Chapter 12
Nanostructures Cluster Models in Solution: Extension to C, BC$_2$N, and BN Fullerenes, Tubes, and Cones

Francisco Torrens
Universitat de València, Spain
Gloria Castellano
Universidad Católica de Valencia, Spain

ABSTRACT

The existence of Single-Wall C-Nanocones (SWNCs), especially nanohorns (SWNHs), and BC$_2$N/Boron Nitride (BN) analogues in cluster form is discussed in solution in this chapter. Theories are developed based on models bundlet and droplet describing size-distribution function. The phenomena present unified explanation in bundlet in which free energy of (BC$_2$N/BN-)SWNCs involved in cluster is combined from two parts: volume one proportional to the number of molecules $n$ in cluster and surface one, to $n^{1/2}$. Bundlet enables describing distribution function of (BC$_2$N/BN-)SWNC clusters by size. From geometrical differences bundlet [(BC$_2$N/BN-)SWNCs] and droplet ($C_{60}/B_{15}C_{30}N_{15}/B_{30}N_{30}$) predict dissimilar behaviours. Various disclination (BC$_2$N/BN-)SWNCs are studied via energetic and structural analyses. Several (BC$_2$N/BN-)SWNC’s ends are studied that are different because of closing structure and arrangement type. Packing efficiencies and interaction-energy parameters of (BC$_2$N/BN-)SWNCs/SWNHs are intermediate between $C_{60}/B_{15}C_{30}N_{15}/B_{30}N_{30}$ and (BC$_2$N/BN-)Single-Wall C-Nanotube (SWNT) clusters: in-between behaviour is expected; however, properties of (BC$_2$N/BN-)SWNCs, especially (BC$_2$N/BN-)SWNHs, are calculated closer to (BC$_2$N/BN-)SWNTs. Structural asymmetry in different (BC$_2$N/BN-)SWNCs characterized by cone angle distinguishes properties of types: P2. BC$_2$N/BN, especially species isoelectronic with C-analogues may be stable.

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INTRODUCTION

Nanoparticles (NPs) interest arose from the shape-dependent physical properties of nanoscale materials (Faraday, 1857; Murphy et al., 2010). Single-wall C-nanocones (SWNCs) were used to study the nucleation/growth of curved C-nanostructures (NSs) suggesting pentagon role. When a pentagonal defect is introduced into a \( C_{\text{graphene}} \) sheet (\( C_{\text{graphene}} \)) via extraction of a 60º sector from the piece a cone leaf is formed. The presence of pentagons in an SWNC apex is analogue of single-wall C-nanotube (SWNT) tip topology. Balaban et al. (1994), Klein (2002) and Klein and Balaban (2006) analyzed the eight classes of positive-curvature graphitic nanocones, and Klein (1992), Misra et al. (2009ab), Balaban & Klein (2009) and Klein & Balaban (2011) examined the Clar theory for conjugated C-NSs. The SWNT ends predicted electronic states related to topological defects in \( C_{\text{graphene}} \) lattice (Tamura & Tsukada, 1995). Kim et al. (1999) observed resonant peaks in the density of states in SWNTs and Carroll et al. (1997), in multiple-wall C-nanotubes (MWNTs).

Krishnan et al. (1997) observed SWNCs with discrete opening angles \( \theta \) of ca. 19, 39, 60, 85 and 113º in C-sample generated by hydrocarbon pyrolysis. Observation was explained by a cone wall model composed of wrapped \( C_{\text{graphene}} \) sheets, where geometrical requirement for seamless connection naturally accounted for semi-discrete character and absolute angles \( \theta \). Total disclinations are multiples of 60º corresponding to number \( P \geq 0 \) of pentagons in SWNC apices. Considering \( C_{\text{graphene}} \)-sheet symmetry and Euler theorem five SWNC types are obtained from continuous \( C_{\text{graphene}} \) sheet matching to \( P = 1 \sim 5 \). Angle results \( \theta = \sin(\theta/2) = 1 - P/6 \), leading to flat discs and caped SWNTs corresponding to \( P = 0, 6 \), respectively; most abundant SWNC with \( P = 5 \) (\( \theta \approx 19^\circ \)) is single-wall C-nanohorn (SWNH). Several configurations exist for given SWNC angle depending on pentagon arrangement. According to isolated pentagon rule (IPR) configurations containing isolated pentagons lead to isomers that are more stable than those including grouped ones (Kroto, 1987); Han & Jaffe (1998) derived another rules from \textit{ab initio} calculations. Covalent SWNCs functionalization with \( \text{NH}_3^+ \) improved solubility (Tagmataris et al., 2006), which was achieved by skeleton (Cioffi et al., 2006, 2007; Pagona et al., 2007b)/cone-end (Pagona et al., 2006a) functionalization and supramolecular \( \pi-\pi \) stacking interactions (Pagona et al., 2006b, 2007a; Zhu et al., 2003) with pyrenes/porphyrins. An MNDO calculation of BN substitutions in \( C_{\text{60}} \) showed that analogous one gave \( B_{30}N_{30} \) (Xia et al., 1992). Atom substitution in \( C_{\text{diamond}} \) by alternating B/N atoms provided BN-cubic (Silaghi-Dumitrescu et al., 1993). BN-hexagonal (h) resembles \( C_{\text{graphite}} \) since it consists of fused planar six-membered \( B_2N_2 \) rings; however, interlayer B–N interactions exist. Hamilton et al. (1993, 1995) and Loiseau et al. (1996) visualized BN nanotubes. Rubio et al. (1994) proposed BN-h. Bourgeois et al. (1999, 2000) and Terauchi et al. (2000) observed BN nanocones, and Mota et al. (2003) and Machado et al. (2003abc, 2004, 2005) calculated them; most abundant ones presented 240/300º disclinations. Thesing et al. (2006) computed BN/AlN nanotube junction. Calculations of \( BC_2N_2 \) tubules (Miyamoto et al., 1994) and \( C_{\text{graphene}} \)-like onion/nanotube production using layered materials (e.g., \( WS_2 \) (Tenne et al., 1992), \( MoS_2 \) (Margulis et al., 1993), \( BC_2N \), \( BC_3 \) (Weng-Sieh et al., 1995), BN (Chopra et al., 1995)) allowed structures with oxidation resistance and low thermal/electronic conductivities. The NSs of pyrolytically grown \( B,C,N \), were studied: concentration profiles along/across tubes revealed that B, C and N are separated into C/BN domains; compound provides materials that are useful as robust nanocomposites (NCs) and semiconductor devices enhanced towards oxidation (Kohler-Redlich et al., 1999; Madden, 2009; Terrones et