Theory of superconductivity of carbon nanotubes and graphene

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We present a new mechanism of carbon nanotube superconductivity that originates from edge states which are specific to graphene. Using on-site and boundary deformation potentials which do not cause bulk superconductivity, we obtain an appreciable transition temperature for the edge state. As a consequence, a metallic zigzag carbon nanotube having open boundaries can be regarded as a natural superconductor/normal metal/superconductor junction system, in which superconducting states are developed locally at both ends of the nanotube and a normal metal exists in the middle. In this case, a signal of the edge state superconductivity appears as the Josephson current which is sensitive to the length of a nanotube and the position of the Fermi energy. Such a dependence distinguishes edge state superconductivity from bulk superconductivity.

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Superconductivity in carbon nanotubes (NTs) has been attracting much attention due to its high superconducting transition temperature, $T_c \gtrsim 10$ K. However, it is well-known that superconductivity in low dimensional (quasi-1D) systems is difficult to produce due to low density of states (DOS), strong quantum fluctuations and other phenomena in such systems. Moreover, metallic NTs exhibit ballistic transport properties at low temperatures, which suggests a weak electron-phonon (el-ph) interaction for the conducting electrons. It is surprising that superconductivity is realized in NTs at such high values of $T_c$. The mechanism of NT superconductivity is a critical issue and determining it will be a valuable contribution not only to NT science but also to nanotechnology.

Superconductivity has been observed in different types of NTs. Tang et al. reported $T_c \sim 15$ K for single-wall NTs (SWNTs) having a diameter of 0.4 nm. Takesue et al. found an abrupt drop in the zero-bias resistance at 12 K for multi-wall NTs (MWNTs) having an outer diameter of $\sim 10$ nm. It is not straightforward to explain the results obtained in experiments. For instance, the DOS at the Fermi energy of a SWNT appears to be too small to give rise to such high $T_c$. Kamide et al. and Barnett et al. considered that curvature of $(5,0)$ SWNTs may increase the DOS. However, a large DOS may induce charge density wave (CDW) before superconductivity occurs. Connétable et al. showed that $(5,0)$ and $(3,3)$ SWNTs undergo a CDW transition at temperatures above room temperature. Thus, small diameter SWNTs may be insulators. Moreover, the curvature effect is negligible for MWNTs. The origin of NTs superconductivity can not be explained by curvature-induced DOS and a new explanation is needed.

Here, we focus our attention on the large local DOS (LDOS) given by edge states which are intrinsic to graphene. The edge states are electronic localized states that exist around the zigzag edge of graphene and a SWNT. The energy dispersion of edge states is sensitive to the length of a nanotube and the position of the Fermi energy. LDOS depends on the energy bandwidth ($W$) of the edge states. Recent experiments involving scanning tunneling microscopy/spectroscopy (STM/STS) at the zigzag edge of graphene, and angle-resolved photo-emission spectroscopy (ARPES) of Kish graphite, showed that the edge states are located below the Fermi energy and have a finite $W$. Although edge states of NTs have not been observed so far, it is possible to consider the edge states of a SWNT with a zigzag edge as well as those of a graphene sheet.

In this letter, we calculate $T_c$ as a function of $W$ and $E_F$, and obtain an appreciable values for $T_c$ of the edge states of zigzag SWNTs and graphene. As a result, we predict that the superconductivity of a SWNT is given by a natural superconductor/normal metal/superconductor junction (SNS) system, in which superconducting states develop locally at both ends of the SWNT and a normal, ballistic state exists in the middle of the SWNT. Remarkably, the bulk part of a SWNT need not be superconducting since Josephson supercurrent flows in the middle as a result of the proximity effect when the superconducting edge states have different phases at both ends. We note that proximity-induced supercurrents have been observed in Ta/SWNTs/Au and Nb/MWNTs/Al systems. The Josephson current of a metallic zigzag SWNT depends on the length ($L$) and temperature ($T$). The amplitude of the current is proportional to $\exp(-L/\xi_N)$ when $T < T_0$ where $T_0 \sim 20 \mu m/K$ and $\xi_N \sim 10^3 K/T$ nm is the coherence length. A length dependence of the current distinguishes edge-state superconductivity from bulk super-
conductivity.

The edge-state superconductivity has the following advantages in explaining the experiment performed by Takesue et al., \([2]\) (1) the edge states are robust against static surface deformation which is relevant for CDW instability, \([17, 18]\) (2) the el-ph interaction for the edge states is strong compared with that for delocalized states, and (3) \(T_c\) is sensitive to \(W\) and the energy position of \(E_F\), which are all consistent with the fact that the superconductivity is sensitive to the junction structures of the Au electrode/MWNTs. \([2]\) Enhancement of \(T_c\) is given mainly by the vibrations of carbon atoms in the direction of the SWNT axis where \(\mathbf{k} = 2 \mathbf{a}_2 - \mathbf{a}_1\) is the translation vector. \([20, 21]\) When we incorporate the next nearest-neighbor (nnn) transfer integral \(\gamma_n\) into the Hamiltonian, the energy dispersion of the edge states becomes \(E(k) = \gamma_n(2 \cos k + 1)\) \((2\pi/3 < k < 4\pi/3)\) where the value of \(\gamma_n = 0.3\) eV is adopted. \([20, 22]\) The calculated results explain the STS \([10, 11]\) and ARPES \([12]\) experiments. Hereafter we treat \(W = \gamma_n\) and the position of the Fermi energy as independent parameters.

The el-ph interaction for the edge states shows a different behavior from that for delocalized states. The el-ph interaction consists of on-site and off-site deformation potentials. \([23]\) It is pointed out that, for a backward scattering of delocalized states, the on-site and off-site deformation potentials on two sublattices cancel with each other due to a phase difference of the wavefunction at the two sublattices. \([24]\) This is why metallic NTs show a ballistic transport property. However, the cancellation of the on-site deformation potential does not work for the edge states since the wavefunction of the edge state has an amplitude only on one of the two sublattices. Furthermore, because of a lack of translational symmetry at the edge, a strong el-ph interaction for optical phonon modes is expected for the edge. Thus the understanding of the el-ph interaction for the edge states is essential for the present problem.

The el-ph interaction is given by

\[
\mathcal{H}_{\text{int}} = \frac{1}{\sqrt{N_0}} \sum_{k, k', \mathbf{q}, \nu} \alpha_{kk'}^\nu (\mathbf{q}) (b_{\mathbf{q}, \nu} + b_{\mathbf{q}, \nu}^\dagger) c_k^{\dagger} c_k,
\]

where \(N_0\) is the number of carbon unit cells in a SWNT, and \(\alpha_{kk'}^\nu (\mathbf{q})\) is the el-ph coupling connecting two edge states \(k\) and \(k'\) by \(\nu\)-th phonon mode with momentum \(\mathbf{q}\). Due to the momentum conservation along the edge, \(k' = k + q (q \equiv \mathbf{q} \cdot \mathbf{a}_1)\), while the wavevector perpendicular to the edge \(q_3 (\equiv \mathbf{q} \cdot \mathbf{T})\) is needed to sum over the Brillouin zone. We calculate \(\alpha_{kk'}^\nu (\mathbf{q})\) using the deformation potential, \(\delta V = -\sum_{i} \nabla v(R_p) \cdot \mathbf{u}(R_p)\), where \(\mathbf{u}(R_p)\) is the displacement vector and \(v(R_p)\) is the pseudo-potential of a carbon atom at \(R_p\). The present pseudo-potential is used for calculating resonance Raman intensity in which the calculated results explain chirality and diameter dependence of Raman intensity quantitatively. \([22]\) \(\mathbf{u}(R_p)\) can be expanded by phonon normal modes as

\[
\mathbf{u}(R_p) = \sum_{\nu} (A^\nu(q)/\sqrt{2N_0}) (b_{\mathbf{q}, \nu} + b_{\mathbf{q}, \nu}^\dagger) e^{\mathbf{q}\cdot \mathbf{R}_p} e^{i\mathbf{q} \cdot \mathbf{R}_p},
\]

where \(e_{\mathbf{q}}(R_p)\) is the normalized eigenvector at \(R_p\) and \(A^\nu(q) = h/\sqrt{m \omega_{\nu}}(\mathbf{q})\) is the phonon amplitude. From \(\langle \Psi (\mathbf{k}) | \delta V | \Psi (\mathbf{k}) \rangle\), we obtain \(\alpha_{kk'}^\nu (\mathbf{q}) = A^\nu(\mathbf{q}) M_{kk'}^\nu (\mathbf{q})/\sqrt{2}\), where \(M_{kk'}^\nu (\mathbf{q})\) is the el-ph matrix element defined by

\[
M_{kk'}^\nu (\mathbf{q}) \equiv -\sum_{p \neq 0} \langle \Psi (\mathbf{k}) | \nabla v(R_p) | \Psi (\mathbf{k}) \rangle \cdot e_{\mathbf{q}}(R_p) e^{i\mathbf{q} \cdot \mathbf{R}_p}.
\]

Putting Eq. (1) to Eq. (3), we see that \(M_{kk'}^\nu (\mathbf{q})\) consists of the on-site \(\langle \phi(R) | \nabla v(R_p) | \phi(R) \rangle\) and off-site \(\langle \phi(R) | \nabla v(R_p) | \phi(R) \rangle\) atomic deformation potentials \((R_p \neq R_i)\). The off-site atomic deformation potential does not contribute to \(M_{kk'}^\nu (\mathbf{q})\) because \(\langle \phi(R_p) | \nabla v(R_p) | \phi(R) \rangle\) vanishes for \(R_p \in A - R_i \supset [\mathbf{a}_1]\). We note that Eq. (3) includes the effect of boundary. To show this, we illustrate several carbon atoms \((R_p > 0)\) near the zigzag edge and a fictitious atom \((R_p < 0)\) in Fig. (1a). The on-site deformation potential at \(R_3\) is given mainly by the vibrations of carbon atoms at \(R_2\) and \(R_3\) as

\[
-e_{\mathbf{q}}(R_p) e^{i\mathbf{q} \cdot \mathbf{R}_p}.
\]

This on-site deformation potential would
be canceled by the fictitious carbon atom at $R_{-1}$ since 
$e_{q}^{0}(R_{p})$ ($p = -1, 2, 3$) points at the same direction. 
Namely, the on-site deformation potential is enhanced at 
the edge. This enhancement may be a reason why the tunnel 
current is unstable at the edge. [10]

For a $(n, 0)$ SWNT, $k$ for the edge states becomes 
discrete as $k(i) = 2\pi/3 + 2\pi i/n$ ($i = 1, \ldots, n/3 - 1$) due 
to the periodic boundary condition around the axis. We 
denote an edge state by the integer $i$ and write $M'_{k,i}(q)$ 
as $M'_{q}(q)$ for simplicity. Putting $k(i)$ to $\xi(q)$, we 
obtain $\xi(k) \lesssim d_{i}/2$ where $d_{i} \equiv n|a_{1}|/\pi$ is 
diameter for the SWNT.

In Fig. 1(b) and (c), we plot $|M'_{q}(q)|$ and $|M'_{\nu}(q)|$, 
respectively, for the $(60, 0)$ SWNT ($d_{i} \approx 5$ nm). $|M'_{q}(q)|$ 
is chosen as an example that $\xi(q) \sim 22\AA$ and $\xi(q) \sim 
4.4\AA$ are much longer than the carbon-carbon bond 
length $a_{cc} \sim 1.4\AA$, while $|M'_{\nu}(q)|$ is chosen as another 
example that $\xi(q) \sim 2.4\AA$ and $\xi(q) \sim 0.9\AA$ are 
comparable to $a_{cc}$. As for acoustic modes, the LA mode 
couples strongly to the edge state. The oTA mode contributes 
to $|M'_{q}(q)|$, whereas the iTA mode is negligible. Since 
the LA and oTA modes change the area of a hexagonal 
lattice, they contribute to on-site deformation potential. 
For optical modes, the iTO and LO modes are important. 
$|M'_{\nu}(q)|$ decreases with increasing $q_{t}$, while $|M'_{\nu}(q)|$ 
increases with increasing $q_{t}$. As shown in Fig. 1(c), the 
deformation potential is stronger for the smaller 
localization length. The behavior of the iTO and LO modes 
is due to the boundary deformation potential. To prove 
this, we show in the inset, the matrix element without 
the boundary, which is defined by Eq. 3 including (fictitious) 
carbon atoms at $p < 0$ in Fig. 1(a). The boundary 
deformation potential depends on the direction of $e_{q}^{0}$ 
and the magnitude is maximum when $e_{q}^{0}$ is parallel to $T$. 
$e_{q}^{0}$ has a large element parallel to $T$ when $q_{t} > \sqrt{3}q$ 
($q_{t} > \sqrt{3}q$) as shown as a vertical line in Fig. 1(b) and (c). 
On the other hand, $e_{q}^{0}$ is perpendicular to the SWNT 
axis (or parallel to $a_{1} \times T$) and the boundary effect of 
the oTO mode does not appear in $|M'_{\nu}(q)|$.

Now we apply $|\alpha'_{k,q}(q)|$ to the Eliashberg equation. 
The Eliashberg equation includes the effects of phonon 
retardation and electron self-energy, which are not taken 
into account in the BCS theory. [23, 26] The phonon 
retardation is included by the Matsubara frequency: $\omega_{n} = 
k_{B}T(2n + 1)\pi$ where $n$ is integer and $|\omega_{n}| \leq \omega_{D}$ 
where $\omega_{D} = 0.2$ eV is the Debye energy. [8] Since the gap 
function, $\Delta(k, i\omega_{n})$, vanishes at $T_{c}$, the Eliashberg 
equation can be linearized at $T_{c}$ to get the gap equation:

$$
\Delta(k, i\omega_{n}) = \frac{2k_{B}T_{c}}{N_{u}} \sum_{k',\nu,q,u,v} |\alpha'_{k,q}(q)|^{2} \omega_{\nu}(q) 
\times \frac{\omega_{\nu}(q)}{(\omega_{\nu} - \omega_{m})^{2} + \omega_{\nu}^{2}(q)} G(k', i\omega_{n}),
$$

where $G(k, i\omega_{n})$ is a thermal Green function of electron, 
$G(k, i\omega_{n}) = (i\omega_{n} - (E(k) - E_{F} - \Sigma(k, i\omega_{n}))^{-1}$. Here,

$$\Sigma(k, i\omega_{n})$$

is the self-energy, which is determined self-consistently by

$$\Sigma(k, i\omega_{n}) = \frac{2k_{B}T_{c}}{N_{u}} \sum_{k',\nu,q,u,v} |\alpha'_{k,q}(q)|^{2} \omega_{\nu}(q) 
\times \frac{\omega_{\nu}(q)}{(\omega_{\nu} - \omega_{m})^{2} + \omega_{\nu}^{2}(q)} G(k', i\omega_{n}).
$$

After calculating $\Sigma(k, i\omega_{n})$ in Eq. (5), we solve Eq. (4).

In Fig. 2 we show $T_{c}$ as a function of $W$ for $(n, 0)$ 
SWNTs with $n = 30, 60$, and 90, where we assume $E_{F} = 
-W/2$. $T_{c}$ decreases with increasing $W$ and $T_{c}$ vanishes 
at critical values, $W_{c}$. The increase of $W$ corresponds to 
the decrease of the LDOS around the Fermi energy. The 
values of $W_{c}$ are 0.46 eV and 0.37 eV, respectively for $n = 
30$ and $n \geq 60$. Those values of $W_{c}$ are close to $\gamma_{n}$ (the 
dashed line in Fig. 2). When $n (d_{i})$ is relatively small, all 
edge states couple strongly to the boundary deformation 
potential since $\max(\xi) \lesssim d_{i}/2$. The strong el-ph coupling 
for $n = 30$ makes $W_{c}$ larger than that for $n \geq 60$. It is 
also noted that excluding optical modes makes $T_{c}$ and $W_{c}$ 
both smaller. In this case, we obtain $T_{c} \sim 70$ K at $W = 0$ 
eV and $W_{c} \sim 0.21$ eV for $n = 60$. Although the values of 
$A'_{\nu}(q)$ for optical modes are smaller than those of acoustic 
modes, the iTO and LO modes contribute to Eqs. (4) and (5) 
because of the large values of $|M'_{\nu}(q)|$ due to the boundary 
deformation potential. A large value of $n$ corresponds to the 
zigzag edge of graphene. Remarkably, $T_{c}$ for $n = 120$ has 
a curve quite similar to $T_{c}$ for $n = 90$. This suggests that $T_{c}$ 
converges and $n = 90$ is large enough to represent a graphene.

It is important to note that the calculated $T_{c}$ is 
sensitive to the energy position of $E_{F}$. We plot $T_{c}$ as a 
function of $E_{F}$ for a $(60, 0)$ SWNT with $W = \gamma_{n}$ in 
the inset of Fig. 2. When $E_{F}$ exists at the top of the energy 
band of the edge states, $T_{c}$ becomes less than 1 K. When $E_{F} \sim 0.1$ eV, $T_{c}$ decreases rapidly since the inelastic 
scattering process is suppressed by the absence of the 
scattered state. This is a reason why $T_{c}$ is sensitive to 
the position of $E_{F}$. We also calculated $T_{c}$ for extended 
states around the Fermi energy of the $(60, 0)$ SWNT 
using the Eliashberg equation. The calculated $T_{c}$ is 
less than 0.1 K. Thus the extended states do not contribute 
to $T_{c}$.

The observed $T_{c}$ should be smaller than our estimation. 
In fact, a lattice defect along the edge decreases LDOS 
and reduces $T_{c}$. The Coulomb repulsive interaction might 
decrease $T_{c}$, too. Fujita et al. showed that the edge states 
develop a local ferro-magnetism in the presence of a large 
Hubbard $U$ comparable to $W$. [8] Since the edge states 
are localized at the edge, they might have a quantum fluc-
tuation intrinsic to 1D system. The Tomonaga-Luttinger 
liquid theory may be suitable to calculate the correlation 
function.

In summary, using the Eliashberg equation, we clarify 
that $W$ and $E_{F}$ position is sensitive to $T_{c}$ of the edge 
states in SWNTs and graphene. The rather high value
FIG. 1: (Color online) (a) Carbon atoms at \( R_{p>0} \) near the zigzag edge, and a fictitious carbon atom at \( R_{-1} \) are illustrated to show an enhancement of the on-site deformation potential at the boundary. The boundary deformation potential is large for optical modes whose \( e_{\nu}^q \) is parallel to \( T \). (b,c) \( |M_{ij}^\nu(q)| \) of the \((60,0)\) SWNT with (b) \( k(1)(=7\pi/10) \rightarrow k(4)(=4\pi/5) \) and (c) \( k(6)(=13\pi/15) \rightarrow k(9)(=29\pi/30) \) are plotted as a function of \( q_t \) where \( q = \pi/10 \). The inset is the matrix element including (fictitious) carbon atoms at \( R_{p<0} \). Three solid/dashed curves represent acoustic/optical phonon modes: oTA/oTO (green), iTA/iTO (blue) and LA/LO (red). The vertical dashed lines represent \( q_t = \sqrt{3} \).

FIG. 2: The dependence of \( T_c \) on \( W \) is plotted for \((30,0)\), \((60,0)\) and \((90,0)\) zigzag SWNTs. The Fermi energy is assumed to be located at the center of the band (\( E_F = -W/2 \)). The nnn hopping gives \( W = 0.3 \) eV. (inset) The dependence of \( T_c \) on \( E_F \) for the \((60,0)\) SWNT with \( W = \gamma_a \).

of \( T_c \) obtained is a result of LDOS enhancement by the edge states, and the on-site and boundary deformation potentials of the el-ph interaction for the edge states. If nanotube superconductivity is given by el-ph interaction, the edge-state superconductivity is a unique candidate since \( T_c \) of the bulk is negligible. Edge (surface) state superconductivity is potentially a key concept for designing superconductors on the nanometer scale.

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