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1. Introduction

1.1. Literature review

Boron nitride nanotubes (BNNTs) have a structure similar to carbon nanotubes, but with different properties [1] due to the polarity of B-N bonds. In the past, high-quality BNNTs have been synthesized at high temperatures using arc discharges [2, 3], laser ablation [4-6], and inductively-coupled plasma (ICP) torches [7–9]; at relatively low temperatures, BNNT synthesis has been performed via ball-milling [10] and

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Boron nitride nanotube precursor formation during high-temperature synthesis: kinetic and thermodynamic modelling

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Abstract

We performed integrated modelling of the chemical pathways of formation for boron nitride nanotube (BNNT) precursors during high-temperature synthesis in a B/N_2 mixture. Integrated modelling includes quantum chemistry, Quantum-classical molecular dynamics, thermodynamic modelling, and kinetic approaches. We demonstrate that BN compounds are formed via the interaction of molecular nitrogen with small boron clusters, rather than through interactions with less reactive liquid boron. (This process can also be described as N2 molecule fixation.) Liquid boron evaporates to produce these boron clusters (B_m with $m \leq 5$), which are subsequently converted into $B_m N_n$ chains. The production of such chains is crucial to the growth of BNNTs because these chains form the building blocks of bigger and longer BN chains and rings, which are in turn the building blocks of fullborenes and BNNTs. Additionally, kinetic modelling revealed that B_4N_4 and B_5N_4 species in particular play a major role in the N₂ molecule fixation process. The formation of these species via reactions with B_4 and B_5 clusters is not adequately described under the assumption of thermodynamic equilibrium, as is demonstrated in our kinetic modelling. Thus, the accumulation of both B₄N₄ and B₅N₄ depends on the background gas pressure and the gas cooling rate. Long BN chains and rings, which are precursors of the fullborene and BNNT growth, form via self-assembly of components B_4N_4 and B_5N_4 . Our modelling results—particularly the increased densities of B_4N_4 and B_5N_4 species at higher gas pressures—explain the experimentally observed effect of gas pressure on the yield of highquality BNNTs. The catalytic role of hydrogen was also studied; it is shown that HBNH molecules can be the main precursor of BNNT synthesis in the presence of hydrogen.

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)



chemical vapor deposition [11–13]. High-temperature synthesis by arc discharges or ICP torches involves the injection of N₂ gas and B powder into the plasma zone first [7], where the gas temperature is high enough (>8000 K [8]) to completely vaporize the boron powder while the molecular nitrogen stays intact [14]. The gas then flows into the cooler afterglow zone, where synthesis of BNNTs occurs. In this zone, the gas temperature drops precipitously at a rate of about $\sim 10^5$ K s⁻¹ [8]. It was experimentally observed that the growth of BNNTs begins at ~ 3000 K [9]; therefore, to accurately predict how BNNTs form in these high temperature synthesis scenarios, we have made an effort to predict the gas composition as the mixture cools down from 8000 to 2000 K.

There are many aspects of BNNT growth that are not well understood [15]. Three growth mechanisms have previously been discussed in the literature: root growth [4, 8], open-end growth [16], and growth by self-assembly [17].

In the root growth model, BNNTs grow on the surface of boron droplets, and growth occurs at the point of attachment to the droplet (the root). Boron droplets are formed at temperatures (\sim 4100 K at 1 atm. [18]) significantly higher than the temperature of BNNT growth, so droplet formation occurs earlier in the gas cooling process. According to the root-growth mechanism, atomic nitrogen, molecular nitrogen, or B–N gas species are dissolved in the droplets, and these molecules feed the growth of BNNTs [9, 17, 19].

A related mechanism of BNNT formation is open-end growth, in which B–N compounds react with an unattached end of a BNNT. The other end of the nanotube may be attached to a boron droplet, though not necessarily [16].

The third mechanism, growth by self-assembly, was discussed in [17]. Based on molecular dynamic (MD) simulations, Han and Krstic suggested that BNNT formation can occur without boron droplets via the self-assembly of small species with B–N bonds, such as BN dimers. However, the production of these species with B–N bonds was not investigated. Here, we have focused on precursor formation for this self-assembly mechanism of BNNT growth.

In our early research [14] it was shown that small B–N species such as BN, B₂N, and N₂B are generated in boron and nitrogen gas mixtures. However, the thermodynamic equilibrium densities of all small B–N compounds considered in that study were shown to be very low compared to the densities of molecular N₂ and liquid boron at temperatures suitable for BNNT growth (\sim 2600 K). Considering our earlier research, which demonstrated that N₂ molecules do not directly react with liquid boron droplets [19], *it remained unclear how N₂ molecules and liquid boron are converted into compounds that contain B–N bonds. The main goal of this study is to understand this crucial step of nitrogen fixation in the BNNT synthesis process.*

1.2. Our contribution

In our previous thermodynamic approach [14] we studied the B–N mixture composition at equilibrium and we only considered small species that contain B–N bonds (BN, B_2N , N_2B). In this study, we significantly expanded the number of

B–N species under consideration, adding $B_m N_n$ chains and $B_n N_n$ fullborenes (section 2.2). We showed that at temperatures near 2600 K or slightly higher, particular $B_m N_n$ chain species have the highest densities in the reaction mixture, while at T < 2600 K fullborenes become the major component. The densities of small B–N gas species, such as BN, N_2B and B_2N , have a maximum value at temperatures near the boron condensation point (4100 K at 1 atm) and drop quickly as the gas cools. This contradicts previous assumptions that these species act as direct precursors for BNNT growth [14, 17, 19]. In summary, the densities of the small B–N species are very low near the BNNT growth temperature (~2600 K), but the densities of $B_m N_n$ chains at this temperature are high. Therefore, we conclude that the latter are precursors in the formation of BNNTs.

In addition, we show that these $B_m N_n$ chains are synthesized via reactions between molecular nitrogen and small boron clusters (B_m with $m \leq 5$) at temperatures ranging from the temperature of BNNT growth (~ 2600 K) to the boron condensation point (4100 K at 1 atm.). This process is the mechanism for N₂ fixation during high temperature BNNT synthesis. Liquid boron droplets act as a source of B_m clusters in the gas phase, but do not themselves fix nitrogen molecules. Small boron clusters in gas phase should have a higher reactivity than liquid boron, and smaller clusters should have a higher reactivity than larger clusters [20]. (For example, the reactivity of B_7^+ clusters with N₂O is much smaller compared to that of B_6^+ clusters.) This is due to the fact that larger boron clusters are more coordinatively saturated (have fewer dangling bonds). Further research is needed to systematically study the transformation of $B_m N_n$ chains into BNNTs, and to investigate additional details regarding the role of boron droplets in this transformation. (See the Discussion section.)

We also report that the effectiveness of the fixation of N_2 depends on the process conditions. *Namely, it is shown that boron consumption and* B_mN_n *chain generation can be enhanced by increasing the background gas pressure, by slowing the gas cooling rate, and by decreasing the initial boron fraction in the reaction mixture.*

1.3. Organization of the paper

The organization of the paper is as follows: details of the computational methods used and the results of modeling are discussed in section 2. This includes an investigation into the binding energy and thermodynamic stability of B_mN_n clusters by calculation of their Gibbs free energies in section 2.1, global modelling of the equilibrium mixture composition in section 2.2, quantum chemistry (QC) studies of the reaction pathways for N₂ fixation in section 2.3, global kinetic modelling of the N₂ fixation process with time-dependent reaction rates in section 2.4, and finally Quantum–classical molecular dynamics (QCMD) simulations of small B_mN_n chains aggregating into larger B_mN_n chains in section 2.5. Discussion of the results and conclusions are addressed in sections 3 and 4, respectively.

2. Computational results

Here we describe the multiple approaches used to model BNNT precursor formation. First, we determined the composition of the gas mixture as a function of temperature for pressures of 1 atm and higher under the assumption of thermodynamic equilibrium. This method is referred to throughout the paper as the 'thermodynamic approach.' Next, chemical kinetic calculations were carried out to check whether or not the assumption of thermodynamic equilibrium is valid during typical gas cooling conditions for BNNT synthesis.

Thermodynamic and kinetic modelling requires the calculation of chemical potentials (the standard Gibbs free energy $\Delta_f G^0$) and rate constants for each relevant reaction. These were obtained through DFT (density functional theory) QC calculations using the GAMESS software package [21]. We used an unrestricted WB97X-D [22, 23] hybrid functional and the 6-311 + G(2dp) basis set. For large $B_n N_n$ clusters, where n > 13, the Gaussian-16 software package [24] and 6-31 + G(d) basis set were used.

Reaction paths, some of which are described in section 2.3, were investigated using DFT methods, and in some cases MCSCF (multi-configuration self-consistent field) methods [25] were also used to verify the DFT approach. The MCSCF method includes single- and double-excitations (MCSCF-SD) with 30776 configuration state functions in the active space. The geometries of all considered structures were first optimized using DFT and then, if applicable, further optimized using MCSCF-SD, at which point single point energy calculations were carried out using MCSCF with single-, double- and triple-excitations (MCSCF-SDT) without further optimization. All transition states (TSs) were identified by the presence of one imaginary frequency in the Hessian matrix and by an IRC method (intrinsic reaction coordinate).

Reaction paths for molecules larger than BNBN were optimized using the DFT method only, as MCSCF calculations are more computationally intensive. Further details on the applicability and accuracy of DFT approaches are discussed in the supplementary material (available online at stacks.iop.org/NANO/32/475604/mmedia), on an example of BN₂ molecule formation [26].

The calculated rate constants k_i of the gas phase reactions, which are used in the kinetic model (section 2.4), can be found in the supplementary materials. All rate constants are presented in the Arrhenius form:

$$k_i = A_i * (T/298.15)^n * \exp\left(-\frac{E_a(i)}{k_B T}\right).$$
(1)

The reaction activation barrier of a given reaction, $E_a(i)$, is the total electronic energy difference between the transition state (saddle point on a potential energy surface) and the reactants (or product). Reactants, products and transition states were localized on the potential energy surface (PES) using WB97X-D DFT functional. PES of the reaction pathways relevant to the N₂ fixation process can be found in figure 4. The reactions of B₁₂N₁₂ and B₂₄N₂₄ monocyclic

rings folding into the corresponding fullborenes can be found

in the supplementary materials. The pre-exponential factors used in calculating the rate constants were calculated using Eyring equation [27]

$$A'_{i} = \frac{k_{B}T}{h} \times \left(\frac{Z_{tot}^{TS}}{Z_{tot}^{Re}}\right),\tag{2}$$

where k_B , T and h are Boltzmann's constant, Planck's constant, and temperature, respectively. Z_{tot}^{TS} and Z_{tot}^{Re} are the overall partition functions of the transition state and reactant geometries. A'_i is a function of temperature; it was fitted using the standard form in a temperature range from 2000 to 6000 K:

$$A'_{i} = A_{i} \left(\frac{T}{298.15}\right)^{n}.$$
 (3)

The partition functions were calculated using a harmonic oscillator approximation by the GAMESS software package.

A schematic diagram of the calculation methods used in our research is presented in figure 1. A DFT approach was used to study the reactions leading to N₂ molecular fixation and the process of B_nN_n chains folding into the corresponding fullborene structure, as well as to calculate rate constants for these reactions and standard Gibbs free energies of formation $(\Delta_f G^0)$ for the new B–N compounds. The calculated $\Delta_f G^0$ and the rate constants were used as parameters in thermodynamic and kinetic modelling, respectively.

QCMD was used to investigate reactions involving the merging of B_3N_3 rings into longer chains and fullborenes. The self-consistent charge density functional tight binding (SCC-DFTB) approximation was used while performing these simulations. All SCC-DFTB [28] simulations were conducted using the DFTB + [29] software package. The 'matsci-0-3' parameter sets were used for the simulations. These parameter sets are created using semi-relativistic, self-consistent charge Slater–Koster tables [30, 31]. Periodic Boundary Conditions and Nose–Hoover thermostat were applied for all calculations. The results of QCMD simulations were visualized using the software Jmol [32].

2.1. Thermodynamic analysis: stability of B-N clusters

Before investigating the composition of the gas mixture at thermodynamic equilibrium, we first discuss general trends in the stability of B–N monocyclic rings, linear chains, and fullborenes. The geometries of the studied species are depicted in the supplementary materials and in figure 2(a). We begin by considering the initial reactants which eventually produce these B–N clusters through the nitrogen fixation process:

$$mB + \frac{n}{2}N_2 \to B_m N_n. \tag{4}$$

For a variety of B–N monocyclic rings, linear chains, and fullborenes, we performed DFT calculations of the binding energy per reactant, defined as:

$$\Delta E_{norm} = \frac{E(B_m N_n) - mE(B) - \frac{n}{2}E(N_2)}{m + \frac{n}{2}},$$
 (5)



Figure 1. Schematic diagram describing computational techniques which were used in our research.

where $E(B_m N_n)$, E(B), and $E(N_2)$ are the total electronic energies (calculated using WB97X-D DFT functional) of the product and reactant molecules (corrected for the zero-point vibrational energy of each molecule). A plot depicting the value of ΔE_{norm} and its dependence on the size of the B–N clusters is shown in figure 2(a).

The rate of change of ΔE_{norm} as a function of B–N cluster size is large when the clusters are small. However, the strain of the clusters decreases with elongation, and for long chains (m > 13), ΔE_{norm} only weakly depends on the cluster size.

Only chains and rings with $m \leq 13$ were considered. We assume that the longer chains will be less stable at high temperatures, given that ΔE_{norm} weakly depends on chain length for long chains, and that the entropy-related factor in the standard Gibbs free energy of the chains should increase as the length of the chain increases. Carbon chains of comparable size have been observed in [33–36]. In these studies carbon clusters C_n were generated by laser desorption, after which various isomers of C_n were identified by mass-spectrometry and ion chromatography. This analysis showed that carbon chains with linear structure exist up to C_{10}^+ . Reference [37] performed a similar investigation of the equilibrium mixture composition with carbon chains smaller than n = 9.

The standard Gibbs free energies of gas phase $B_m N_n$ species depend on ΔE_{norm} according to the following equation [31]:

$$\Delta_{f} G^{0}(B_{m}N_{n}) = \left(m + \frac{n}{2}\right) \Delta E_{norm} - k_{B}T \left[\ln\left(Z(B_{m}N_{n})\right) - m * \ln\left(Z(B)\right) - \frac{n}{2} * \ln\left(Z(N_{2})\right)\right] + m * \Delta_{f}G^{0}(B(gas)),$$
(6)

where Z is the total partition function, k_B is the Boltzmann constant, and $\Delta_f G^0(B(gas))$ is given in the NIST database [18].

The contribution of ΔE_{norm} into $\Delta_f G^0$ is significantly greater for species with $m \ge 4$. (See figure 2(a).) As a result, the standard Gibbs free energy of larger species like B₄N₄ and B₅N₄ monotonically decreases as temperature decreases, as is evident in figure 2(b). In contrast, for smaller species such as BNBN and B₃N₂, the standard Gibbs free energy is a nonmonotonic function of temperature and has a minimum near the boron condensation point.

2.2. Thermodynamic modeling: equilibrium mixture composition

Having calculated the standard Gibbs free energy for each B-N species, we then minimized the total Gibbs free energy to determine the composition of the gas mixture at thermodynamic equilibrium for a variety of different temperatures; for further details see [14]. The results of this thermodynamic modeling are shown in figure 3.

The densities of long ($m \ge 4$) $B_m N_n$ chains peak in a narrow temperature range, approximately between 2400 and 2800 K at 1 atm, and between 2400 and 3600 at 10 atm.

For the purpose of the thermodynamic modeling, we used $B_{44}N_{44}$ fullborenes to represent BNNTs. Real BNNTs are significantly larger than the $B_{44}N_{44}$ clusters, and are more thermodynamically stable at low temperatures. Thus, BNNTs are more likely final products. However, the $B_{44}N_{44}$ clusters are suitable proxies for larger BNNT molecules in these thermodynamic calculations, as their formation begins at T < 2600 K, which corresponds to the temperature suitable for BNNT formation (figure 3).



Figure 2. Binding energy of $B_m N_n$ clusters (ΔE_{norm}) per reactant (m = n or n+1), dependent on the cluster size and geometry (a). Calculated standard Gibbs free energies of formation (b).

 B_m clusters with $m \le 5$ have much higher densities than larger B_m clusters for all temperatures. Thus, only these species are considered as sources of boron in our modeling of the N₂ fixation process. As shown in the next sections, these boron clusters participate in reactions with N₂ to form BNBN, B₃N₄, B₄N₄ and B₅N₄ molecules.

The thermodynamic calculations show that liquid boron is fully consumed by the time the gas has cooled to the boron solidification temperature ($\sim 2300 \text{ K}$ [18]). (See figure 3.) The equilibrium mixture composition at 1 atm and 10 atm is shown in figures 3(a) and (b). Note that liquid boron disappears at temperatures below 2800 K at 1 atm and below 3600 K at 10 atm. This demonstrates that higher pressures promote liquid boron consumption.

The addition of H_2 into the B/N_2 mixture leads to the formation of a significant amount of HBNH (iminoborane) molecules, as shown in figure 3(c). Note that similar to the B–N rings and chains, HBNH density increases with decreasing



Figure 3. Typical equilibrium densities for a variety of molecules for (a) a B/N_2 mixture at 1 atm, (b) a B/N_2 mixture at 10 atm, and (c) a $B/N_2/H_2$ mixture at 1 atm.

temperature until BNNT growth begins. Correspondingly, this molecule can play a key role in the synthesis of BNNTs in the presence of hydrogen. (See discussion section.)

2.3. Reaction pathways for N_2 fixation via interaction with B_2 , B_3 , B_4 , and B_5 clusters

The B_m clusters with $m \leq 5$ have the highest densities after boron condensation, as discussed in the previous section. Here, we present a detailed chemical mechanism for N_2 fixation via reactions with these clusters and describe the relevant energies and geometries along the reaction pathways.

Calculated reaction paths of nitrogen fixation resulting in the production of BNBN, B_3N_2 , B_4N_4 and B_5N_4 are shown in figure 4. It requires several steps to achieve the most stable geometry, which corresponds to a global minimum on the PES. The highest barriers to dissociation for BNBN, B_3N_2 , B_4N_4 and B_5N_4 are significantly larger for the larger molecules (2.5, 4.8, 5.8 and 6.0 eV, respectively).

The reaction path for the transformation of B₂ and N₂ dimers into BNBN is depicted in figure 4(a). Four transition states (TSs) have been localized (TS1, TS2, TS3, TS4) using both DFT and MCSCF methods. The first reaction step is the formation of a linear BBNN molecule, which proceeds through a fairly low energy barrier (~ 0.23 eV). It should be noted that the BBNN molecule structure is located in a deep local minimum on the PES (figure 4(a)). This explains experimental data presented in [32], where BBNN molecule formation has been observed in addition to the formation of the more stable BNBN molecule. The second step through TS2 is the highest barrier along the reaction pathway in the forward direction, and results in the formation of a planar BBN_2 molecule. In the third step the BBN_2 molecule is transformed into a planar B₂N₂ molecule through TS3. The B₂N₂ molecule is the most unstable isomer and it is transformed into the linear BNBN molecule through TS4. Note that both DFT and MCSCF approaches reproduce qualitatively the same reaction path for BNBN molecule formation. For reactions with larger clusters shown in figures 4(b)-(f), only a DFT approach was used.

This modelling demonstrates that reactions between small B_m clusters N_2 dimers result in nitrogen fixation and B_- N molecule generation without the presence of atomic nitrogen. Such mechanisms require less energy than the atomization of N_2 dimers; while the N_2 bond energy is 9.8 eV, the highest barrier towards BNBN molecule formation from the proposed series of reactions described above is only 1.10 eV.

Calculated rate constants (see equation (1)) for the reaction steps presented in figure 4 can be found in the supplementary materials. These rate constants are used in the kinetic modeling described in the next section.

2.4. Kinetic modeling of N₂ fixation

In this section we consider kinetic modeling of the formation of BNBN, B_3N_2 , B_4N_4 and B_5N_4 species through reactions between N_2 molecules and B_2 , B_3 , B_4 and B_5 clusters, respectively. Based on the chemical reaction pathways established in the previous section, reaction rate constants were determined and the kinetic equations describing the time evolution of species' densities were numerically solved. The systems of differential equations describing BNBN, B_3N_2 , B_4N_4 , and B_5N_4 formation are presented below.

2.4.1. BNBN generation

$$\frac{dC_{BBNN}(t)}{dt} = \vec{k1}C_{B2}^{eq}(t)C_{N2}(t) - (\vec{k1} + \vec{k2})C_{BBNN}(t) + \vec{k2}C_{BBN2}(t),
\frac{dC_{BBN2}(t)}{dt} = \vec{k2}C_{BBNN}(t) - (\vec{k2} + \vec{k3})C_{BBN2}(t) + \vec{k3}C_{B2N2}(t),
\frac{dC_{B2N2}(t)}{dt} = \vec{k3}C_{BBN2}(t) - (\vec{k3} + \vec{k4})C_{B2N2}(t) + \vec{k4}C_{BNBN}(t),
\frac{dC_{BNBN}(t)}{dt} = \vec{k4}C_{B2N2}(t) - \vec{k4}C_{BNBN}(t).$$
(7a)

2.4.2. B_3N_2 generation

$$\frac{dC_{B3N2(1)}(t)}{dt} = \vec{k1}C_{B3}^{eq}(t)C_{N2}(t) - (\vec{k1} + \vec{k2})C_{B3N2(1)}(t) + \vec{k2}C_{B3N2(2)}(t),$$

$$\frac{dC_{B3N2(2)}(t)}{dt} = \overline{k2}C_{B3N2(1)}(t) - (\overline{k2} + \overline{k3})C_{B3N2(2)}(t) + \overline{k3}C_{B3N2(3)}(t),
\frac{dC_{B3N2(3)}(t)}{dt} = \overline{k3}C_{B3N2(2)}(t) - (\overline{k3} + \overline{k4})C_{B3N2(3)}(t) + \overline{k4}C_{B3N2}(t),
\frac{dC_{B3N2}(t)}{dt} = \overline{k4}C_{B3N2(3)}(t) - \overline{k4}C_{B3N2}(t).$$
(7b)

2.4.3. B₄N₄ generation

$$\frac{dC_{B4N2(1)}(t)}{dt} = \overline{k1}C_{B4}^{eq}(t)C_{N2}(t) - (\overline{k1} + \overline{k2})C_{B4N2(1)}(t) \\ + \overline{k2}C_{B4N2(2)}(t),$$

$$\frac{dC_{B4N2(2)}(t)}{dt} = \overline{k2}C_{B4N2(1)}(t) - (\overline{k2} + \overline{k3})C_{B4N2(2)}(t) + \overline{k3}C_{B4N2(3)}(t),$$

$$\frac{dC_{B4N2}(t)}{dt} = \overline{k3}C_{B4N2(2)}(t) - (\overline{k3} + \overline{k4}C_{N2}(t))C_{B4N2}(t) + \overline{k4}C_{B4N2}(t),$$

$$\frac{dC_{B4N4(1)}(t)}{dt} = \overline{k4}C_{N2}(t)C_{B4N2}(t) - (\overline{k4} + \overline{k5})C_{B4N4(1)}(t) + \overline{k5}C_{B4N4(2)}(t),$$

$$\frac{dC_{B4N4(2)}(t)}{dt} = \overline{k5}C_{B4N4(1)}(t) - (\overline{k5} + \overline{k6})C_{B4N4(2)}(t) + \overline{k6}C_{B4N4(3)}(t),$$

$$\frac{dC_{B4N4(3)}(t)}{dt} = \overline{k6}C_{B4N4(2)}(t) - (\overline{k6} + \overline{k7})C_{B4N4(3)}(t) + \overline{k7}C_{B4N4}(t)$$

$$\frac{dC_{B4N4(1)}}{dt} = \overline{k7}C_{B4N4(3)}(t) - \overline{k7}C_{B4N4}(t).$$

$$(7c)$$

2.4.4. B_5N_4 generation

$$\frac{dC_{B5N2(1)}(t)}{dt} = \vec{k1}C_{B5}^{eq}(t)C_{N2}(t) - (\vec{k1} + \vec{k2})C_{B5N2(1)}(t) + \vec{k2}C_{B5N2(2)}(t),$$
$$\frac{dC_{B5N2(2)}(t)}{dt} = \vec{k2}C_{B5N2(1)}(t) - (\vec{k2} + \vec{k3})C_{B5N2(2)}(t)$$

$$+ \overleftarrow{k3}C_{B5N2(3)}(t),$$

$$\frac{dC_{B5N2(3)}(t)}{dt} = \overrightarrow{k3}C_{B5N2(2)}(t) - (\overleftarrow{k3} + \overrightarrow{k4})C_{B5N2(3)}(t)$$

$$+ \overleftarrow{k4}C_{B5N2}(t),$$



Figure 4. Calculated reaction paths of N_2 molecule fixation in the reactions with B_2 (a), B_3 (b), B_4 ((c) and (d)), and B_5 ((e) and (f)).

$$\frac{dC_{B5N2}(t)}{dt} = \vec{k4}C_{B5N2(3)}(t) - (\vec{k4} + \vec{k5}C_{N2}(t))C_{B5N2}(t) + \vec{k5}C_{B4N4(1)}(t),$$

$$\frac{dC_{B5N4(1)}(t)}{dt} = \vec{k5}C_{N2}(t)C_{B5N2}(t) - (\vec{k5} + \vec{k6})C_{B5N4(1)}(t) + \vec{k6}C_{B5N4(2)}(t),$$

$$\frac{dC_{B5N4(2)}(t)}{dt} = \overrightarrow{k6}C_{B5N4(1)}(t) - (\overleftarrow{k6} + \overrightarrow{k7})C_{B5N4(2)}(t) + \overleftarrow{k7}C_{B5N4(3)}(t),$$

4

$$\frac{dC_{B5N4(3)}(t)}{dt} = \vec{k7}C_{B5N4(2)}(t) - (\vec{k7} + \vec{k8})C_{B5N4(3)}(t)
+ \vec{k8}C_{B5N4}(t),
\frac{dC_{B5N4}(t)}{dt} = \vec{k8}C_{B5N4(3)}(t) - \vec{k8}C_{B5N4}(t).$$
(7d)

. In these systems of equations, the rate constants of forward and reverse reactions ($\vec{k}i$ and $\vec{k}i$) are related to the TS_i transition states in figure 4. The rate constants depend on temperature, which in turn is assumed to be linearly decreasing with time via a constant gas cooling rate (\dot{T}_0) :

$$T(t) = T_0 - \dot{T}_0 \times t.$$
(8)

Thus, both the rate constants and equilibrium densities of B_m clusters depend on temperature, which in turn depends on a gas cooling rate. Essentially, both rate constants as well as densities of B_m clusters depend on time.

The equilibrium densities of B_m clusters were obtained using the following equation:

$$C_{Bm}^{eq}(t) = C_B^{eq}(t)^m \times K_f(B_m), \tag{9}$$

where $K_f(B_m) = \exp\left(-\frac{\Delta G(B_m)}{RT}\right)$ is the calculated equilibrium constant of B_m formation from boron atoms in gas and C_B^{eq} is the equilibrium density of boron atoms in gas phase. The latter was calculated according to the Clausius–Clapeyron

relation:

$$C_B^{eq}(t) \approx \frac{P}{RT(t)} \times \exp\left(-\frac{\Delta_f G(B, T(t))}{RT(t)}\right), \qquad (10)$$

where $\Delta_f G(B, T(t)) = \Delta_f G^0(B, T(t)) + RT(t) \ln\left(\frac{P}{P_0}\right)$ and $\Delta_f G^0(B, T(t))$ is the standard Gibbs free energy of formation for atomic boron at 1 atm.

The densities of BNBN, B_3N_2 , B_4N_4 and B_5N_4 at chemical equilibrium (C^{eq}) were calculated using the system of equations (7*a*)–(7*d*), taking into account that $\frac{dC(t)}{dt} = 0$ for all species:

$$C_{BNBN}^{eq}(T(t)) = \frac{\sum_{i=1}^{4} \vec{k}_i}{\sum_{i=1}^{4} \vec{k}_i} C_{B2}^{eq}(T(t)) C_{N2}^{eq}(T(t))$$
$$= \frac{\sum_{i=1}^{4} \vec{k}_i}{\sum_{i=1}^{4} \vec{k}_i} C_{B2}^{eq}(T(t)) (1 - x_0(B)) \frac{P}{RT}.$$
 (11a)

$$C_{B3N2}^{eq}(T(t)) = \frac{\sum_{i=1}^{4} \vec{k}_i}{\sum_{i=1}^{4} \vec{k}_i} C_{B3}^{eq}(T(t)) C_{N2}^{eq}(T(t))$$
$$= \frac{\sum_{i=1}^{4} \vec{k}_i}{\sum_{i=1}^{4} \vec{k}_i} C_{B3}^{eq}(T(t)) (1 - x_0(B)) \frac{P}{RT}.$$
 (11b)

$$C_{B4N4}^{eq}(T(t)) = \frac{\sum_{i=1}^{7} \vec{k}_i}{\sum_{i=1}^{7} \vec{k}_i} C_{B4}^{eq}(T(t)) C_{N2}^{eq}(T(t))^2 = \frac{\sum_{i=1}^{7} \vec{k}_i}{\sum_{i=1}^{7} \vec{k}_i} C_{B4}^{eq}(T(t)) (1 - x_0(B))^2 \left(\frac{P}{RT}\right)^2.$$
(11c)

$$C_{B5N4}^{eq}(T(t)) = \frac{\sum_{i=1}^{8} k_i}{\sum_{i=1}^{8} \bar{k}_i} C_{B5}^{eq}(T(t)) C_{N2}^{eq}(T(t))^2$$
$$= \frac{\sum_{i=1}^{8} \bar{k}_i}{\sum_{i=1}^{8} \bar{k}_i} C_{B5}^{eq}(T(t)) (1 - x_0(B))^2 \left(\frac{P}{RT}\right)^2.$$
(11d)

The condensation point (T_B) depends on boron partial pressure $(x_0(B)P)$. We define T_B as a temperature at which $\Delta_f G(B, T(t)) = 0$.

The results of the kinetic modeling are presented in figure 5 for the temperature range between the boron solidification (2300 K) and condensation points ($T_{\rm B}$). The fraction of liquid boron (x_{LB}) is a fraction of boron atoms in liquid state, which was defined as

$$x_{LB} = \left(x_0(B)\frac{PV}{RT_B} - 4C_{B4N4}(t) - 5C_{B5N4}(t)\right)\frac{RT(t)}{PV}.$$
 (12)

It is evident from figure 5 that the fractions of B_4N_4 and B_5N_4 species deviate significantly from the chemical equilibrium values at $T < T_B$ for atmospheric and higher pressures. As a result, kinetic simulations predict that liquid boron is not fully consumed before boron solidification at 1 atm pressure (figures 5(a) and (b)), assuming that the typical gas cooling rate during BNNT synthesis is 10^5 K s⁻¹ [8]. This differs from the complete liquid boron consumption predicted by earlier thermodynamic calculations in section 2.2.



Figure 5. N₂ fixation process during a gas cooling under kinetic control ($\dot{T}_0 = 10^5 \text{ K s}^{-1}$) at different conditions: (a) 45% B and 1 atm, (b) 5% B and 1 atm, (c) 5% B and 10 atm.

According to equations (11c) and (11d), high pressure (10 atm) and a low initial boron fraction ($x_0(B) = 5\%$) is required in order to significantly enhance B_4N_4 and B_5N_4 production via liquid boron consumption (figure 5(c)). Liquid boron consumption (LBC) is an important issue to consider for the

production of high quality BNNTs. (See discussion section). Here, the LBC at the boron solidification point (2300 K) has been estimated using the following expression:

$$LBC = \frac{x_0(B) - x_{LB}(2300 \text{ K})}{x_0(B)}.$$
 (13)

As shown in figure 6, LBC increases with higher pressures and slower gas cooling rates. Total consumption of all liquid boron is possible only with a low initial boron fraction and at pressures higher than 1 atm (figure 6(a)). Indeed, even with an initial boron fraction of $x_0(B) = 0.01$, not all liquid boron will be consumed if the pressure is only 1 atm. This insight agrees with experimental observations of boron droplets encapsulated in BN shell structures at 1 atm [7]. (See discussion.)

The effect of the gas cooling rate on LBC is effectively demonstrated in figure 6(b). It is shown that the gas cooling should be 10 times slower ($\sim 10^4$ K s⁻¹) than the typical cooling rate in order to significantly increase LBC.

2.5. QCMD simulation of small chains aggregation

We used DFTB + modeling to investigate the interaction of small B₃N₃ rings with each other. We showed that planar collisions of these B3N3 molecules lead to the formation of one big monocyclic B₁₂N₁₂ ring. This result supports our thermodynamic modeling, which indicated that longer B-N chains, both cyclical and linear, are more stable than shorter B–N chains at T < 3000 K. We suggest that B_4N_4 and B_5N_4 clusters will aggregate into larger chains through mechanisms similar to the one explored in the case of B₃N₃. Nonplanar collisions of these rings lead to the formation of $B_{12}N_{12}$ and $B_{24}N_{24}$ fullborenes in the shape of nanocages [38]. Thus, the smaller B-N rings tend to combine very quickly (on a nanosecond timescale) into longer chains and fullborenes. This confirms our assumption that the rate-limiting step of BNNT precursor formation is the N2 fixation process resulting in formation of small $B_m N_n$ chains ($B_4 N_4$ and $B_5 N_4$). Once these small chains form, the production of longer chains and subsequent synthesis of fullborenes and BNNTs proceeds rapidly during a gas cooling.

2.6. Rings folding into fullborenes

A detailed mechanism of BNNT formation from the B–N precursors is beyond the scope of this research. However, the reaction paths for the transformation of $B_{12}N_{12}$ and $B_{24}N_{24}$ chains (monocyclic rings) into the corresponding fullborene structures have been calculated (figure 7). The rate constants corresponding to these transformations can be found in supplementary materials. The $B_{12}N_{12}$ fullborene formation is shown in figure 7(a). Five steps have been found on this reaction path. The first three reaction steps are the transformation of the monocyclic ring into a planar graphitic sheet, and the following two steps involve the folding of the B–N plane into a 3D fullborene via TS4 and TS5.

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Figure 6. Liquid boron consumption (LBC) versus initial boron fraction at (a) different pressures and (b) gas cooling rates.

The formation of a $B_{24}N_{24}$ fullborene proceeds through 16 transition states (figure 7(b)). The geometries of the 15 intermediate structures are shown in figure 7(c). The first 12 steps describe the formation of a planar graphitic structure consisting of B_3N_3 hexagonal rings (see $B_{24}N_{24}$ (12) in figure 7(b).) The subsequent steps describe the transformation of the planar structure into a 'cup' shaped structure (see $B_{24}N_{24}$ (15) in figure 7(b).) and eventually into the 3D fullborene. All barriers of the forward reactions are less than 3.1 eV, and the geometry of the $B_{24}N_{24}$ fullborene corresponds to a very deep well on the PES (10.5 eV), which is higher than the bond energy of N_2 .

It should be noted that our reaction paths for fullborene formation bear a resemblance to the mechanism of fullerene formation proposed in [33–35]. In that study, various C_n cations were generated by laser desorption and identified based on mass-spectrometry, ion chromatography data, and QC calculations [34–36]. From this analysis, it was determined that the growth of fullerenes follows the following reaction steps: chains \rightarrow monocyclic rings \rightarrow polycyclic rings \rightarrow fullerenes [35]. According to our simulations, small chains form longer monocyclic rings via collisions with each other (section 2.5), and the monocyclic rings fold into fullborenes



Figure 7. Calculated reaction path (potential energy surface) of transformation of (a) $B_{12}N_{12}$ and (b) $B_{24}N_{24}$ monocyclic rings into the corresponding fullborenes. (c) The reactant, product and intermediate structures of the reaction path of transformation of $B_{24}N_{24}$ monocyclic ring into the corresponding fullborene.

via a series of transformations very similar to those described above (figure 7): monocyclic ring \rightarrow bicyclic ring \rightarrow polycyclic rings \rightarrow graphitic sheet \rightarrow 'cup' shaped structure \rightarrow fullborene.

The graphitic and 'cup' shaped structures described by our modelling of fullborene growth were not observed in the fullerene growth experiment [35]. This discrepancy can be explained by the low energy barriers along the reaction path near these structures. Indeed, according to our DFT calculations, these structures ($B_{24}N_{24}$ (12) and $B_{24}N_{24}$ (15) in figure 7(b).) are transformed into fullborenes through TS13–TS15, and the barriers corresponding to these transitions are quite low, while the barriers to backwards reactions from the fullborene structures are quite large. Thus, the graphitic and 'cup' shaped isomers are most likely short-lived intermediates on the reaction path leading to fullborene (or fullerene) formation and therefore difficult to detect experimentally.

It is interesting to note that the smallest C_n fullerene which observed in [33, 35] has n = 30. In addition, the vast majority of C_n clusters with n > 50 have folded into fullerenes [35]. This phenomenon can be explained by comparing the reaction barriers in the decomposition of the two fullborenes examined in our modelling. The highest reaction barrier in the decomposition of $B_{24}N_{24}$ is much higher than that of $B_{12}N_{12}$ (5.9 versus 10.5 eV in figures 7(a) and (b)). Thus, the stability of fullborenes significantly increases with cluster size. Similarly, smaller fullerenes should be less stable than bigger ones, which explains the fact that C_n fullerenes with n < 30 were not observed in [33, 35].

3. Discussion

As we discussed in section 2.6 the fullborene formation during high temperature BNNT synthesis should proceed through the formation of the following structures: small B–N chains \rightarrow monocyclic rings \rightarrow bicyclic rings \rightarrow polycyclic rings \rightarrow graphitic sheet \rightarrow 'cup' shaped structure \rightarrow fullborene. Our research aims to study in detail the synthesis of the first structure (small B–N chains) through N₂ fixation.

Here it has been shown that N₂ molecules can react with B_m clusters to produce small $B_m N_n$ chains, and the main reaction products are B_4N_4 and B_5N_4 chains (section 2.4). The source of these B_m clusters is liquid boron, and thus the consumption of these B_m clusters by the nitrogen fixation process results in the consumption of liquid boron. Under the (not valid) assumption that thermodynamic equilibrium is achieved throughout gas cooling process, all liquid boron is consumed. (See figure 3.) Removing the assumption of thermodynamic equilibrium, we show that consumption of all liquid boron is only achieved under the conditions of high pressure and low initial boron fraction. Correspondingly, the formation of small $B_m N_n$ chains occurs in a non-equilibrium (kinetic) regime and depends on the gas cooling rate and pressure. The effect of pressure was reported by the Zettl group [7], where it was concluded that boron is not completely consumed by reactions with N₂ at 1 atm pressure. As a result, shell structures of BN around boron droplets ('nanococoons') are observed. At pressures above 2 atm the prevalence of these nanococoons begins to decrease and at pressures above 3 atm nanococoon formation is significantly suppressed, assisting in high purity BNNT synthesis. The observed boron consumption trend is consistent with the kinetic modeling results shown in figures 5 and 6, where it can be seen that the liquid boron consumption is hindered at 1 atm pressure. As a result, not all boron is converted into B_4N_4 and B₅N₄ chains. Higher pressures enhance B₄N₄ and B₅N₄



Figure 8. Mechanisms of BNNTs growth: (a) root growth, (b) open-end growth and (c) self-assembling.

production and liquid boron can be fully consumed even at 2 atm (figure 6(a)).

It should be noted that the complicated process of boron droplet nucleation prior to the agglomeration phase is not considered here. Only boron clusters B_m with $m \leq 6$ and liquid boron were considered in this study. The clusters were shown to contribute to nitrogen fixation, while the liquid boron did not [19]; contributions from larger B_m clusters were not studied. However, they may also play a role in nitrogen fixation, either directly or indirectly. The cluster size at which these contributions to nitrogen fixation are no longer important has not been determined, though previous studies have established that clusters as large as B_{13} are capable of reacting with N₂ [9].

During the nucleation stage, the small B_m clusters are in equilibrium with the bigger boron clusters, not with liquid state as suggested in our current kinetic model. Because the larger boron clusters are not accounted for in our model, the densities of smaller boron clusters may be underestimated near the nucleation point in our calculations. Considering that the nucleation burst typically occurs at temperatures ~300 K below the nucleation point [39], we believe that the kinetic model underestimates the rate of B_4N_4 generation near the boron boiling point (figure 5(b)) since the nucleation burst is not taken into account.

The study of the growth process of BNNTs is beyond the scope of our research, but some steps were taken in this direction. Namely, we showed using DFTB + simulations (section 2.5) that the small B–N chains form longer B–N rings. The reaction paths leading to the folding of B–N rings into fullborenes is shown in in section 2.6. We propose that the formation of fullerenes and fullborenes occurs through a series of similar structural transformations.

Despite this structural similarity, fullborenes should be less stable than fullerenes. Blasé *et al* [40] showed that fullborene caps consist of metastable squares due to the greater

stability of B–N bonds compared to B–B and N–N bonds. In other words, stabilized fullborenes and BNNTs are capped by metastable sites (squares), and can therefore attach to each other by these sites to form elongated structures. This process was reported to occur for the $B_{12}N_{12}$ fullborene [41]. This indicates that fullborenes are less stable than BNNTs, because the longer structure of the nanotubes consists mainly of stable hexagonal rings, so the effect of the metastable sites on the stability of whole tube is insignificant.

Our thermodynamic modelling (section 2.2) predicts that fullborene formation begins at temperatures less than 2600 K, about the same temperature at which BNNT growth begins [9]. Thus, if fullborenes are generated in the gas mixture they will collide and form more stable elongated structures, eventually resulting in the growth of BNNTs. This process resembles the self-assembling mechanism proposed in [17, 42]. (Or see figure 8(c).) These studies have reported that BN dimers, BNH, HBNH, and $B_3N_3H_3$ molecules can selfassemble into BN nanostructures (cages, flakes, and tubes) without the presence of boron droplets. It was also observed that BN chains are the first to appear in the B–N reaction mixture. This is consistent with our result that B_mN_n chains are precursors to the growth of BNNTs.

Note, a way to synthesize the BN chains had not been experimentally discovered despite the fact that potential applications of BN chains were theoretically studied [43]. Moreover, the very fact that BN chains exist had not been discussed until they were experimentally observed above hexagonal boron nitride sheets [44]. According to our data, synthesis of BN chains is a difficult process since the chains are stable only within a narrow temperature range (section 2.2).

Another BNNT growth mechanism previously explored in the literature [4, 8] is the root growth mechanism. In this process, B_mN_n chains or fullborenes are dissolved in boron droplets, and BNNT growth proceeds outwards from the droplet surface as shown in figure 8(a). The same setup, wherein the BNNT is attached to a boron droplet at one end, also supports another mechanism for BNNT growth. In this process, B_mN_n chains and fullborenes can react with the metastable site at the tube-end, resulting in tube elongation. This resembles the open-end growth mechanism described in [16]. (See figure 8(b).)

Previously, hydrogen was reported to have a catalytic role in BNNT synthesis [8]. Here, we considered the effect of hydrogen using a thermodynamic approach, and showed that iminoborane (HBNH) molecules can be produced in large quantities. (See figure 3(c).) It should be noted that HBNH was detected in a diborane/ammonia arc discharge [45] and in reactions between atomic boron and NH₃ [46]. The mechanisms of HBNH formation and HBNH incorporation into BNNT molecules were previously studied using QC methods [47]. It was shown that HBNH molecules are a possible precursor in the production of borazine [42] as well as BNNTs [42, 47]. In addition, as shown in section 2.6, the graphitic and 'cup' shaped structures are not stable. The hydrogen atoms will close the vacancies on the terminal B and N atoms, stabilizing these structures.

4. Conclusion

We have proposed a chemical reaction pathway for BNNT growth and precursor formation. We showed that the critical (rate-determining) step in BNNT synthesis is N_2 fixation, which primarily occurs during the reaction of N_2 with small B_4 and B_5 clusters, causing the formation of B_4N_4 and B_5N_4 chains. Subsequent chain elongation occurs via collisions of B_4N_4 and B_5N_4 with each other, and these larger chains are in turn precursors to fullborene and BNNT growth. The process described here stands in contrast with the common assumption that small molecules such as BN, B_2N , and BN_2 are the main precursors to BNNT formation.

We also showed that high pressures and slow gas cooling rates enhance N_2 fixation and correspondingly enhance liquid boron consumption, creating good conditions for high quality BNNT synthesis. The addition of hydrogen into the reaction mixture can also enhance N_2 fixation. It was shown that HBNH molecules are present in the mixture at thermodynamic equilibrium, and probably play an important role in BNNT synthesis.

Further research on BNNT synthesis and the nitrogen fixation process will be facilitated by the information presented in the supplementary material: this includes rate constants for the dissociative adsorption of N₂ on small B_m clusters (m = 2-5), as well as rate constants for the reactions leading to folding of B₁₂N₁₂ and B₂₄N₂₄ monocyclic rings into their corresponding fullborenes. These rate constants can be used for kinetic modeling of fullborene formation. In addition, the standard Gibbs free energy of formation for B_nN_n monocyclic rings, B_{n+1}N_n linear chains, and B_nN_n fullborenes can be found in supplementary materials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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