Carbon 125 (2017) 509–515

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Superconductivity in ultra-thin carbon nanotubes and carbyne-nanotube composites: An ab-initio approach

C.H. Wong [a, *], E.A. Buntov [a], M.B. Guseva [b], R.E. Kasimova [a], V.N. Rychkov [a], A.F. Zatsepin [a]

[a] Institute of Physics and Technology, Ural Federal University, Yekaterinburg, Russia
[b] Faculty of Physics, Moscow State University, Moscow, Russia

ARTICLE INFO

Article history:
Received 24 July 2017
Received in revised form
13 September 2017
Accepted 19 September 2017
Available online 20 September 2017

ABSTRACT

The superconductivity of the 4-Å single-walled carbon nanotubes (SWCNTs) was discovered more than a decade ago, and marked the breakthrough of finding superconductivity in pure elemental undoped carbon compounds. The van Hove singularities in the electronic density of states at the Fermi level in combination with a large Debye temperature of the SWCNTs are expected to cause an impressively large superconducting gap. We have developed an innovative computational algorithm specially tailored for the investigation of superconductivity in ultrathin SWCNTs. We predict the superconducting transition temperature of various thin carbon nanotubes resulting from electron-phonon coupling by an ab-initio method, taking into account the effect of radial pressure, symmetry, chirality (N,M) and bond lengths. By optimizing the geometry of the carbon nanotubes, a maximum T_c of 60 K is found. We also use our method to calculate the T_c of a linear carbon chain embedded in the center of (5,0) SWCNTs. The strong curvature in the (5,0) carbon nanotubes in the presence of the inner carbon chain provides an alternative path to increase the T_c of this carbon composite by a factor of 2.2 with respect to the empty (5,0) SWCNTs.

1. Introduction

The observation of superconductivity in 4-Å single wall carbon nanotubes arrays (SWCNTs) was first reported back in 2001 [1], and further confirmed by more detailed experiments [2]. The superconducting transition temperature T_c was observed with onset at 15 K. In a purely one-dimensional (1D) material the electrons form Cooper pairs at the onset superconducting transition temperature, however the low-dimensionality causes strong thermal and quantum fluctuations leading to phase slips events, which cause finite resistance at any non-zero temperature [3]. This scenario has been theoretically well described in the framework of the Langer-Ambegaokar-McCumber-Halperin (LAMH) theory [3,4]. Fortunately, this limitation of 1D superconductors can be overcome by arranging the superconducting nano-elements in the form of closely packed arrays of parallel wires [1,5–7,10]. The Josephson interaction induced by quantum tunneling of Cooper pairs stabilizes then the superconducting phase order parameter and triggers a dimensional crossover from a 1D fluctuating state at high temperatures to a 3D phase coherent state with vanishing electrical resistance [5–10]. By drawing a parallel to the geometry of the non-superconducting graphene, a strong curvature of the graphene sheet is believed to be the main ingredient to activate the superconductivity in thin carbon nanotubes [1,11]. The BCS theory states that a large electronic density of states (DOS) at the Fermi level and a high Debye frequency are the essential ingredients for a high T_c in the case of classical phonon-mediated BCS superconductors [8]. 1D metallic elements feature van Hove singularities in their electronic density of states (DOS) at Fermi level, and if by chance such a singularity could appear at, or in the vicinity of the Fermi level very high T_c values could result. The Fermi level may be further tuned by application of pressure or electric gate voltages [12], and in addition the superconductivity of SWCNTs may be further tunable through the lateral tube-to-tube distances and bond lengths. However, the synthesis of high quality carbon nanotubes thinner than 4 Å in diameter represents a challenge [13]. In addition, no theoretical model predicting the superconducting transition temperature T_c of the SWCNTs accurately was reported so far, despite of numerous first principle calculations that have been reported for SWCNTs [14,15]. In view of this, we have developed a powerful theoretical model to accurately predict superconducting parameters of thin carbon nanotubes. In addition, we address linear carbon chains, whose existence has been questioned for a long time due to its

* Corresponding author. Tel.: +7 9068158342.
E-mail address: ch.kh.vong@urfu.ru (C.H. Wong).

https://doi.org/10.1016/j.carbon.2017.09.077
0008-6223/

energetic instability [16]. However, linear carbon nanowires protected by double walled carbon nanotube (DWCNT) have been fabricated successfully recently [16], and we will study how the interaction between the chain and the nanotube can cause superconductivity in such a carbon composite. In our simulation the carbon nanowire is surrounded by a (5,0) SWCNTs. The (5,0) SWCNTs features a threshold radius, which means that no extra covalent bond is established radially between the carbon nanowire and the nanotube.

2. Computational methods

The BCS pairing Hamiltonian, $H_{pair} = \sum_{k\sigma} E_k n_{k\sigma} + \sum_{kl} V_{kl} c^*_{k\uparrow} c^*_{k\downarrow} c_{l\uparrow} c_{l\downarrow}$, is made up of the single particle energy E_k relative to the Fermi energy. The interaction V_{kl} changes the state of particle from $(l\uparrow, -l\downarrow)$ to $(k\uparrow, -k\downarrow)$. The creation operators, $c^*_{k\uparrow}$ and $c^*_{k\downarrow}$, refer to spin up and down respectively, while the particle number operator is represented by $n_{k\sigma}$ and σ is the spin index [8]. The ground state of the BCS wavefunction ψ_G is expressed as

$$|\psi_G\rangle = \prod_{k=k_1....k_M} \left(u_k + v_k c^*_{k\uparrow} c^*_{k\downarrow}\right)|\varphi_0\rangle$$

where $|\varphi_0\rangle$ is the vacuum state with the absence of particles. As $|u_k|^2 + |v_k|^2 = 1$, the $|u_k|^2$ means the unoccupied probability. In BCS material the energy gap is k independent and hence we may define $\Delta = \Delta_k = -\sum_l V_{kl} u_l v_l$ [8]. The interaction term is originated from the electron phonon scattering in the expression of $H_{e-ph} = \sum_{kk'\sigma\lambda} g_{kk'\lambda} C^\dagger_{k\sigma} C_{k'\sigma}((a_\lambda(\mathbf{q}) + a^\dagger_\lambda(-\mathbf{q}))$ [8,11]. The $C_{k\sigma}$ and λ result from linear combinations of the eigenfunctions and polarizations. The $g_{kk'\lambda}$ is related to the electrostatic integral and lattice vibrations. The $a^\dagger_{q\lambda} a_{q\lambda} + \frac{1}{2}$ refers to the quantum number of the phonons, where $\mathbf{q} = \mathbf{k} - \mathbf{k}' + \mathbf{G}$ and $\mathbf{G}$ correspond to a reciprocal lattice vector [12].

For circular materials like SWCNT, the attractive force acting on the electrons needs to be modified due to the increase of the effective atomic number $Z_{effective}$ [17].

$$Z_{effective} = Z \frac{\sum_r^R U_c(r)}{\sum_r^R U_p(r)}$$

The Bloch theorem ensures that the wavefunctions of electron ψ can be written in the form of $\psi(r + R) = e^{ik\cdot R}\psi(r)$ where k is the wave number and R is a lattice vector. By comparing the attractive potential between the circular U_c and planar U_p shapes, the $Z_{effective}$ is obtainable.

The prediction of the T_c is acquired by computing the scale factor $\frac{T_{c(A)}}{T_{c(B)}} = \frac{\Delta_A(0)}{\Delta_B(0)}$, because $\Delta(0) \propto T_c$ per electron [8]. If the T_c of the material B is known, the T_c of the material A is predictable according to our semi-phenomenological scale-factor approach. However, the $u_l v_l$ depend on Δ and hence another transfer function is needed: According to the BCS theory, the energy gap is expressed as $\Delta_k = -\frac{1}{2}\sum V_{kl} \frac{\Delta_l}{(\Delta_l^2 + E_k^2)^{0.5}}$ [8]. The derivation of the transfer function starts from calculating the trial energy gap Δ^T, which originates from the electrons at the Fermi level only. In this particular situation the Δ^T is directly proportional to the interaction term after the vanishing of E_k. Then the transfer function, i.e. $u_l^T v_l^T$ as a function of electron energy is interpreted, which will be substituted into $\Delta_k^{corrected} = -\sum_{kl} V_{kl} u_l^T v_l^T$ to correct the energy gap. However, the scale factor approach is valid if it satisfies the condition that the Debye energy $\hbar\omega_D \gg \Delta$. Otherwise, the BCS occupational fraction will not drop sharply to zero when the electron energy increases [8].

We apply the scale factor approach to calculate the T_c of SWCNTs arranged in the form of a hexagonal array. Each SWCNT can be imagined as a rolled-up graphene sheet forming the shape of a tube. As a result, the phonon wavefunction in a SWCNT $\chi(\omega_x^{planar}, \omega_y^{planar}, \omega_z^{circular})$ becomes related to graphene $\chi(\omega_x^{planar}, \omega_y^{planar})$ and linear carbon nanochains $\chi(\omega_x^{linear})$ of the same bond lengths. We consider two types of repeating units in graphene as illustrated in Fig. 1. The effective spring constants $(K_x^{planar}, K_y^{planar})$ of the upper and lower repeating units in graphene are resolved into the x and y axis, respectively.

As the bond length of graphene is about 143 p.m., we make use of the GGA functional [18,19] to simulate the dispersion curve and the phonon density of states in the linear carbon chain under the same bond distance of 143 p.m. based on the finite displacement method in which the corresponding supercell cut-off radius is 0.5 nm [20]. In addition, the electronic DOS of the reference carbon chain is simulated by the GGA functional in the Dmol^3 package [21]. The lateral chain-to-chain separation between the isolated carbon chains is 1340 p.m. By comparing the linear repeating unit made by the four nearest carbon atoms along the reference linear carbon chain with the known dimensionless spring constant K_x^{linear}, the vibrational frequency of the graphene is interpretable after computing the ratio of the resultant spring constant of the graphene relative to the reference chain using the classical mass-spring formula of $\frac{\sqrt{(K_x^{planar} K_x^{planar} + K_y^{planar} K_y^{planar})}}{K_x^{linear}}$ [12]. In other words, the

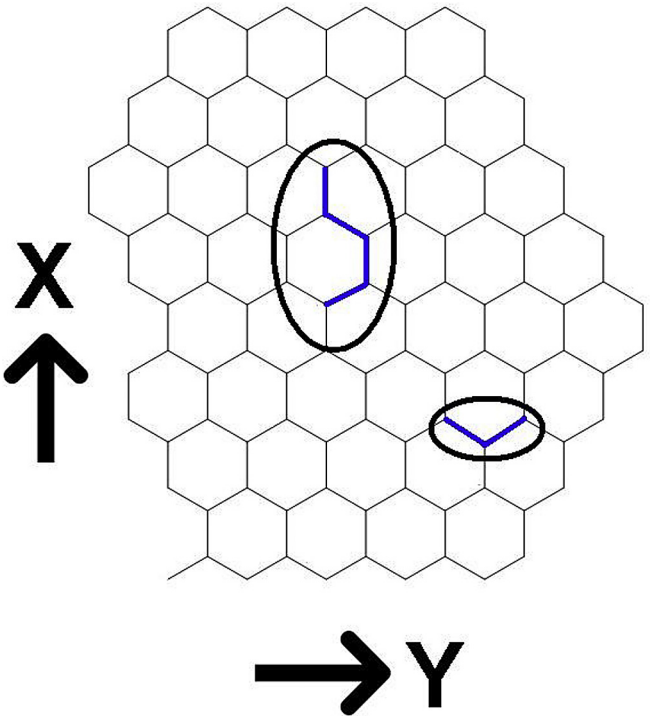

Fig. 1. Illustration of the structure of graphene. Two types of repeating units of graphene are shown in thicker lines.