Simulation of chemical bond distributions and phase transformation in carbon chains

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

[a] Institute of Physics and Technology, Ural Federal University, Ekaterinburg, 620002, Russia
[b] Faculty of Physics, Moscow State University, Moscow, 119991 Russia

ARTICLE INFO

ABSTRACT

In the present work we develop a Monte Carlo algorithm of the carbon chains ordered into 2D hexagonal array. The chemical bond of the chained carbon is computed from 1 K to 1300 K. Our model confirms that the beta phase is more energetic preferable at low temperatures but the system prefers to switch into alpha phase at high temperatures. Based on the thermal effect on the bond distributions of the carbon chains, the bond softening temperature is observed at 500 K. The bond softening temperature is higher in the presence of interstitial doping but it does not change with the length of nanowire. The elastic modulus of the carbon chains is 1.7 TPa at 5 K and the thermal expansion is $+7 \times 10^{-5}$ K^{-1} at 300 K via monitoring the collective atomic vibrations and bond distributions. Thermal fluctuation in terms of heat capacity as a function of temperatures is computed in order to study the phase transition across melting point. The heat capacity anomaly initiates around 3800 K.

1. Introduction

The carbon nanomaterials had been studied in the past few decades [1,2]. It provides a large variety of applications in daily life. One kind of carbon material, carbon nanotube, was proven to give impressive elastic modulus [2]. Carbyne seems like another strong material as well [3]. A recent theoretical study of Young's modulus of carbyne, a parallel carbon chains with kinks, gives a breakthrough at over 1 TPa which draws a lot of attentions to material scientists [3]. We therefore develop a novel Monte Carlo algorithm to model 10 carbyne chains in form of hexagonal array. Thermal expansion is essential important to nano-electronics [4] and different thermal elongations of the nanomaterials make a strong impact on the reliability of the nano-electronics [2]. However, the sign of thermal expansion is different in various carbon materials [5—7]. The coefficient of thermal expansion of fullerene is positive [7] while the coefficient turns into negative in free standing graphene due to out-of-plane vibrations [5]. Despite the sophisticated concepts behind the thermal expansion in various carbon materials, the arrangement of different types of covalent bond is one of the most crucial parameters to determine thermal expansion. Following the arguments of energy minimization, our work enables to study the thermal effect on the chemical bond and atomic distributions of the carbon chains and presumably identifies the bond softening temperature, thermal expansion and elastic modulus. As the variety of bond distributions alternate the energy state of the carbon chains, the average energy will be analyzed in beta (i.e. $\ldots = C = C = C = \ldots$) and alpha (i.e. $\ldots - C \equiv C - C \equiv \ldots$) phase respectively. In the second part of the simulation, we will study the factors affecting the bond softening temperature of the carbyne. The melting transition across the carbyne via heat capacity as a series of temperatures will be implemented as well. Many Monte Carlo calculations of the material science only limits in dimensionless temperature such as magnetic spin interactions [11—14,17,20,21], therefore a plenty of theoretical works have been bounded into DFT only to predict the physical properties of carbyne [8—10]. However, using Monte Carlo method to study the carbyne is not fully established and therefore our group creates an alternative path to make it works in the Kelvin! The simulation involves 10 carbyne chains ordered in the 2D hexagonal array and each nanowire carries 50 carbon atoms (unless otherwise specify).

2. Simulation model

The first part of the Monte Carlo simulation calculates the redistribution of the covalent bond at various temperatures but meanwhile readjusting the new atomic coordinates with help of Metropolis algorithm [11—14].

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

Assume the scattering time is temperature independent, the Hamiltonian H is

$$H = e^{-T/T_{bj}} \sum_{m=1}^{M} \sum_{n=1}^{N-1} \left| E_{m,n,j} e^{-\frac{\left(r_{m,n}-r_{m,n,j}^{eq}\right)}{0.5 r_{m,n,j}^{eq}}} - E_2 \right| + e^{-T/T_{bj}} \sum_{m=1}^{M}$$

$$\times \sum_{n=1}^{N-1} J_A (\cos\theta + 1)^2 - 4\phi \left[\sum_{n,m} \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12} \right]$$

where M, N, E_2, T are the total number of chains, the total number of carbon in each chain, double bond energy and temperature respectively. The formation in single, double and triple bond corresponds to $j = 1, 2$ and 3 respectively. The j is a stochastic variable in the simulation. The r is computed in Cartesian coordinate and $r_{m,n,j}^{eq}$ is equilibrium position. For example, $r_{5,18,1}^{eq}$ refers to the equilibrium position of 18th atom along 5th chain which is connected by single bond. The temperature to break the covalent bond T_{bj} is determined by $E_j = k_B T_{bj}$ where Boltzmann constant $k_B = 1.38 \times 10^{-23} JK^{-1}$. The Van der Waal's energy E_{vdw} is the only interaction between the adjacent carbon chains with the sample length τ_s. Based on the hexagonal structure, periodic boundary condition applies along XY plane so that every carbon atom interacts laterally with the three nearest neighbors via Van der Waal's force as shown in Fig. 1.

The inter-chain separation is 0.3 nm. The Van der Waal's constant, ϕ and σ, are calculated in combination [15,18] with $\tau_s \frac{dE_{vdw}^2}{d\tau_s^2} = \frac{1}{\zeta}$ and $\frac{dE_{vdw}}{dx}\Big|_{x^{eq}} = 0$. A measure of the volume changes as a response to the pressure changes at constant temperature T and entropy S are almost the same in solid, i.e. $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \sim -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$. It makes the negligible distinction between isothermal compressibility ζ and isentropic compressibility [15] and hence $\zeta \sim \frac{1}{\rho v^2}$ is applicable here. After all, the calculation yields the ϕ and σ are $8.1 \times 10^{-23} J$ and $1.23 \times 10^{-10} m$ respectively. We set the angular energy J_A to be 600 kJ/mol but the actual angular energy will be weakened by $(\cos\theta + 1)^2$. For example, $J_A(\cos\theta + 1)^2$ equals to 0 in the straight carbon chain because the pivot angle formed by three adjacent carbon atoms is 180°. The single bond, double bond and triple bond
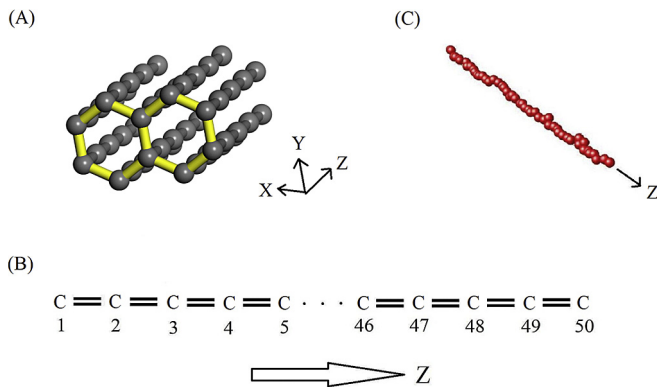
(A)   (C)

(B)

$$C = C = C = C = C \cdots C = C = C = C = C$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \qquad 46 \quad 47 \quad 48 \quad 49 \quad 50$$

$\Longrightarrow Z$

Fig. 1. A - The 3D view of the carbon chains. The yellow color which does not represent covalent bond marks the hexagonal structure. For clarity reason, only 5 atoms (instead of 50 atoms) are drawn in each chain. **B -** The chains are propagating along z axis at initial condition. **C –** The simulation results of one of the carbon chains at 300 K with the averaged atomic spacing of 134.8pm along Z axis. (A colour version of this figure can be viewed online.)

energy at 300 K are 348 kJ/mol, 614 kJ/mol and 839 kJ/mol respectively [16]. The $C - C, C = C$ and $C\equiv C$ bond length are $r_{m,n,1}^{eq} = 154$ pm, $r_{m,n,2}^{eq} = 134$ pm and $r_{m,n,3}^{eq} = 120$ pm respectively [16].

In the model all carbons are initially connected by double bond and separated by 134pm. At each Monte Carlo step the carbon is selected randomly. The selected atom starts to move to new coordinate and also change the types of covalent bonds. The kinematics of the selected carbon with atomic mass M is governed by $dz = \pm p\tau \sqrt{\frac{k_B T}{M}}$ at any temperature T. Here the scattering time τ of the atom is defined as the time to travel the covalent radius. The root-mean square-velocity of the carbon within one period of motion along Z axis is calculated by Hamiltonian of 1D harmonic-oscillator separately [15]. As a result, τ is around $1.96 \times 10^{-13} s$ at room temperature. As the rate of collision may amend from place to place due to stochastic process, the random number so called frictional factor p, varies from 0.01 to 0.99 to represents the Stochastic collision. The dz is positive if the random number R_z within 0 and 1 is greater than 0.5. However, once the R_z is less than or equal to 0.5, the dz becomes negative. Similarly, the sign of dx and dy are controlled by their corresponding random number R_x and R_y between 0 and 1 respectively. The $dx > 0$ if $R_x > 0.5$, otherwise the $dx < 0$. The same cut-off value, 0.5, is applied to the sign convention along Y axis. The out-of-chain vibration is likely weaker than the in-chain vibration. As a result, $dx = dy = \frac{k_B T}{(E_{m,n,1}+E_{m,n,2}+E_{m,n,3})/3} dz$. Another random number $0 \leq R_{bond} \leq 1$ controls the types of covalent bonds, the selected $C = C$ double bond is allowed to switch into $C\equiv C$ triple bond ($R_{bond} \geq 0.5$) or $C - C$ single bond ($R_{bond} < 0.5$).

When temperature becomes higher, the selected site may be switched to single bond, triple bond or remain in double bond according to the energy minimization and Octet rule [13]. Only 8 electrons are allowed in the outermost shells in presence of the Octet rule and no lone pair electron is allowed to generate. We also include the possibility that once the double bond is excited to either single or triple bond, it can revert back to double bond. The strength of covalent bond is softened by thermal energy in parallel. If the energy difference E_{diff} is less positive, the selected atom is allowed to be in motion and/or change the types of covalent bonds simultaneously. Otherwise, it returns to the previous status [17]. Thermal energy is another routine to influence the selected atom [11]. If the new random number $0 \leq R_B \leq 1$ is smaller than Boltzmann probability $e^{-E_{diff}/k_B T}$ [12], the selected carbon will move and/or amend the types of covalent bonds as well. The process will continue until equilibrium. As a remark, the $k_{m,n,j}$, T_{bj} and $x_{m,n,j}^{eq}$ will be amended if the types of covalent bonds is swapped. The interactions are effective in the nearest neighbor only. No metropolis step applies to the 1st carbon atom in each chain as a fixed boundary condition on one end. The Monte Carlo simulation is iterated 100000 times (unless specified otherwise) at each temperature.

The calculation of the elastic modulus is based on the Hamiltonian below. The work $W_{external}$ exerted on the chains is defined as the product of the mechanical deformation dz and applied force F_z along the chain axis.

$$H = e^{-T/T_{bj}} \sum_{m=1}^{M} \sum_{n=1}^{N-1} \left| E_{m,n,j} e^{-\frac{\left(r_{m,n}-r_{m,n,j}^{eq}\right)}{0.5 r_{m,n,j}^{eq}}} - E_2 \right| + e^{-T/T_{bj}} \sum_{m=1}^{M}$$

$$\times \sum_{n=1}^{N-1} J_A (\cos\theta + 1)^2 - 4\phi \left[\sum_{n,m} \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12} \right] + W_{external}$$