text{bi}}}{\Delta_{\text{mono}}} = \exp \left\{ \frac{9\pi t^2_2}{4V\varepsilon_F} \frac{1 + \Delta}{(1 + \varepsilon_F)} \right\}, \tag{16}
\]
where \(\Delta = t/\varepsilon\) in the low-doping regime may be exponentially big. This result is a direct consequence of the qualitative difference between the spectra of charge carriers in single- and bi-layer graphene. While in the mono-layer graphene the spectrum is massless and the density of of states vanishes when the concentration of carriers decreases \(\varepsilon \to 0\) in the bilayer graphene the carriers have a finite effective mass and the density of states in the limit \(\varepsilon \to 0\) is finite.

4. Summary

We have shown that the interlayer carrier transfer in graphene may be of crucial importance in creation of superconducting condensate. It is interesting to notice that in the same way the low-energy behavior of the density of states plays a pivotal role in electron-hole pairing and forming the exciton dielectric phase graphene. In the mono-layer graphene such a phase can form only in the presence of strong magnetic field which effectively reduces to 1D the charge carrier motion and in this way enhances Coulomb attraction (magnetic catalysis \cite{21}). In the bi-layer graphene the presence of interlayer hopping makes inessential applying the magnetic field.

In our opinion, the strengthening of superconductivity in multiwalled nanotubes may be also due to the interlayer electron hopping. The charge carriers in multiwalled nanotubes have a finite effective mass and as a result the density of states is finite as \(\varepsilon \to \varepsilon_F\). It follows also from our model that the critical temperature in a mono-layer graphene (singlewalled nanotube) increases when the doping increases. Moreover the critical temperatures of mono- and bi-layer graphenes (as well as the critical temperatures of single- and multiwalled CNT) equalize when \(\varepsilon_F \gg t_\parallel\).

The above developed theory does not take into account the Coulomb interaction between electrons. It is well known, however, that this interaction it decreases the critical temperature of conventional 3D superconductors. The decisive factor here is a screening of Coulomb interaction in metals. In the case under the consideration we meet with a qualitatively new situation when not only the low-dimensional character of charge transport (quasi 1D in CNT and 2D in graphene) is important but the size and the shape of the objects (radius of CNT, relative shift of sheets in graphene and so on) as well. Quite recent studies of the screening of Coulomb interaction in non-polar systems \cite{22} showed that in low dimensions and small finite-size systems this screening deviates strongly from conventionally assumed. For example, in one dimension at small and intermediate distances the Coulomb interaction is anti-screened thereby strongly reducing the gradient of the Coulomb interaction. It is also shown in \cite{22} that in finite-size systems due to weak dependence of the effective Coulomb interaction on the distance between the electrons the correlation effects are reduced and the mean-field approach works well because the correlation effects are reduced and the mean-field approach works well. Note also that increasing the number of walls in CNT (number of layers in graphene) is to some extent equivalent to increasing of their dimensionality. So the superconducting effects are enhanced in these systems.

Appendix A

The aim of this Appendix is to calculate the density of quasiparticle states
\[
\rho(\varepsilon) = \frac{1}{4\pi^2} \int d|k|\delta[|\varepsilon - \varepsilon_{\text{cond}}(k)|] \tag{A.1}
\]
for the case of bi-layer graphene. Here \( \varepsilon_{\text{cond}}(k) \) is given by Eq. (14) and the two-dimensional character of the system is taken into account. From Eq. (A.1) we get

\[
\rho(\varepsilon) = \frac{1}{4 \pi} \int_{0}^{2\pi} d\delta \int_{t_{\parallel 2}}^{x_{\max}} dx \delta \left[ (x - x_{+})(x - x_{-}) \right],
\]

where the maximal wave vector \( k_{\text{max}} \) is determined from the condition that the total number of states in the conduction band is equal to the number of elementary cells \( N \). By using the new variable \( k = [x^{2} - (t_{\parallel} / 2)] / (3t_{1} / 2)^{2} \), we obtain

\[
\rho(\varepsilon) = \frac{4}{9\pi t_{2}^{2}} \int_{0}^{x_{\max}} d\delta [(x - x_{+})(x - x_{-})],
\]

where

\[
x_{\pm} = (1/2)[-2t_{2}^{2} / t_{2}] \pm \sqrt{4t_{1}^{4} / t_{2}^{2} + (8t_{2}^{2} / t_{2}) (e + t_{||} / 2) + t_{1}^{2}}\]

are the roots of the equation \( \varepsilon_{\text{cond}}(k) = 0 \) and the notation \( x_{\max} = (t_{\parallel} / 2)^{2} + t_{1}^{2} k_{\text{max}}^{2} \) is introduced. As a result we get

\[
\rho(\varepsilon) = \frac{2}{9\pi t_{2}^{2}} \left[ 1 - \frac{1}{\sqrt{1 + (t_{2} / t_{1})^{2} e}} \right] \sim \frac{1}{t_{1}^{2}} \quad (A.2)
\]

From Eq. (A.2) we obtain that for the mono-layer graphene (when the interlayer hopping is absent, \( t_{\parallel} = 0 \)) the density of states takes the form

\[
\rho_{1L}(\varepsilon) = \frac{2}{9\pi t_{2}^{2}} \left[ 1 - \frac{1}{\sqrt{1 + (2t_{2} / t_{1})^{2} e}} \right] \sim \frac{\varepsilon}{t_{1}^{2}} \quad (A.3)
\]

In the two-layer case (when one can neglect the intra-sublattice hopping \( t_{2} \)) we have the following expression for the density of states

\[
\rho_{2L}(\varepsilon) = \frac{4}{9\pi t_{1}^{2}} (t_{1} + 2\varepsilon)_{\varepsilon \rightarrow 0} \sim \frac{t_{1}}{t_{2}^{2}} \quad (A.4)
\]

Comparing Eqs. (A.3) and (A.4), we see that the ratio

\[
\rho_{1L}(\varepsilon) / \rho_{2L}(\varepsilon)_{\varepsilon \rightarrow 0} \sim \varepsilon / t_{\parallel}
\]

is small as long as \( \varepsilon \ll t_{\parallel} \).

Similar enhancement of density of states one can expect, as it was mentioned above, under the transition from singlewalled to multiwalled nanotubes. Indeed, it is easy to see that due to a massless character of the carrier dispersion in the singlewalled nanotube the density of states \( \rho_{SW}^{\max}(\varepsilon) \sim 1 / t_{1} \) while in the multiwalled nanotube the carriers have a finite effective mass and the density of states \( \rho_{NT}^{SW}(\varepsilon) \sim 1 / \sqrt{\varepsilon} \), fastly growing for small \( \varepsilon \).