

# Bardeen-Cooper-Schrieffer Formalism of Superconductivity in Carbon Nanotubes

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## Abstract

We develop the Bardeen-Cooper-Schrieffer (BCS) formalism for the superconductivity of carbon nanotubes. It is found that the superconducting transition temperature  $T_c$  of single-wall carbon nanotubes decreases exponentially with the increase of the tube diameter because the density of states near the Fermi energy is inverse proportional to the tube diameter. For the multi-wall carbon nanotubes, the Cooper paring hopping between layers enhances the superconducting correlation and increase the superconducting transition temperature, which is consistent with the experimental observation.

*Key words:* BCS theory; Carbon nanotube

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## 1 Introduction

Carbon nanotubes (CNs) have promised a great potential application in nanotechnology.[1] In recent years, superconductivity has been observed experimentally in the single-wall carbon nanotubes (SWCN), the rope of SWCNs,[2] and the multi-wall carbon nanotubes (MWCN)[3] by the low-temperature transport measurements. For the individual SWCN and the rope of SWCN, the superconducting transitions have been observed at a temperature below 1K.[2] For the end-bonded MWCNs, the superconducting transition temperature reaches  $6 \sim 12K$ ,[3] which is much higher than that of the individual SWCN and the rope of SWCN. This implies that the interlayer coupling may enhance the superconducting correlation.[3] The investigation of the magnetic properties reveals that the superconductivity emerges at temperatures below 15K for a small diameter tube (4 angstrom) embadded in a zeolite.[4]

From a theoretical point of view, it is still not very clear how to understand the mechanism of superconductivity in CNs. Generally, CNs may be regarded as a one-dimensional material (1D). The 1D systems face some obstructions that prevent the emergence of superconductivity, such as Luttinger liquid states with a repulsive electron-electron interaction[5] and Peierls phase transition. However, one believes that the proximity effect could play an essential role in superconductivity state in CNs.[2] Another scenario on superconductivity of CNs is obtained by the effective low-energy theory for interacting electrons in metallic SWCN, which predicts that SWCNs can be described as a Luttinger liquid with an attractive electron-electron interaction.[6] The breathing modes specific to CNs can be the origin of a strong electron-phonon coupling giving rise to attractive electron-electron interactions.[6] A short-range attractive electronic interaction originates from the exchange of phonons.[7] The single-particle hopping between neighboring nanotubes in a rope is strongly suppressed because the different helical structure of nanotubes, in general, leads to the mismatching of the atoms between tubes. The intertube coherence is established mainly through the tunneling of Cooper pairs, which enhances the superconducting correlation.[7] Exactly speaking, CN is a quasi-one-dimensional system. The energy band contains some split bands near Fermi level. The inter-layer coupling in MWCNs could play an important role in superconductivity of CNs. Superconductivity in CNs should be intrinsic [6,7] and the nature of superconductivity in CNs is still attributed to Bardeen-Cooper-Schrieffer(BCS) mechanism.[8] Thus, the BCS formalism for CNs is still an interesting issue.

In this paper, we will develop a formalism of MWCNs based on BCS theory, and discuss the superconducting correlation and the critical temperature. In the section II, we will propose a BCS Hamiltonian of MWCNs in the tight-binding approximation. We will give a mean field solution of this Hamiltonian, the self-consistent equations on the superconducting energy gap and the superconducting transition temperature of MWCN in the section III. Finally, we will give a discussion and conclusion.

## 2 BCS Hamiltonian

Since the intrinsic superconductivity is observed in SWCNs one may believe that the effective electron-electron interaction is attractive to form the Cooper pairs in the SWCN. We consider a general BCS Hamiltonian of MWCN constructed from a coupling multi-layer BCS Hamiltonian.[9] The single electron hopping between layers is estimated to be much weaker than the Cooper pair hopping between layers due to the mismatching of atoms between layers.[7,2] The Cooper pair hopping between layers dominates the interaction between layers.[2] Thus, the BCS Hamiltonian of MWCNs may be expressed in terms

of the coupling SWCN BCS Hamiltonian.

$$H = \sum_{\ell} H_{\ell}(k) + \sum_{\langle \ell, \ell' \rangle} H_{\ell, \ell'}, \quad (1)$$

where

$$H_{\ell}(k) = \sum_{k, \sigma} E_{\ell}(k) c_{k, \ell, \sigma}^{\dagger} c_{k, \ell, \sigma} - \sum_{k, k', \sigma} V_{\ell} c_{k, \ell, \sigma}^{\dagger} c_{k, \ell, \bar{\sigma}}^{\dagger} c_{k', \ell, \bar{\sigma}} c_{k', \ell, \sigma}, \quad (2)$$

is the Hamiltonian of the  $\ell$ th tube. The  $V_{\ell}$  in the second term of Eq.(2) describes the intratube effective electron-electron interaction. The  $H_{\ell, \ell'}$  in the second term of Eq.(1) is the coupling between layers, where the sum  $\langle \ell, \ell' \rangle$  runs only for the nearest layers in the tight-binding approximation. The layer-layer coupling Hamiltonian may be written as

$$H_{\ell, \ell'} = - \sum_{k, k', \sigma} V_{\ell, \ell'} c_{k, \ell, \sigma}^{\dagger} c_{k, \ell, \bar{\sigma}}^{\dagger} c_{k', \ell', \bar{\sigma}} c_{k', \ell', \sigma} \quad (3)$$

where the  $V_{\ell, \ell'}$  in Eq.(3) represents the intertube electron-electron interaction between the  $\ell$ th and  $\ell'$ th layers, which induces the Cooper pairing hopping between layers and are measured relative to the corresponding screened Coulomb potential. The  $c_{k, \ell, \sigma}^{\dagger} (c_{k, \ell, \sigma})$  is the creation (annihilation) operator at the layer  $\ell$  with the spin  $\sigma$ , where the  $\ell = 1, 2, \dots, M$  labels the layers. The  $E_{\ell}(k) = \epsilon_{\ell}(k) - E_F$ , where  $E_F$  is the Fermi energy. We set  $E_F = 0$  for convenience in the following. The  $\epsilon_{\ell}(k)$  is the energy dispersion relation of the layer  $\ell$  for free electrons, which can be obtained by the tight-binding approximation[10]

$$\epsilon_{\ell}(\mathbf{k}) = \pm t \sqrt{1 + 4 \cos \left( \frac{\sqrt{3}k_x^{(\ell)}a}{2} \right) \cos \left( \frac{k_y^{(\ell)}a}{2} \right) + 4 \cos^2 \left( \frac{k_y^{(\ell)}a}{2} \right)}, \quad (4)$$

and their wave vectors are [12]

$$\begin{pmatrix} k_x^{(\ell)} \\ k_y^{(\ell)} \end{pmatrix} = \begin{pmatrix} \frac{a}{2L_{\ell}}(m_{\ell} - n_{\ell})k_{\ell} + \frac{\sqrt{3}\pi a}{L_{\ell}^2}(n_{\ell} + m_{\ell})q_s \\ \frac{\sqrt{3}a}{2L_{\ell}}(m_{\ell} + n_{\ell})k_{\ell} + \frac{\pi a}{L_{\ell}^2}(n_{\ell} - m_{\ell})q_s \end{pmatrix}, \quad (5)$$

where  $a = 2.46\text{\AA}$  is the lattice constant of hexagons. The  $t$  is the intralayer electronic hopping constant. The SWCN is identified by the chiral vector  $\mathbf{C}_h = (n, m)$ , which length  $L_{\ell} = a\sqrt{n_{\ell}^2 + m_{\ell}^2 + n_{\ell}m_{\ell}}$ . The  $(k_{\ell}, q_{\ell})$  in Eq.(5) are quantum numbers of the  $\ell$ th tube. The sum  $\sum_k$  in Eqs.(2) and (3) runs

all states of the nanotubes  $\ell$  and  $\ell'$  in the Briullien zone, which includes the  $k_\ell$  values within  $-\frac{\pi}{T_\ell} < k_\ell < \frac{\pi}{T_\ell}$  and  $q_\ell = 0, 1, \dots N_\ell - 1$ , where  $T_\ell = \sqrt{3}L_\ell/d_{R_\ell}$  is the length of the translational vector of the  $\ell$ th tube being parallel to the tube axis and  $N_\ell = 2L_\ell^2/a^2d_{R_\ell}$  is the number of hexagons per unit cell of the  $\ell$ th tube. The  $d_{R_\ell} = \text{gcd}(2n + m, 2m + n)$  means the greatest common divisor of  $2n_\ell + m_\ell$  and  $2m_\ell + n_\ell$ . For comensurate MWCNs the atoms between layers are matching such that all  $T_\ell$  are equal.[13] The energy band structure of SWNTs depends on the chirality of the tube. The SWCN may be metallic for  $n_\ell - m_\ell = 3i$  or semiconducting for  $n_\ell - m_\ell \neq 3i$ , where  $i$  is an integer.[10]

### 3 Mean field solution

Based on the BCS mean field idea, factorizing the potential terms in Eq.(2) and (3),  $c_{k,\ell,\sigma}^\dagger c_{k,\ell,\bar{\sigma}}^\dagger c_{k,\ell',\bar{\sigma}} c_{k,\ell',\sigma} = \langle c_{k,\ell,\sigma}^\dagger c_{k,\ell,\bar{\sigma}}^\dagger \rangle c_{k,\ell',\bar{\sigma}} c_{k,\ell',\sigma} + c_{k,\ell,\sigma}^\dagger c_{k,\ell,\bar{\sigma}}^\dagger \langle c_{k,\ell',\bar{\sigma}} c_{k,\ell',\sigma} \rangle - \langle c_{k,\ell,\sigma}^\dagger c_{k,\ell,\bar{\sigma}}^\dagger \rangle \langle c_{k,\ell',\bar{\sigma}} c_{k,\ell',\sigma} \rangle$ , we can obtain the mean field form of Hamiltonian

$$H = \sum_{\ell,k,\sigma} \epsilon_\ell(k) c_{k,\ell,\sigma}^\dagger c_{k,\ell,\sigma} - \sum_{\ell,k,\sigma} \Delta_\ell(c_{k,\ell,\sigma}^\dagger c_{k,\ell,\bar{\sigma}}^\dagger + h.c.) + \sum_{\ell,k} \Delta_\ell^\dagger S_{\ell k} \quad (6)$$

where the pair correlation,  $S_{\ell k}$ , has been defined by

$$S_{\ell k} = \langle c_{k,\ell,\sigma} c_{k,\ell,\bar{\sigma}} \rangle, \quad (7)$$

where  $\langle X \rangle$  is the grand canonical average of  $X$ . The superconducting energy gap may be expressed as [9]

$$\Delta_\ell = \sum_k V_\ell S_{\ell k} + \sum_{\ell' \neq \ell} V_{\ell,\ell'} S_{\ell' k}, \quad (8)$$

Using the Bogoliubov transform,

$$\begin{pmatrix} c_{k,\ell,\sigma} \\ c_{-k,\ell,-\sigma}^\dagger \end{pmatrix} = \begin{pmatrix} u_k & v_k \\ -v_k & u_k \end{pmatrix} \begin{pmatrix} \gamma_{k,\ell} \\ \gamma_{-k,\ell}^\dagger \end{pmatrix} \quad (9)$$

to diagonalize the Hamiltonian in Eq.(6), the Hamiltonian can be written as

$$H_{BCS} = E_G + \sum_{\ell,k} \xi_\ell(k) (\gamma_{k,\ell}^\dagger \gamma_{k,\ell} + \gamma_{-k,\ell}^\dagger \gamma_{-k,\ell}), \quad (10)$$

where the ground state energy is

$$E_G = \sum_{\ell,k} (\epsilon_\ell(k) - \xi_\ell(k) + \frac{\Delta_\ell^2}{2\xi_\ell(k)}), \quad (11)$$

and the quasiparticle energy spectrum,

$$\xi_\ell(k) = \sqrt{\epsilon_\ell^2(k) + \Delta_\ell^2}. \quad (12)$$

where  $\ell$  labels the tube, which may be regarded as different energy bands of quasiparticles. Making use of the Bogoliubov transform Eq.(9) and considering the tight-binding approximation, the superconducting energy gap  $\Delta_\ell$  satisfies a set of equations, which matrix form may be written as[9]

$$\begin{pmatrix} \alpha_{1,1} & \alpha_{1,2} & 0 & \cdots & 0 \\ \alpha_{2,1} & \alpha_{2,2} & \alpha_{2,3} & \cdots & \vdots \\ 0 & \alpha_{3,2} & \ddots & \vdots & 0 \\ \vdots & \vdots & \cdots & \alpha_{M-1,M-1} & \alpha_{M,M-1} \\ 0 & 0 & \cdots & \alpha_{M,M-1} & \alpha_{M,M} \end{pmatrix} \begin{pmatrix} \Delta_1 \\ \Delta_2 \\ \vdots \\ \Delta_{M-1} \\ \Delta_M \end{pmatrix} = 0 \quad (13)$$

where

$$\alpha_{\ell,\ell'} = \begin{cases} 1 - V_\ell F(\Delta_\ell) & \text{for } \ell' = \ell \\ -V_{\ell,\ell'} F(\Delta_{\ell'}) & \text{for } \ell' = \ell \pm 1 \\ 0 & \text{others} \end{cases} \quad (14)$$

with

$$F(\Delta_\ell) = \sum_{q=0}^{N_\ell-1} \int_{-\frac{\pi}{T_\ell}}^{\frac{\pi}{T_\ell}} \frac{dk}{\xi_\ell(k)} \tanh\left(\frac{\xi_\ell(k)}{2k_B T}\right) \quad (15)$$

At zero temperature, the Eq.(15) may reduce to  $F(\Delta_\ell) = \sum_{q=0}^{N_\ell-1} \int_{-\frac{\pi}{T_\ell}}^{\frac{\pi}{T_\ell}} \frac{dk}{\xi_\ell(k)}$ .

In principle, numerically solving Eqs.(13) and (15) associated with Eqs.(4),(5) and (12), we can obtain the superconducting paring, superconducting transition temperature and their relationships. The  $F(\Delta_\ell)$  should satisfy Eqs.(13)

and (15). The nontrivial solution of  $\Delta$  requires the determinant of the coefficient matrix being zero. This way to solve numerically the BCS Hamiltonian is exact in the mean field level.

### 3.1 Single-wall carbon nanotubes

In order to give an analytic solution, let us consider the SWCNs first. We note that the density of states (DOS) of metallic tubes per atom can be expressed approximately near Fermi level as [10,11]

$$\rho(E_F) = \frac{4a}{\pi^2 t d}, \quad (16)$$

where  $d$  is the diameter of the tube. Thus, the DOS near Fermi level depends on the diameter of the tubes. The equation of the superconducting energy gap may be written as

$$1 = V\rho(E_F)F_0(\Delta) \quad (17)$$

Since the Debye energy of the phonons  $\hbar\omega_D$  is estimated to be 0.1eV [7], we may neglect the effect of the energy band structure beyond the Fermi level. Thus, the function  $F_0(\Delta)$  may be written as

$$F_0(\Delta) = \int_0^{\hbar\omega_D} \frac{d\epsilon}{\sqrt{\epsilon^2 + \Delta^2}} \tanh\left(\frac{\sqrt{\epsilon^2 + \Delta^2}}{2k_B T}\right) \quad (18)$$

At the critical temperature,  $T = T_c$ , the superconducting paring equals to zero,  $\Delta = 0$ . The integration Eq.(18) can be integrated

$$F_0(0) = \ln\left(\frac{2e^\gamma}{\pi} \frac{\hbar\omega_D}{k_B T_c}\right) \quad (19)$$

where  $\gamma \approx 0.5772$  is Euler constant. Using Eq.(16), (17), and (19), we can obtain the superconducting transition temperature,

$$k_B T_c = \frac{2e^\gamma}{\pi} \hbar\omega_D \exp\left(-\frac{\pi^2 t d}{4aV}\right) \quad (20)$$

Interestingly, the critical temperature  $T_c$  decreases exponentially with the increase of the diameter of the tube. We also obtain the superconducting paring

at zero temperature is  $\Delta(0) = 2\hbar\omega_D \exp\left(-\frac{\pi^2 t d}{4aV}\right)$ . Thus, the superconducting paring can be also expressed approximately as

$$\Delta(T) \approx \begin{cases} \Delta(0) - (2\pi k_B T \Delta(0))^{1/2} e^{-\frac{\Delta(0)}{k_B T}} & \text{for } T \ll T_c \\ 3.06 k_B T_c (1 - \frac{T}{T_c})^{1/2} & \text{for } T \rightarrow T_c \end{cases} \quad (21)$$

Since there is an energy gap at Fermi level for the semiconducting SWCNs, the superconducting state cannot occur in the semiconducting SWCNs. However, it has been found that the layer-layer coupling of MWCNs may induce the semiconductor-metal phase transition.[12,14] Actually, most of MWCNs are metallic due to the interlayer coupling.[13,14] Thus, the superconducting state may occur in MWCNs.

### 3.2 Double-wall carbon nanotubes

For the double-wall carbon nanotubes (DWCN), the Cooper paring equation Eq. (13) can be reduced to [9,16]

$$\begin{pmatrix} 1 - V_1 \rho_1(E_F) F_0(\Delta_1) & -V_{1,2} \rho_2(E_F) F_0(\Delta_2) \\ -V_{2,1} \rho_1(E_F) F_0(\Delta_1) & 1 - V_2 \rho_2(E_F) F_0(\Delta_2) \end{pmatrix} \begin{pmatrix} \Delta_1 \\ \Delta_2 \end{pmatrix} = 0, \quad (22)$$

The effective electron-electron interaction may be assumed to be independent of the chirality of the tube, namely  $V_1 = V_2 \equiv V$  and let  $V_{1,2} = V_{2,1} \equiv V_\perp$ . At  $T = T_c$ , the superconducting paring equals to zero,  $(\Delta_1, \Delta_2) = 0$ , The nontrivial solution of Eq.(22) requires the determinant of the coefficient matrix being zero, in which substituting Eq.(16) into Eq.(22), we can solve two solutions of  $F_0(0)$  of Eq.(22). Based on the hints of the experimental results [2,3] and the similar two-band BCS theory,[9] we may select the smallest solution of  $F_0(0)$ ,

$$F_0(0) = \frac{\pi^2 t}{8(V^2 - V_\perp^2)a} [V(d_1 + d_2) - \sqrt{V^2(d_2 - d_1)^2 + 4V_\perp^2 d_1 d_2}]. \quad (23)$$

Combining Eq.(19), the superconducting transition temperature can be obtained

$$k_B T_c = \frac{2e^\gamma}{\pi} \hbar \omega_D e^{-F_0(0)}. \quad (24)$$

Thus, the interlayer hopping of the Cooper pair enhances the superconducting paring and increases the superconducting transition temperature, which is

consistent with the experimental observation[2,3].

### 3.3 Multi-wall carbon nanotubes

Similarly, we can generalize above way of the DWCN to the MWCN case. Suppose MWCN containing  $M$  layers, to facilitate the analytical solution of  $F_0(0)$ , we assume that  $V_\ell \rho_\ell(E_F) = V_{\ell'} \rho_{\ell'}(E_F) \equiv V \langle \rho(E_F) \rangle$  and  $V_{\ell,\ell+1} \rho_{\ell+1}(E_F) = V_{\ell+1,\ell} \rho_\ell(E_F) \equiv V_\perp \langle \rho(E_F) \rangle$ , where  $\langle \rho(E_F) \rangle = \frac{4a}{\pi^2 t \langle d \rangle}$ . The  $\langle d \rangle$  is the average of the diameter of MWCN,  $\langle d \rangle = \frac{1}{M} \sum_\ell d_\ell$ . At  $T = T_c$ , the determinant of the coefficient of the Eq.(13) can be reduced to the Chebyshev polynomial, which can be solved,[9]

$$F_0(0) = \frac{1}{\langle \rho(E_F) \rangle [V + 2V_\perp \cos(\frac{\pi}{M+1})]}, \quad (25)$$

where we has also selected the smallest solution of the Chebyshev polynomial like the DWCN case.[9] The superconducting transition temperature can be expressed as

$$k_B T_c = \frac{2e^\gamma}{\pi} \hbar \omega_D \exp \left( -\frac{\pi^2 t \langle d \rangle}{4a [V + 2V_\perp \cos(\frac{\pi}{M+1})]} \right) \quad (26)$$

It can be also seen that the Cooper pair tunnelling between layers will enhance the superconducting correlation and increase the critical temperature. This agrees with the experimental observation.[2,3] This theoretical framework provides us an physical understanding of the superconductivity mechanism of CNs even though the result relies on the  $F_0(0)$  solution selected based on the hints of the experiment result[2,3] and the multi-band BCS theory.[9]

Experimentally, the transport measurement of the ropes of SWCNs indicates the superconducting state occurring in the temperature range of  $0.1 \sim 1K$ .[2] The investigation of the magnetic properties for the small radius SWCN ( $4\text{\AA}$ ) reveals that the  $T_c$  can be estimated to be lower than  $15K$ .[4] The transport measurements of the  $Au/MWCN/Au$  junctions indicate that the  $T_c$  reaches to  $6K \sim 12K$ .[3] The theoretical study of the zigzag and armchair SWCNs by the Millan's formula and the *VASP* software package gives that the  $T_c$  is very small,  $10^{-9}K$  for the armchair tube  $(5, 5)$ , but  $55 \sim 75K$  for the zigzag tube  $(5, 0)$ .[15]

As an example of this formalism we list several typical results of the superconducting transition temperature in the table I and compare the first-principle calculation[3] and the experimental results,[2,4,3] where we use the parameters

Table 1  
The superconducting transition temperature of several CNs.

CNs	(n,m)@(n,m)...	$T_c(K)$ <sup>1</sup>	$T_c(K)$ <sup>2</sup>	$T_c(K)$ <sup>3</sup>
SWCN	(4,1)	0.729	57	< 15
SWCN	(5,5)	$9.23 \times 10^{-4}$	$3 \times 10^{-9}$	0.1 ~ 1(SWCN rope)
SWCN	(10,10)	$6.46 \times 10^{-10}$	$2.6 \times 10^{-30}$	
DWCN	(5,0)@(10,0)	2.24		
DWCN	(5,5)@(8,8)	0.043		
TWCN	(5,0)@(10,0)@(15,0)	0.29		6 ~ 12(MWCN junction)
TWCN	(5,5)@(8,8)@(12,12)	0.0069		

<sup>1</sup>our results; <sup>2</sup>the first-principle calculation[15]; <sup>3</sup> experimental results.[2,3,4]

$t = 2.5eV$ ,  $V = 1.2eV$ , and  $V_{\perp} = 0.8eV$ ,  $\hbar\omega_D = 0.1eV$ .[7] For SWCN the first-principle calculation predicts the (5,0) tube being metallic due to the  $\pi^* - \sigma$  coupling.[15] However, in the  $\pi$  electronic tight-binding approximation the (5,0) tube is semiconducting.[10] Thus, we chose a small diameter tube (4,1) ( $\sim 4\text{\AA}$ ) for comparision with the results of the experimental observation [4] and the first-principle calculation.[15] The result we obtain is  $T_c = 0.729K$ , which agrees qualitatively with the experimental result.[2,3,4] For SWCN (5,5), we estimate the  $T_c = 9.23 \times 10^{-4}K$ , which is the same order to another theoretical results,  $T_c = 1.5 \times 10^{-4}K$ .[16] In their theory the electron-phonon interaction is taken into account in detail within the BCS framework. For MWCN the Cooper pair tunnelling between layers also enhances the Cooper pair correlation and increase the superconducting transition temperature. This is also consistent with the experimental observation.[2,3]

#### 4 Discussion and conclusion

Physically, the intratube electronic hopping constant  $t$ , the effective electron-electron interaction  $V_{\ell}$  and the intertube electron-electron interaction  $V_{\ell,\ell'}$  could depend slightly on the chirality and the layer number of the tube.[7,16] Thus, We cannot obtain exactly an analytical solution of  $T_c$ . Nevertheless, above formalism Eqs.(1)~(13) still provides a guideline for the numerical study. From the theoretical point of views, we give the BCS formalism on MWCN and the formula in Eq. (26) tell us that the Cooper pair tunnelling between layers enhances the superconducting correlation and  $T_c$ , which is cconsis-tent with the experimental results[2,3] even though we make some approximations in Eq.(26) for obtaining an analytic formula. Actually, for MWCN the effect of the layer number on  $T_c$  competes with the effect of the diameter of MWCN, which can be seen from Eq.(26). However, the effect of diame-

ter dominates  $T_c$  for the MWCNs that have the layer number more than 4. Hence, the small-diameter double-wall or triple-wall carbon nanotubes could have higher  $T_c$ .

On the other hand, the study of the thermodynamic variables starts from the partition function of the system,  $Z = Tr(e^{-\beta H})$ , where  $\beta$  is the inverse temperature. The free energy may be expressed in terms of  $F = -\beta \ln Z$ . Using Eq.(10), we can obtain

$$F = -\frac{2}{\beta} \sum_{k,\ell} \left[ \ln(1 + e^{-\beta\xi_\ell(k)}) - \epsilon_\ell(k) + \xi_\ell(k) - \frac{\Delta_\ell^2}{2\xi_\ell(k)} \right]. \quad (27)$$

The other thermodynamic variables can be obtained by the thermodynamic relationships between the free energy and the thermodynamic variables, such as the electronic entropy,  $S = -\frac{\partial F}{\partial T}$ , and the specific heat  $C = T \frac{\partial S}{\partial T}$  .[8]

In summary, we have developed a BCS formalism of superconductivity for MWCNs, which give that the superconducting transition temperature  $T_c$  of SWCNs decreases exponentially the tube diameter. The  $T_c$  is very small (less than 1K for the diameter less than 1nm). The Cooper pair tunnelling between layers enhances the superconducting correlation and increases the superconducting transition temperature. The interlayer coupling increases the number of the transverse channels, which suppresses 1D characteristic of CNs due to screening the repulsive electron-electron interaction. Hence, the superconducting long-range order emerges favorably in the small-diameter double-wall or triple-wall carbon nanotubes .

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