

Thermal expansion, elastic modulus and phase transition of carbyne: A stochastic model of chemical bonds distribution

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Abstract:

A plenty of theoretical studies have been conducted by DFT to predict the physical properties of carbon chain. In the present work we develop a powerful Monte Carlo algorithm of the carbon chains ordered into 3D hexagonal array. Our group develops a new routine to probe the phase transition between the alpha and beta carbyne based on the chemical bond and atomic distributions. Our model confirms that the cumulene phase is more energetic preferable at low temperatures but the carbon chain prefers to switch into polyvne phase at high temperatures. The bond softening temperature is observed at 480K. The larger bond softening temperature is observed in the presence of interstitial doping but it does not show length-dependence. The elastic modulus of the carbon chains is 1.7TPa at 5K and the thermal expansion is +70 μ K⁻¹ at 300K via monitoring the resultant atomic vibrations and bond distributions. Thermal fluctuation in terms of heat capacity as a function of temperatures shows that the melting point is around 3800K. The carbon atoms along the carbon nanowire arranged in relaxed state is displayed at the end.

Monte Carlo Simulation:

All carbon atoms are connected by C=C and spaced by 134pm initially at each temperature. The selected atom following the metropolis [1] procedure may move to the new dx, dy, dz and also change the type of bond based on the energy minimization. The inter-chain distance is 0.3nm.

$$H = e^{-T/T_{bj}} \sum_{m=1}^M \sum_{n=1}^{N-1} \left| E_{m,n,j} e^{-\frac{r_{m,n} - r_{m,n}^{eq}}{0.5 r_{m,n}^{eq}}} - E_2 \right| + e^{-T/T_{bj}} \sum_{m=1}^M \sum_{n=1}^{N-1} J_A \cos \theta + 1^2 - 4\varphi \left[\sum_{n,m} \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] + W_{external}$$

$$dz = \pm 3.8 \times 10^{-12} p \sqrt{T} \quad dx = dy = \frac{kT}{E_1 + E_2 + E_3 / 3} dz$$

For example, $r_{12,8,1}$ refers to the equilibrium position of 12th atom along 8th chain which is connected by single bond. The breakdown temperature of the covalent bond T_{bj} is found by $E_j = kT_{bj}$ where k is Boltzmann constant and $J_A = 1 \times 10^{-18} J$. $\sigma = 1.23 \times 10^{-10} m$, $\varphi = 8.1 \times 10^{-23} J$, θ is the pivot angle between the three nearest atoms, W is the mechanical work done with the parallel force $F_z = 8.1 nN$ and p is the frictional factor which is a random number between 0 and 1. N is the total number of atoms along the chain while M is the total number of chains. The type of covalent bond is governed by Octet rules and no lone pair electron is allowed to generate at equilibrium. [2]

Figure 1: (a) The cross section of the hexagonal carbyne. (b) The atomic arrangement of the carbon at initial condition. (c) Simulation results of the relaxed carbon nanowire.

Figure 3: The Peierls transition temperature is increased by the decrease of MPF because more thermal energy is required to rearrange the atomic positions

Figure 5: The melting point of the carbon nanowire is in the range of few thousands Kelvin. The anomaly is activated at 3500K and returns to zero above 6000K.

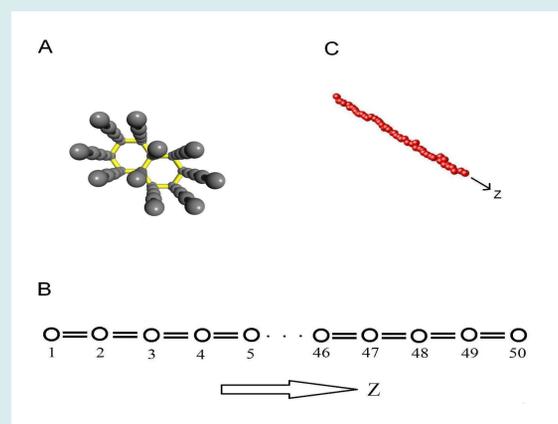


Figure 2: The probability of retaining double bonds reduces upon heating. More single and triple bonds are formed upon heating due to Boltzmann excitation across Peierls transition.

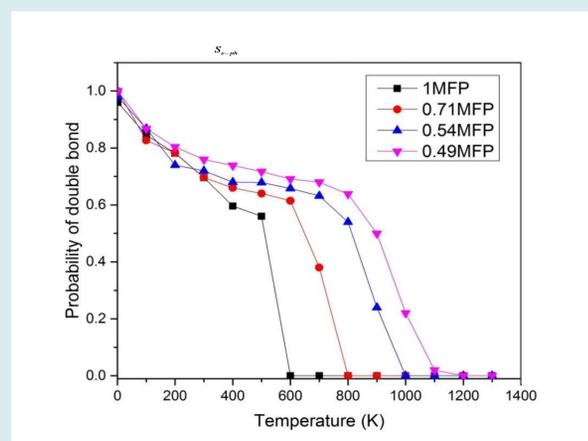
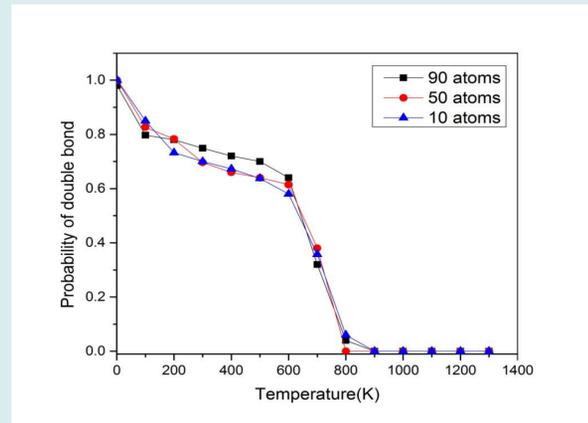
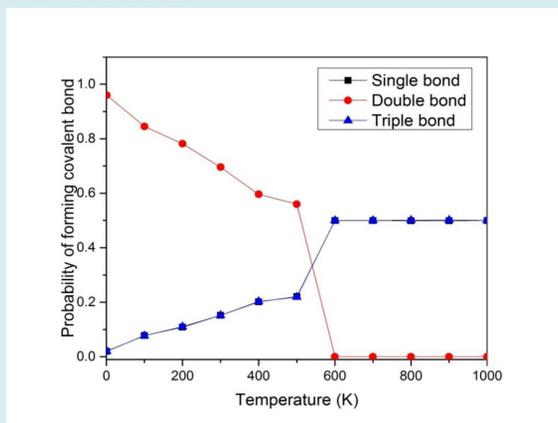
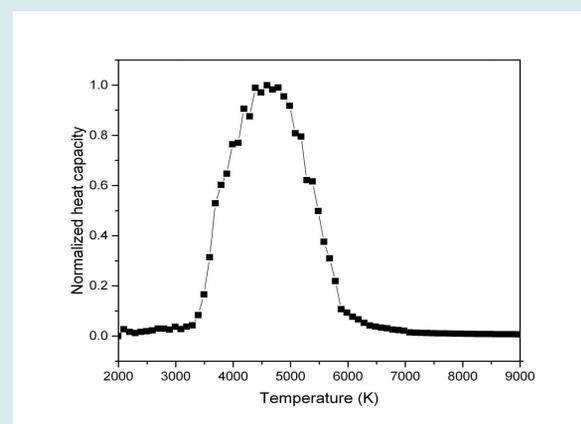


Figure 4: The Peierls transition temperature does not influenced by chain length because the atomic mean free path (0.71MPF) remains unchanged.



References:

- [1] V. V. Prudnikov, et al, Investigation of the effects of aging and temperature dependence of the transverse rigidity of a system in the two-dimensional XY model, The Physics of Metals and Metallography, Volume 115, Issue 12, pp 1186-1193 (2014)
- [2]: C.H.Wong*, E.A. Buntov, V.N. Rychkov, M.B. Guseva, A.F. Zatsepin, Simulation of chemical bond distributions and phase transformation in carbon chains, Carbon, Volume 114, Pages 106-110 (2017)