Quantum-Classical Molecular Dynamics Simulation of Synthesis of Boron-Nitride Nano-Structures at High Temperature, High-Pressure Plasmas

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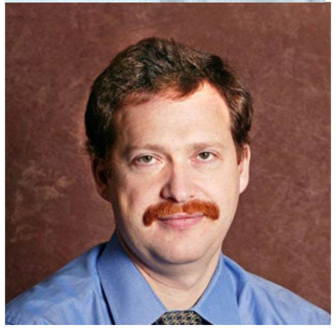
Supported by US DoE, Basic Energy Sciences, through Princeton Plasma Physics Laboratory

Collaboration

PRINCETON UNIVERSITY

Prof. Roberto Car
Carbon



Dr. Igor Kaganovich
Plasma theory

PPPL
PRINCETON PLASMA PHYSICS LABORATORY

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Waseda U.

This research was funded by BES for nanosynthesis in volume of a hot, high pressure plasma through PPPL

U.S. DEPARTMENT OF ENERGY

Computing facilities of IACS, XSEDE, DOE and Nagoya U.

Prof. Stephan Irle,
Nagoya U. and ORNL

Why Boron-Nitride?

- B(5) and N(3) are immediate neighbors of C(4) in periodic table, BN(8) structure is isoelectronic with a bonded carbon structure CC(8)

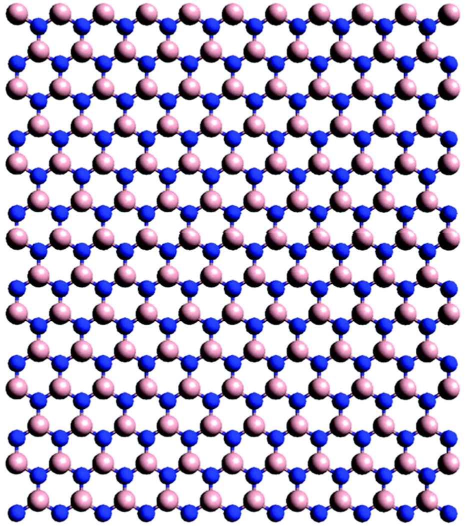
Boron electronic config.
$1s^2 2s^2 2p$

Nitrogen electronic config
$1s^2 2s^2 2p^3$

Carbon $1s^2 2s^2 2p^2$

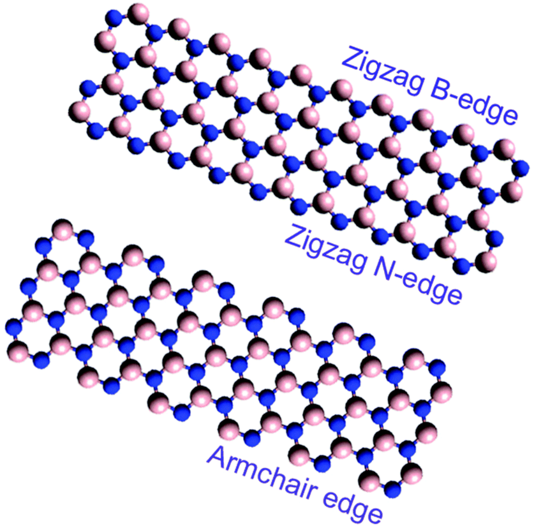
Like graphene

Nanosheet



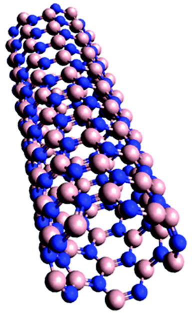
Like carbon

Nanoribbon

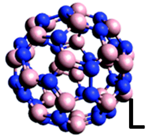


Like CNT

Nanotube



Fullerene



Like carbon

Boron “borrows” one p orbital from nitrogen and then both are like carbon: The carbon story repeats

All identical structures to carbon

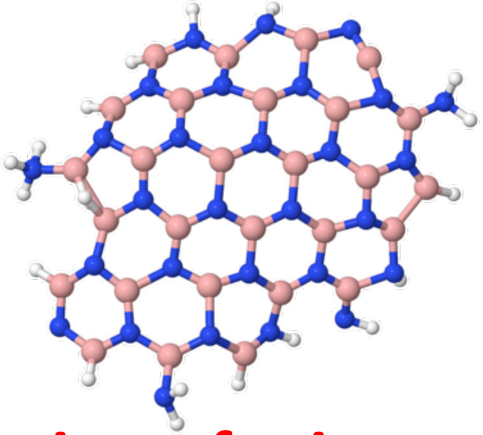
Exceptional properties, similar to CNT and graphene; many applications

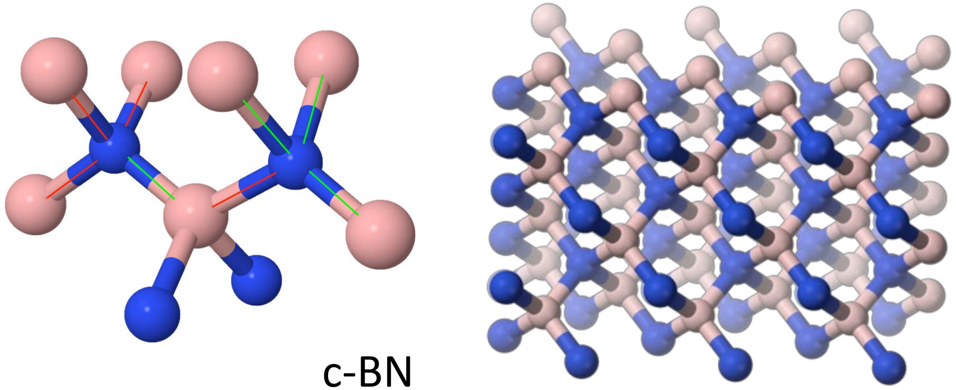
Unlike graphene: Difference in electronegativites (B 2.04; N 3.04) forms ionic bond; 5.9 eV homo-lumo gap : insulator , still good thermal conductor; piezoelectric properties

Why B and N form BN structures (and not B-B, N-N, B-B-N-N,…?)

- B-N bond is energetically favorable (~4 eV) than B-B bond (3.1 eV) and N-N single bond (~1.7 eV).
- Even-numbered rings, made of B and N alterations, are energetically favorable. Odd numbered rings appear as defects.

Each atom in h-BN neighbored by three other atoms.
e.g. when N in center, if one B replaced by N, only single N-N bond can be formed.
Similarly in c-BN, B (or N) is coordinating with 4 atoms of other type.





c-BN

Self-organization of mixture of Bs and Ns will favor creation of BN structures

Oku T, Narita I and Nishiwaki A *Mater. Manuf. Processes*, **2004**, 19, 1215-39.

Then: What were we doing here? How?

- Computationally studied synthesis of boron nitride nanostructures from a hot, high pressure gas containing various combinations of precursors B, N, and H. (typically expected in plasma synthesis)

- Why? To elucidate detailed dynamics of self-assembly mechanisms into clusters and aggregates at various temperatures. understanding the chemical dynamics and predicting the optimal conditions concerning temperature and gas content.

- Achieved by using quantum-classical molecular dynamics (QCMD) simulations based on DFTB quantum chemical potential, implemented in the DC-DFTB-K code (H, Nakai, Waseda U., Tokyo) to study large systems containing about 1300 atoms (10,000 basis functions) in a canonical NVT ensembles for 1 ns, for T’s 1500-6000 K.

Why in plasma?

Usually used process in nanosynthesis is Chemical Vapor Deposition: Temperature < 1000K, deposition on a substrate, various pressure.

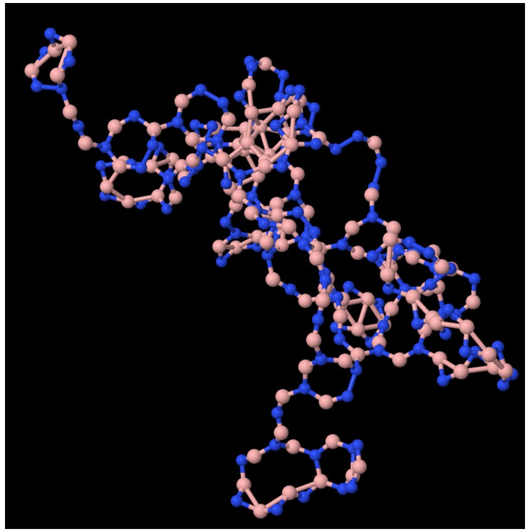
However, experiments on nanosynthesis in hot plasma volume (torch or arc discharge, no substrate) at high pressure showed higher yield of production and defect-free synthesis

Kim et al, 2014: BNNT by feeding h-BN powder, along with N2 and H2 in the torch (8000K).
Hypothesis: BN dissociate, B agglomerate, H prevent N atoms to associate to N2: Final reaction some BNH precursors with B clusters.
Zetl et al, Plasma torch in N2, B feedstock, a few atm, BNNT, BN cages, BN flakes.
Hypothesis: N2 dissociate, react with B clusters

We have tried by theory and simulations to understand this nonequilibrium process and suggest the optimal plasma conditions for the synthesis

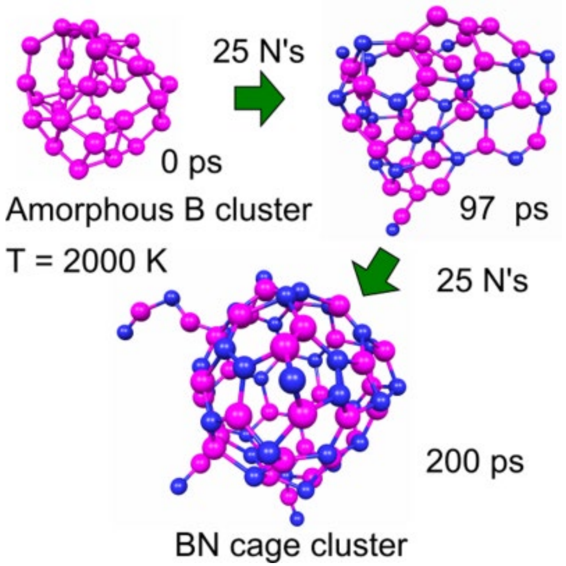
Classical or quantum-mechanical approach?

Using Classical MD, varying various potentials and other parameters, enabling EEM to include dynamics of charging has not resulted in organized but rather to amorphous BN structures



10 ns
1 fs step
Varying T

Inspiration came from Y. Ohta, J. Comp. Chemistry, 2016
Showed that can form small nanocages using QCMD with DFTB



Once we applied QM: The solution for the synthesis in the plasma volume opened

Why quantum-mechanics works here?

Preliminary and ad hoc Hypothesis: Because of the Quantum Entanglement

What is quantum entanglement?
Quantum state of one atom cannot be described independently of all other particles in the system (that is being self-organized in our case), even if they are at large mutual distances. All particle correlated.

Quantum measurement: Whenever dump the coordinates of the particles to the disk (each 4 ps)

The entanglement hypothesis of our self-organized systems is in an initial stage of study!! M. Zack did initial research more than 15 years ago.

Thermodynamics of the process of self-organization

The change in Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$

<0 fo the spontaneous process of synthesis.

Depends on temperature:

When $\Delta S < 0$ and $\Delta H < 0$, the process will be spontaneous at low temperatures and non-spontaneous at high temperatures.

A decrease in system entropy can only occur spontaneously if the entropy change of the surroundings is both positive in sign and has a larger magnitude than the entropy change of the system.

The increase in entropy of the surroundings is accomplished via heat transfer from the system to the surroundings

Big problem is change of the number of particles due to both implantation and loss

Non-equilibrium thermodynamics

Methods

Quantum-Classical Molecular Dynamics
QCMD

Alternative to DFT: Approximate DFT

Density-Functional Tight-Binding: Method using atomic parameters from DFT (PBE, GGA-type), diatomic repulsive potentials from B3LYP

About 2 orders of magnitude faster than DFT

- Seifert, Eschrig (1980-86): minimum STO-LCAO; 2-center approximation
- Porezag, Frauenheim, *et al.* (1995): efficient parameterization scheme: ***NCC-DFTB***


Helmut Eschrig


Gotthard Seifert

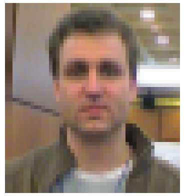

Thomas Frauenheim

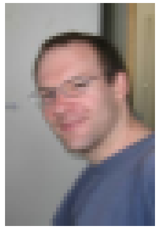
- Elstner *et al.* (1998): charge self-consistency: ***SCC-DFTB***
- Köhler *et al.* (2001): spin-polarized DFTB: ***SDFTB***

$$E^{(NCC-)DFTB} = \sum_{i}^{\substack{valence\\orbitals}} n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B}^{atoms} E_{AB}^{rep}$$

$$E^{(SCC-)DFTB} = E^{(NCC-)DFTB} + \frac{1}{2} \sum_{A \neq B}^{atoms} \gamma_{AB} \Delta q_A \Delta q_B$$

$$E^{S(pin-polarized)DFTB} = E^{(SCC-)DFTB} + \frac{1}{2} \sum_{A}^{atoms} \sum_{l \in A} \sum_{l' \in A} p_{Al} p_{Al'} W_{All'}$$


Marcus Elstner


Christof Köhler

DFTB+

Many groups. Most versatile version of DFTB.

Developed and maintained by the Bremen group for Computational Material Science

B. Aradi, B. Hourahine, and Th. Frauenheim. *DFTB+, a sparse matrix-based implementation of the DFTB method*, J. Phys. Chem. A, **111** 5678 (2007).

1. http://www.dftb.org
2. **DFTB** Porezag, D., T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, *Construction of tight-binding-like potentials on the basis of density-functional theory: application to carbon*. Phys. Rev. B, 1995. 51: p. 12947-12957.
3. **DFTB** Seifert, G., D. Porezag, and T. Frauenheim, *Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme*. Int. J. Quantum Chem., 1996. 58: p. 185-192.
4. **SCC-DFTB** Elstner, M., D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim S. Suhai, and G. Seifert, *Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties*. Phys. Rev. B, 1998. 58: p. 7260-7268.
5. **SCC-DFTB-D** Elstner, M., P. Hobza, T. Frauenheim, S. Suhai, and E. Kaxiras, *Hydrogen bonding and stacking interactions of nucleic acid base pairs: A density-functional-theory based treatment*. J. Chem. Phys,, 2001. 114: p. 5149-5155.
6. **SDFTB** Kohler, C., G. Seifert, U. Gerstmann, M. Elstner, H. Overhof, and T. Frauenheim, *Approximate density-functional calculations of spin densities in large molecular systems and complex solids*. Phys. Chem. Chem. Phys., 2001. 3: p. 5109-5114.
7. **DFTB3** Gaus, M.; Cui, C.; Elstner, M. *DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB)*. J. Chem. Theory Comput., 2011. 7: p. 931-948.

Significant step forward for QCMD is DC-DFTB-K of the group of prof. Hiromi Nakai in Waseda U, Tokyo!

Divide-and-Conquer DFTB: This software is capable, without a significant loss of accuracy!!, to treat larger systems (thousands of atoms) in an acceptable real time.

DC-DFTB-K

Basic References:

[1] H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, and H. Nakai, **Three Pillars for Achieving Quantum Mechanical Molecular Dynamics Simulations of Huge Systems**: Divide-and-Conquer, Density-Functional Tight-Binding, and Massively Parallel Computation, J. Comp. Chem 37, 1983 (2016).

[2] H. Nakai, A. Wibawa Skti, and Y. Nishimura, Divide-and-Conquer-Type Density-Functional Tight-Binding Molecular Dynamics Simulations of Proton Diffusion in a Bulk Water System, J. Phys. Chem, B 120, 217 (2016).

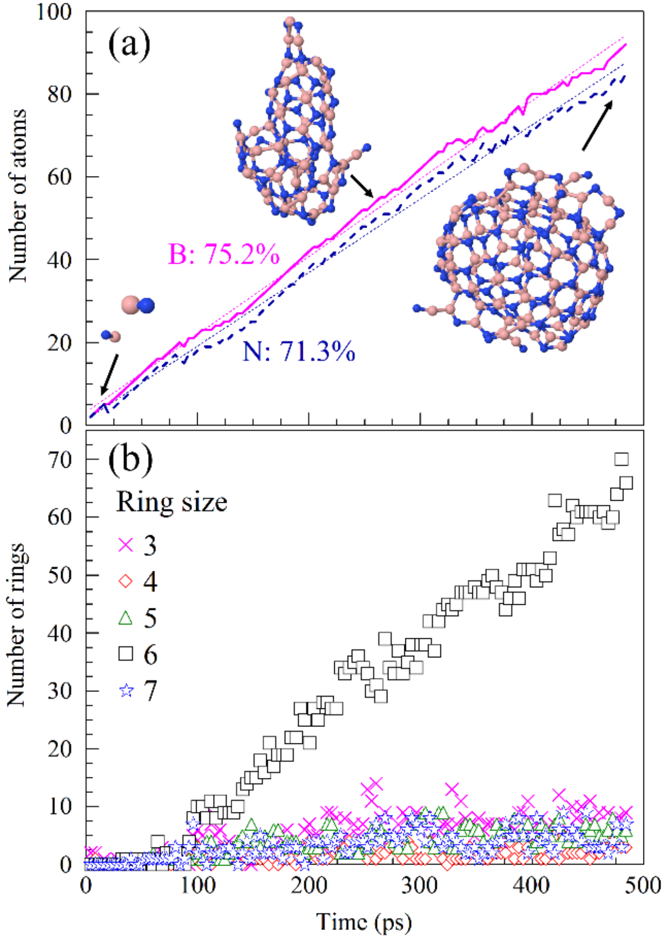
1) DC method => linear-scaling computation with respect to the sys size;
2) DFTB theory, which avoids the explicit two-electron integral evaluation while keeping reasonable accuracy,
3) Massively parallel computation.

The computational efficiency assessed including systems up to **one million atoms**.

This method is reaching N-scaling

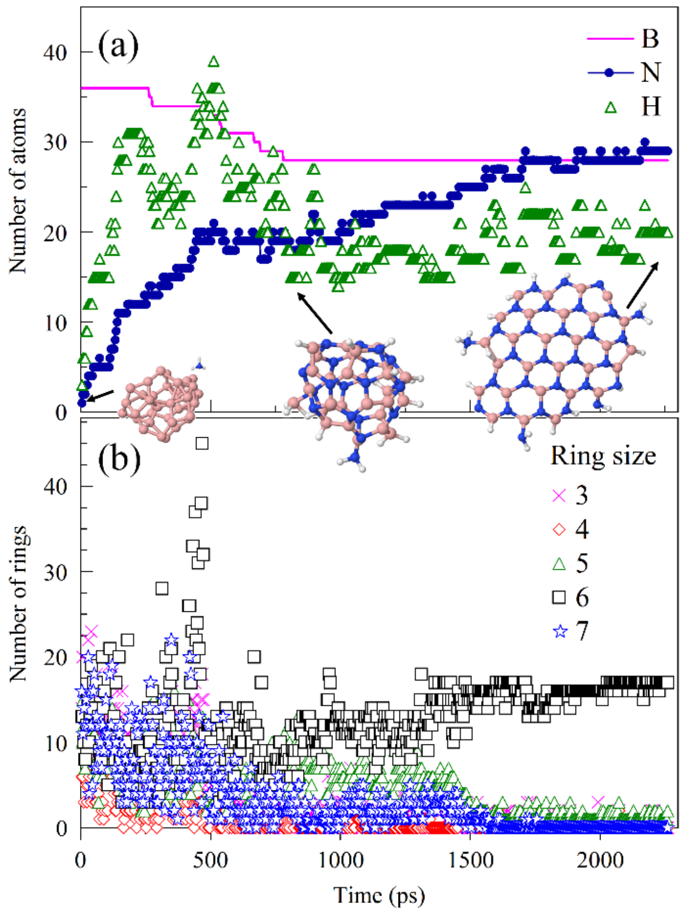
RESULTS

Nanocage formation



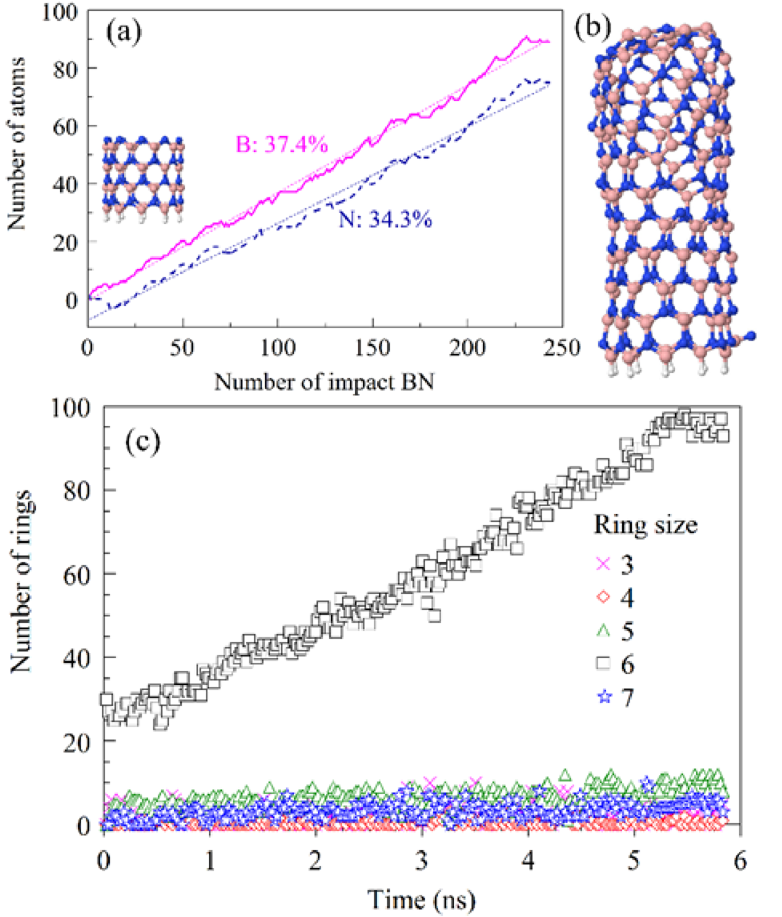
Formation of a BN nanocage by self-organization of BN diatomic molecules. Snapshots are taken at t=0, t=264 ps and t=480 ps, respectively. The implantation rate is derived by linear regression. (a) Number of atoms and (b) number of rings are plotted as a function of time.

Nanoflake formation



Evolution of B36 boron cluster irradiated by NH3 molecules into the flat nanostructure. Three snapshots are taken at t=0, t=800 ps and t=2260 ps, respectively. (a) Number of atoms and (b) number of rings are plotted as a function of time.

BNNT growth



Growth of BNNT from a zig-zag template. (a) Increased number of atoms in BNNT. (b) Grown BNNT after 5.8 ns. (c) Evolution of ring types. Growth of BNNT is completed by self-organization of a BN side chains, which migrated and accumulated at the top end of the tube. T and flux critical qunatities.

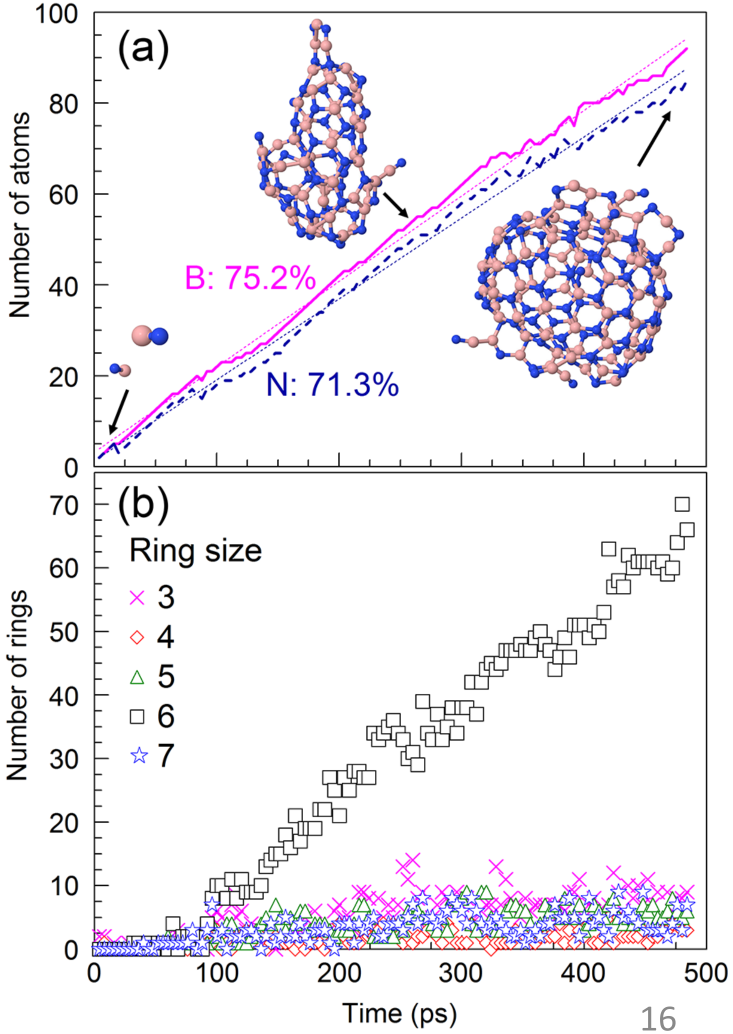
Synthesis of BN fullerene from BN dimers

- Stockfeed by of BN dimers at high temperature and concentration (pressure).

BN chains:

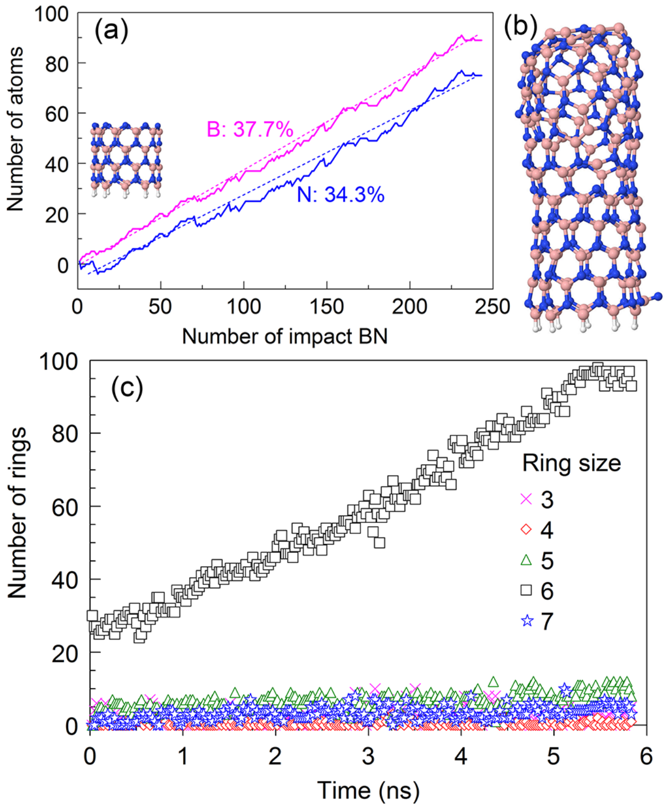
1. branch
2. aggregate

T = 2000K
4ps/BN molecule
P ~ 327 torr

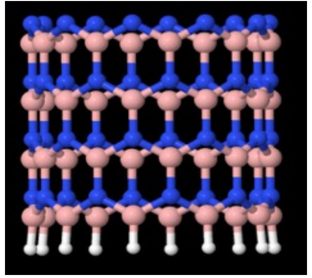


Growth of a BNNT from a zig-zag template

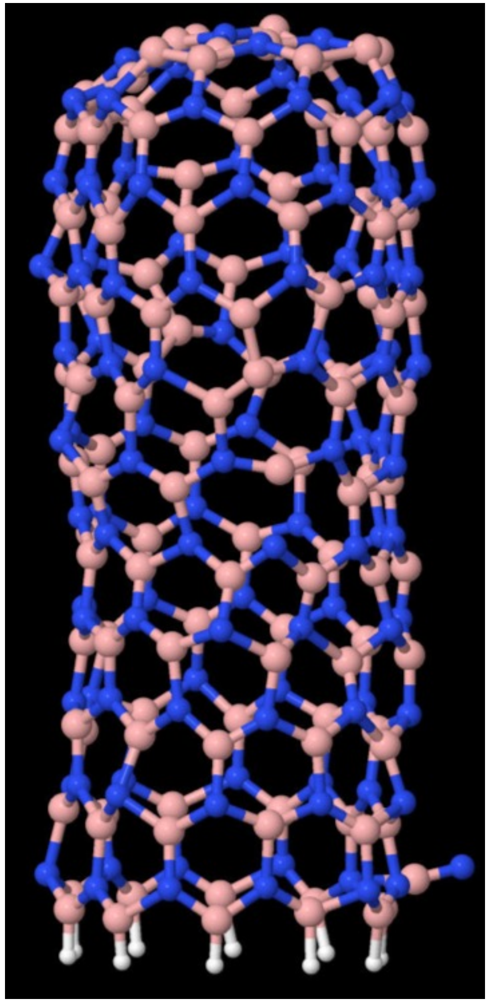
- Side chains formed by BN molecules.
- BNNT grows by self-organizations of the BN side chains
  - migrate and accumulate at the top of the tube by proper T
  - Lowering flux of feedstock provides extra time for migration of side chains



T=2500K
24 ps/molecule
p~65 torr

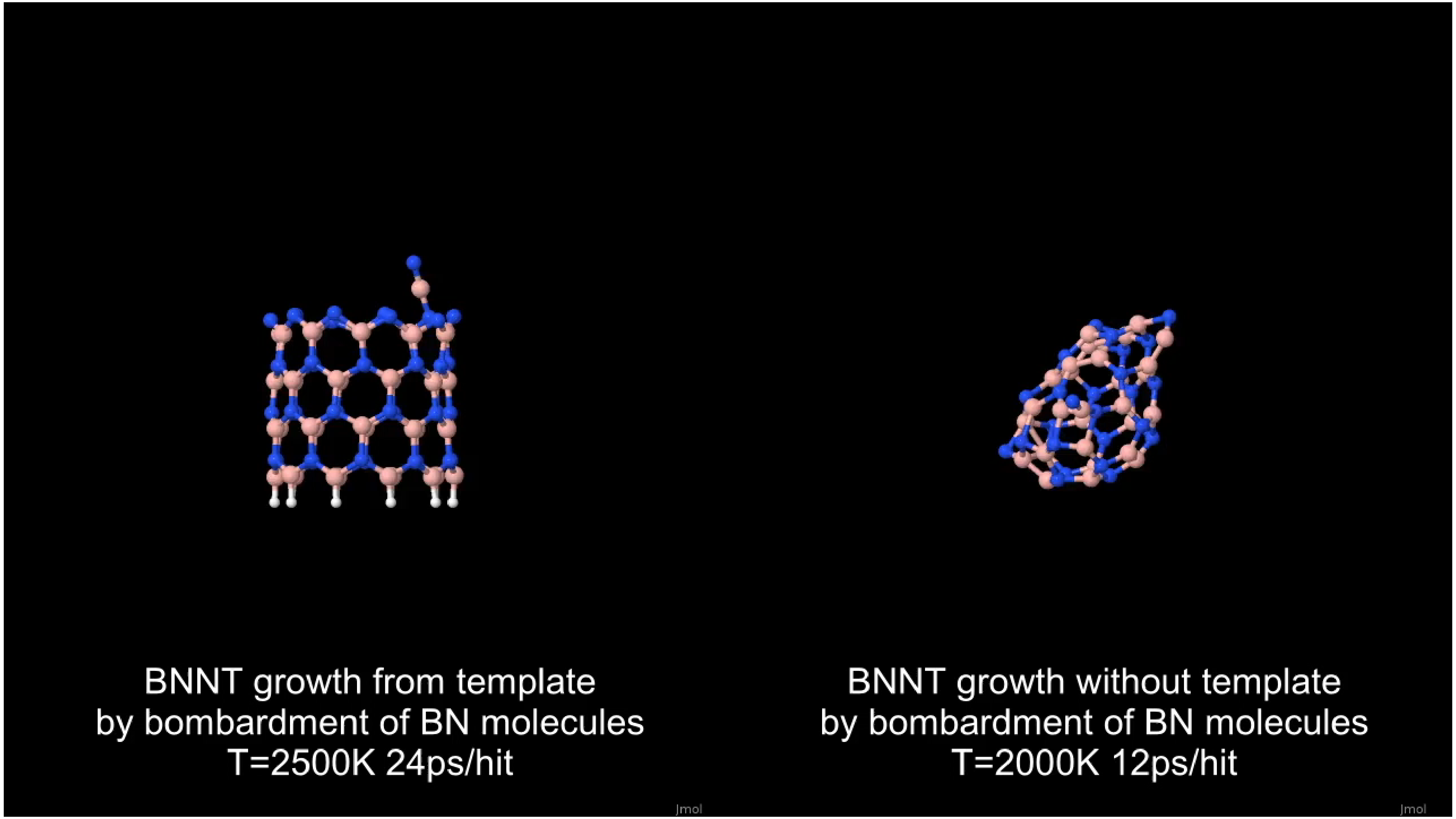


Template



Product

Need to break the symmetry to build a BNNT



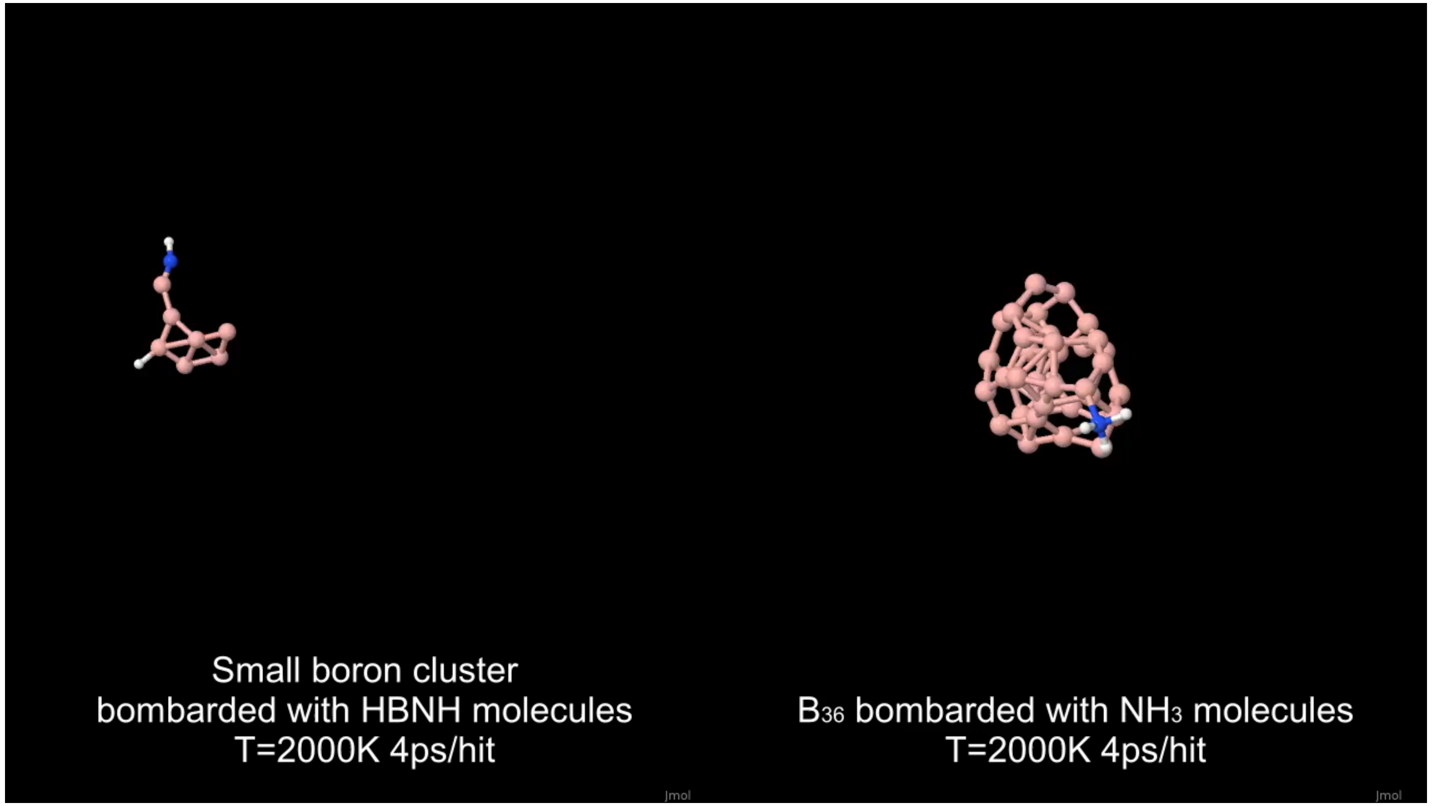
BNNT growth from template
by bombardment of BN molecules
T=2500K 24ps/hit

BNNT growth without template
by bombardment of BN molecules
T=2000K 12ps/hit

Hydrogen rich feedstock leads to the 2D structures

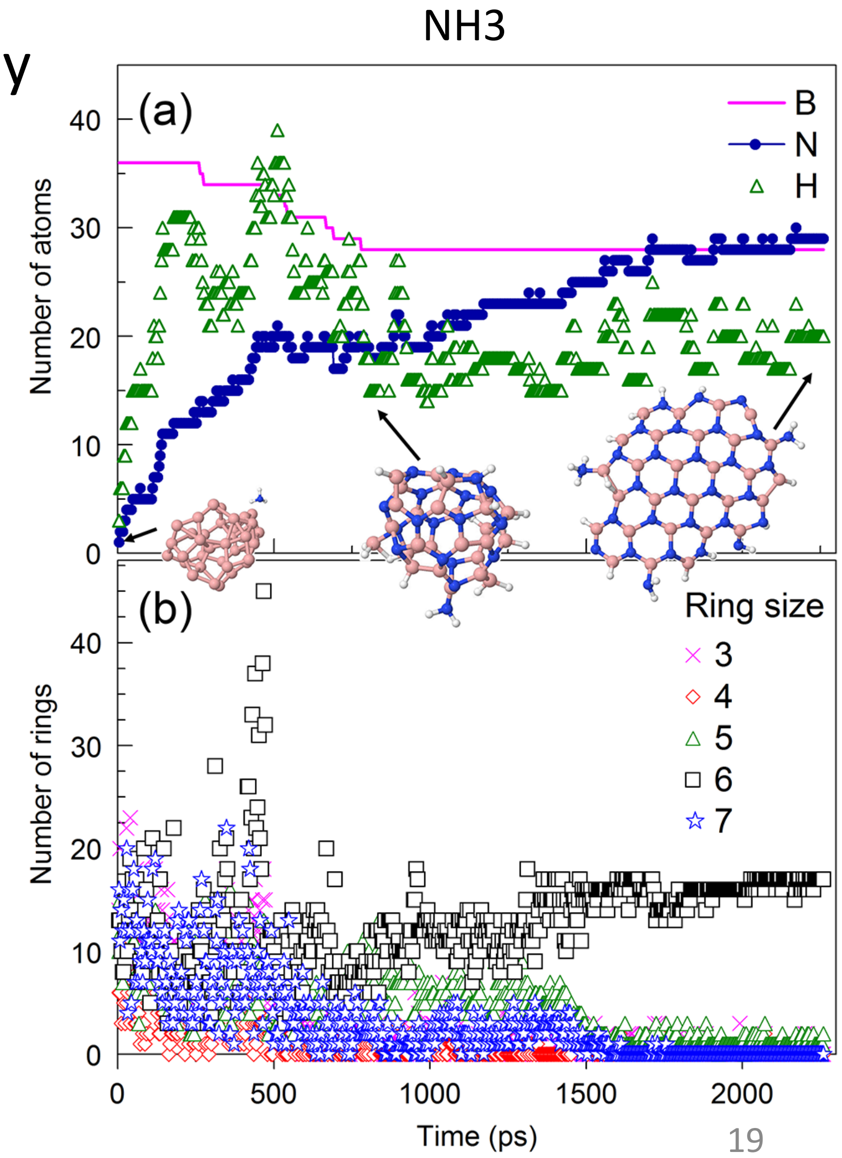
- NH_3 and HBNH
- on boron cluster

Cage opens with edge saturated by hydrogen.



Small boron cluster
bombarded with HBNH molecules
T=2000K 4ps/hit

B_{36} bombarded with NH_3 molecules
T=2000K 4ps/hit



Growth of c-BN by particle irradiation at ambient pressure

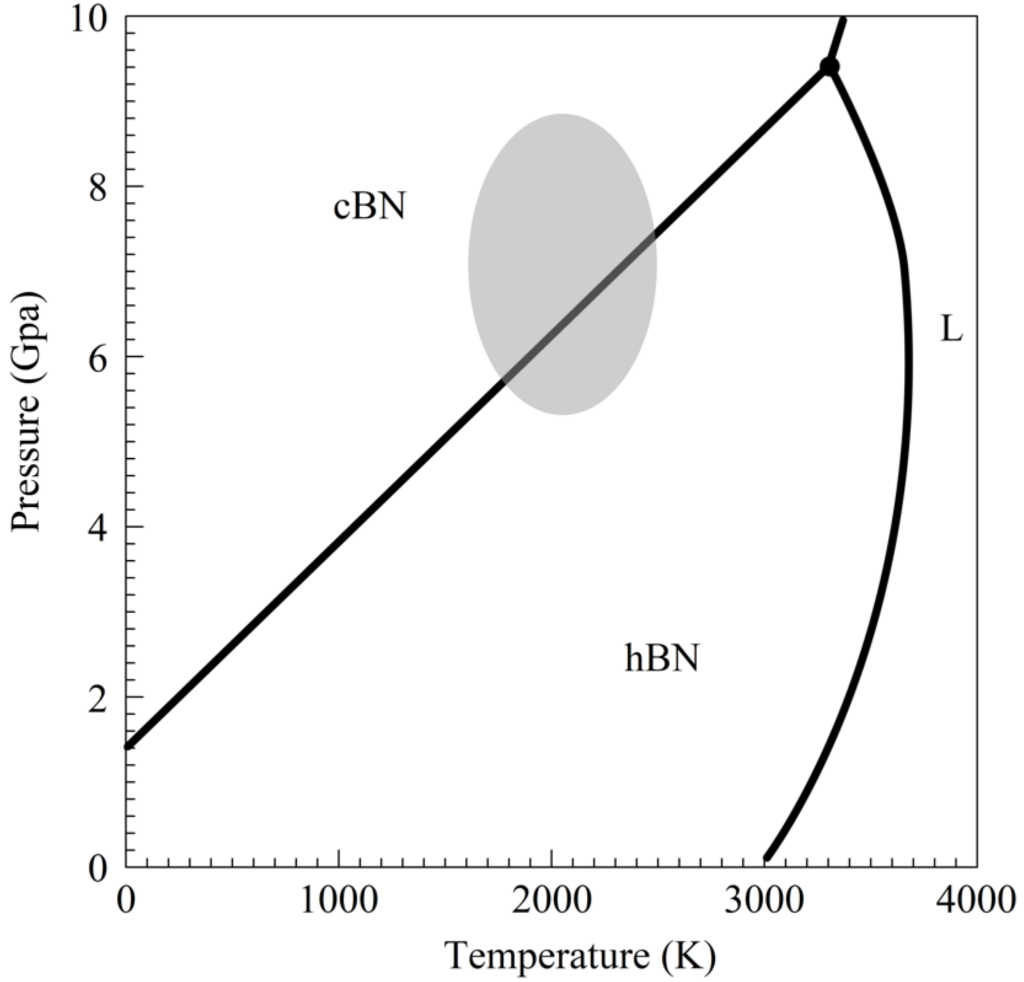
Surface tension induces the high internal pressure

- Surface effects become dominant when cluster gets smaller.
- Young-Laplace equation:

$$P_i = 2\gamma / r$$

  - $\gamma \sim 3J/m^2$, $r \sim 1\ nm \longrightarrow \mathrm{P} \sim 6\ \mathrm{GPa}$

- At 2000K, 6GPa is sufficient to bring c-BN to stable phase.
- H changes the hybridization of B and N atoms, catalyze the transition to c-BN.

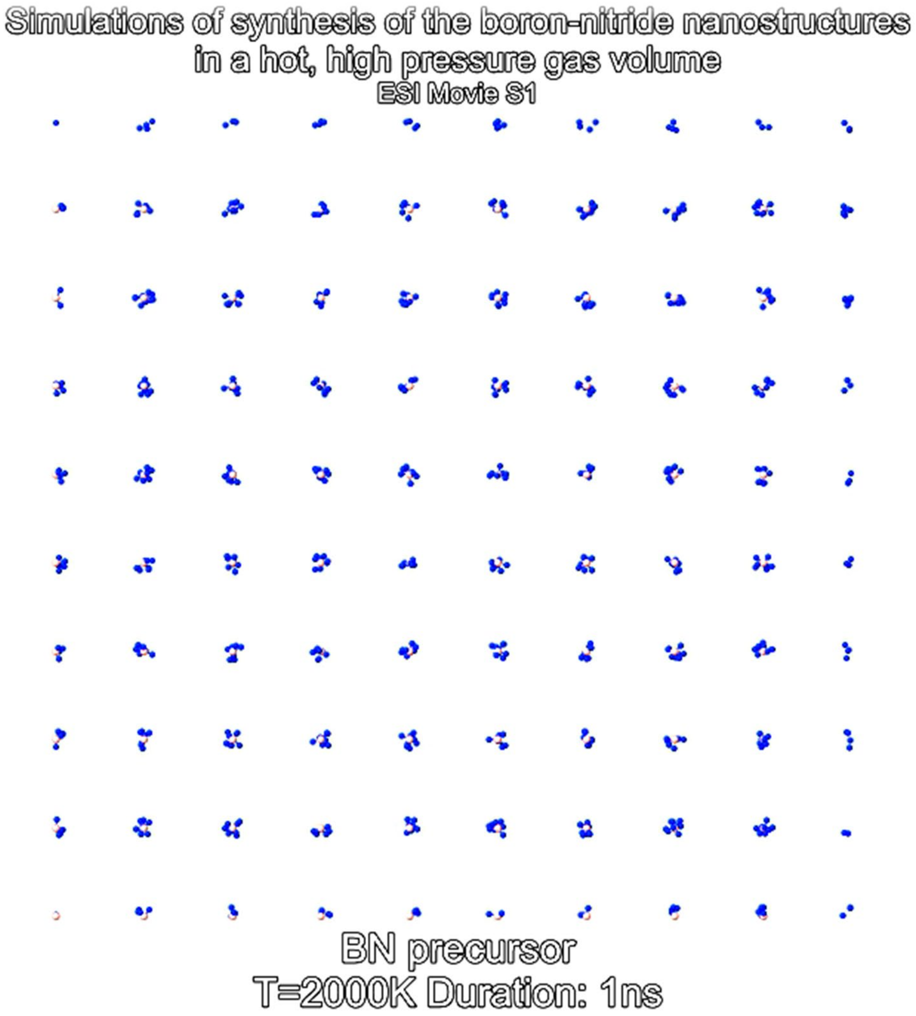


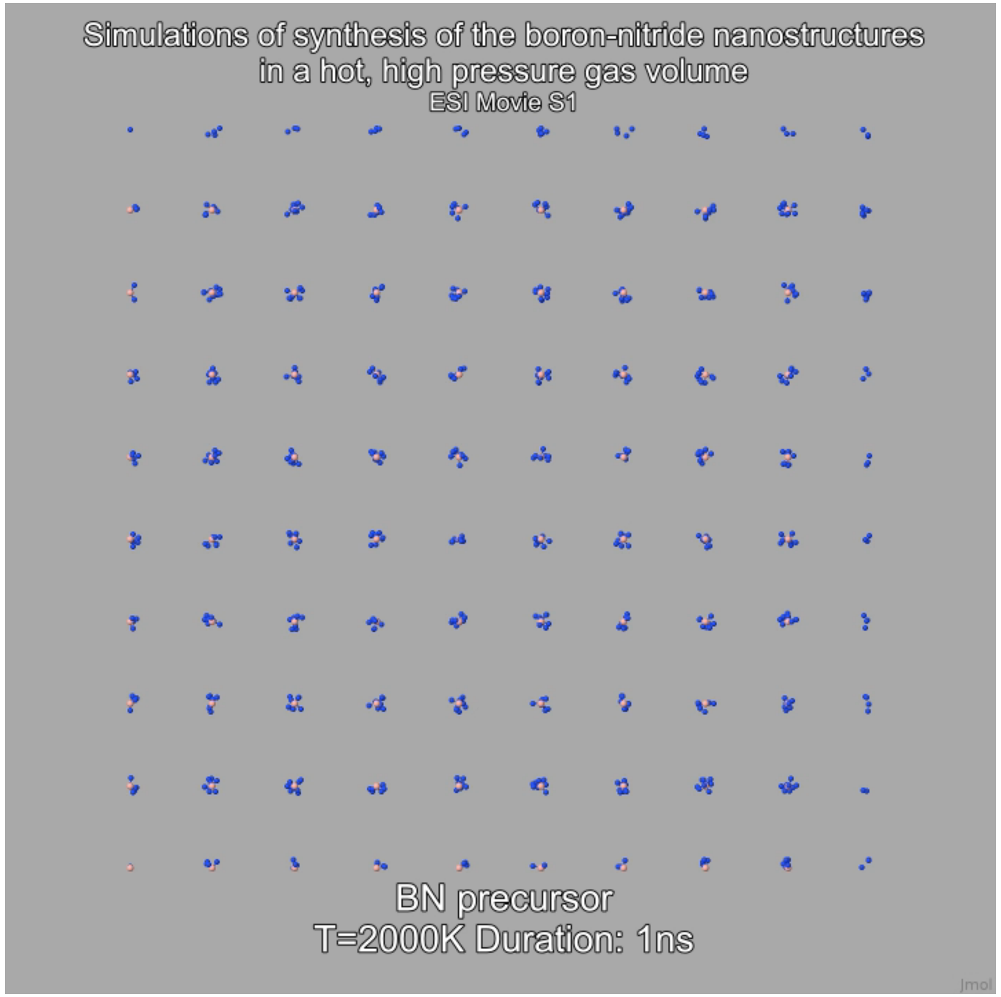
How do we achieve synthesis of the BN nanostructures form the “soup” of precursors?

Systems: Typically 1300 atoms, enclosed in a box of lateral dimension ~10 nm, with 3D periodicity. This resulted in particle density of $n \sim 10^{21}$ cm^{-3} , i.e. initial pressure $p = nkT \sim 1.4 \times 10^4 \times T$ (Pa), which means 270 bars at 2000K. This large initial pressure promotes reactive collisions frequency, accelerating the self-assembly process during the short time of 1 ns. The pressure decreases since n decreases by agglomeration. All system ran for 1 ns, with time-step of 1 fs.

Basic Toll: Quantum mechanics, Quantum-classical molecular dynamics, using DFTB, utilized through the new code, DC-DFTB-K, developed at Waseda University, Tokyo, by Prof. Nakai and collaborators. This code accelerated standard DFTB calculation by close to an order of magnitude (for our systems). Still, each point (defined by a precursor and a temperature) required about one week of calculation

Finding optimal precursors and temperature for the BN synthesis from a hot, high pressure gas





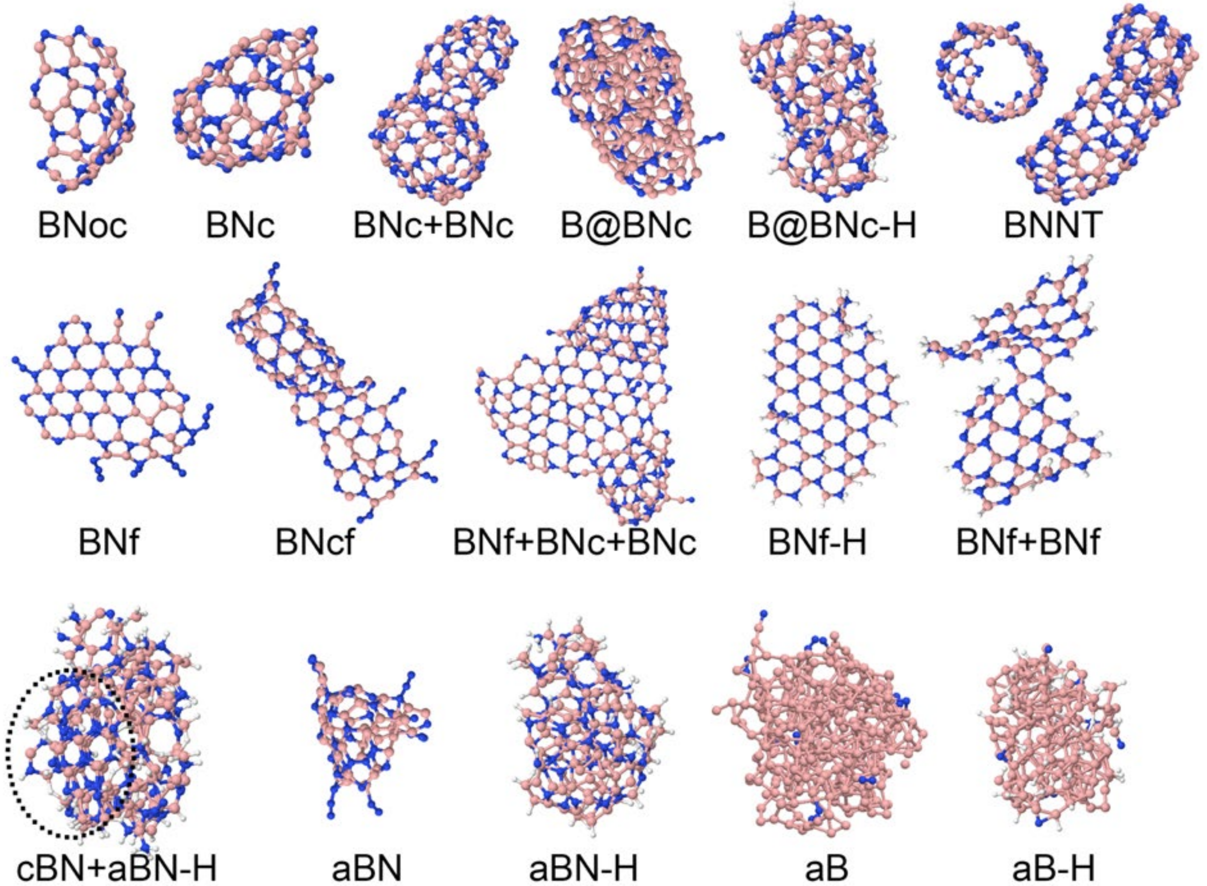
Precursor systems and major products

11 configurations of precursors containing B and N, at 1500K-6000K
Simulations done by DC-DFTB-K

11 precursor systems

Group	Subgroup	Content	Symbol
A	A1	1/2B 1/2N	B-N
		1/3B 2/3N	B-2N
		2/3B 1/3N	2B-N
		1/4B 3/4N	B-3N
	A2	BN	BN
B	B1	1/3B 1/3N 1/3H	BNH/111
		1/4B 1/2N 1/4H	BNH/121
		1/2B 1/4N 1/4H	BNH/211
	B2	4/5BN 1/5H	BN-H
		HBNH	HBNH
		$B_3N_3H_6$	Borazine

Major products



Initial pressure ~100 atm: increase the collision probability

Ratings of precursor systems for optimal synthesis of sp^2 BN structures

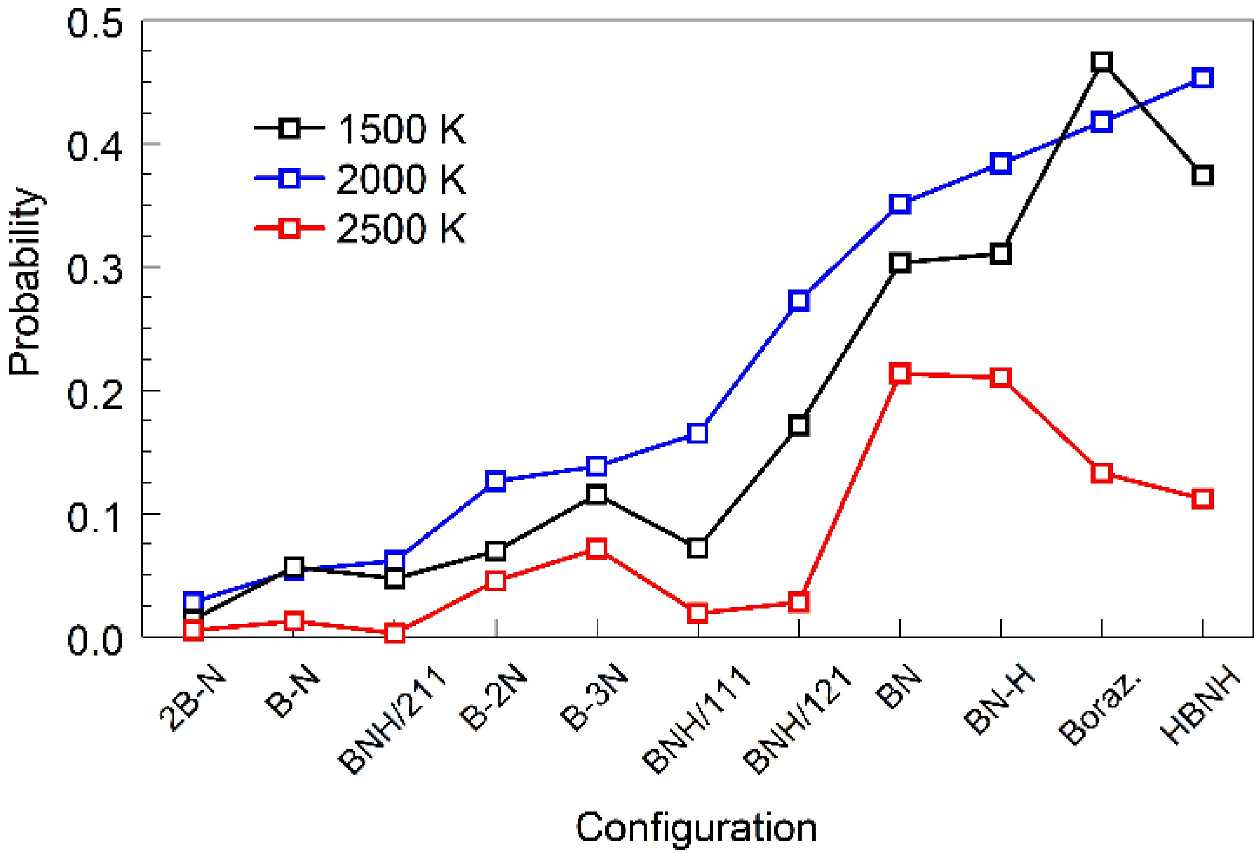
Probability of synthesis of h-BN structure form precursor X at T is product of probability of hexagon formation at time t and probability of formation of B into sp2 ideal hybrid

- PSQ: parameter of the synthesis quality

$$P(X,T) = P_{hex}(X,T)P_{sp2}^{B}(X,T)$$

$$P_{hex} = \frac{N_{hex}}{N_{hex}^{\max}} \qquad P_{sp2}^{B} = B_{sp2} \big/ N_{B}$$

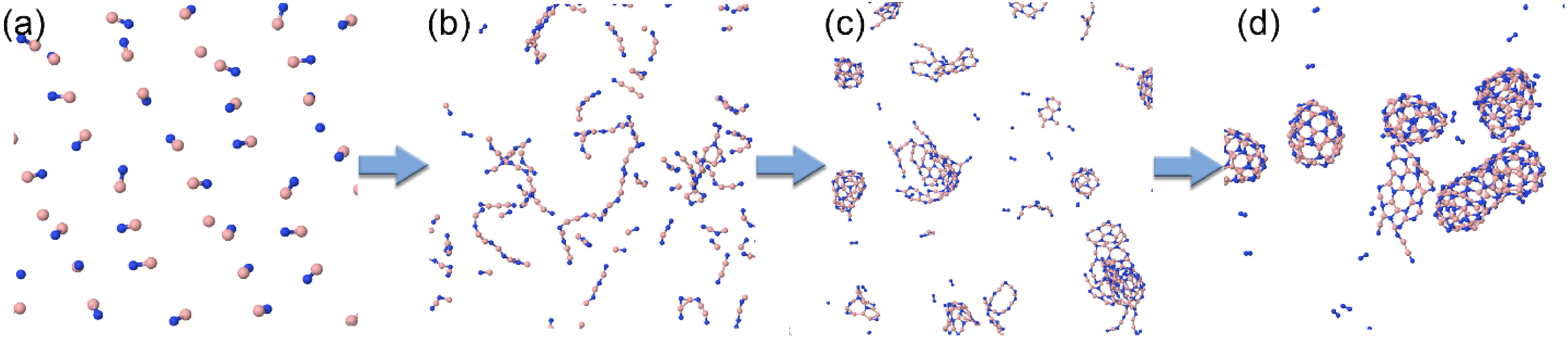
$$N_{hex}^{\max} = \frac{B_{sp2} + N_{sp2}}{2} + 2(B_{sp3} + N_{sp3})$$



- Best choices:
- 2000K
- BN, BN-H, Borazine and HBNH

Stages of structure evolution for BN precursor system

- BN molecules form BN chains (sp);
- Chains branch (sp, sp^2);
- Branched chains join into various sp^2 BN structures



0 ns 0.03 ns 0.13 ns 1 ns

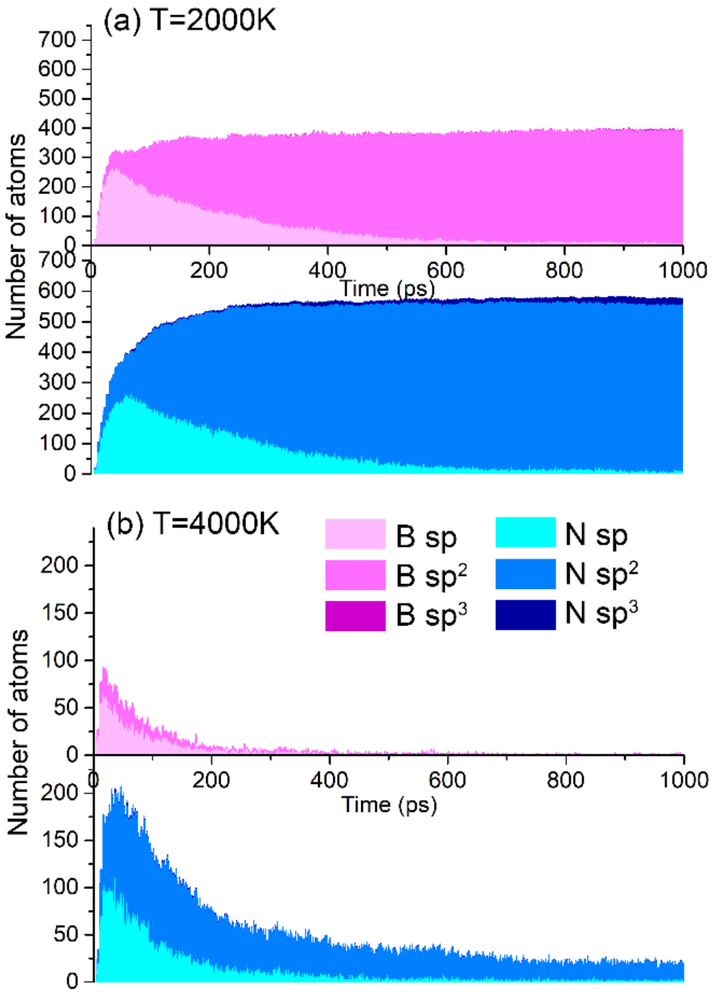
Evolution of B & N atoms hybridization

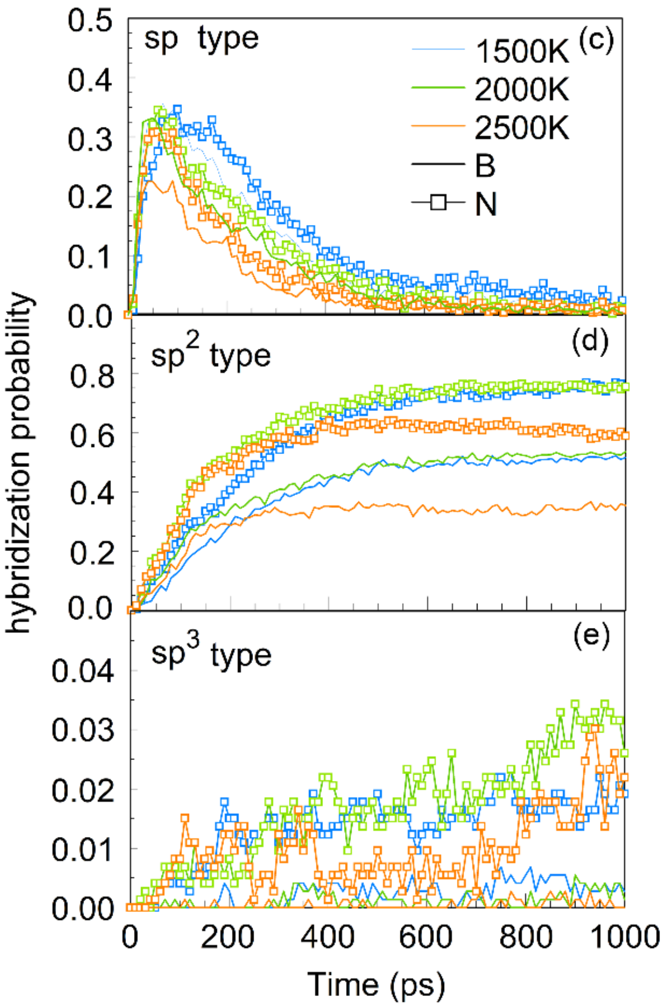
- Sharp increase of sp atoms

  ➔ fast creation of BN chains

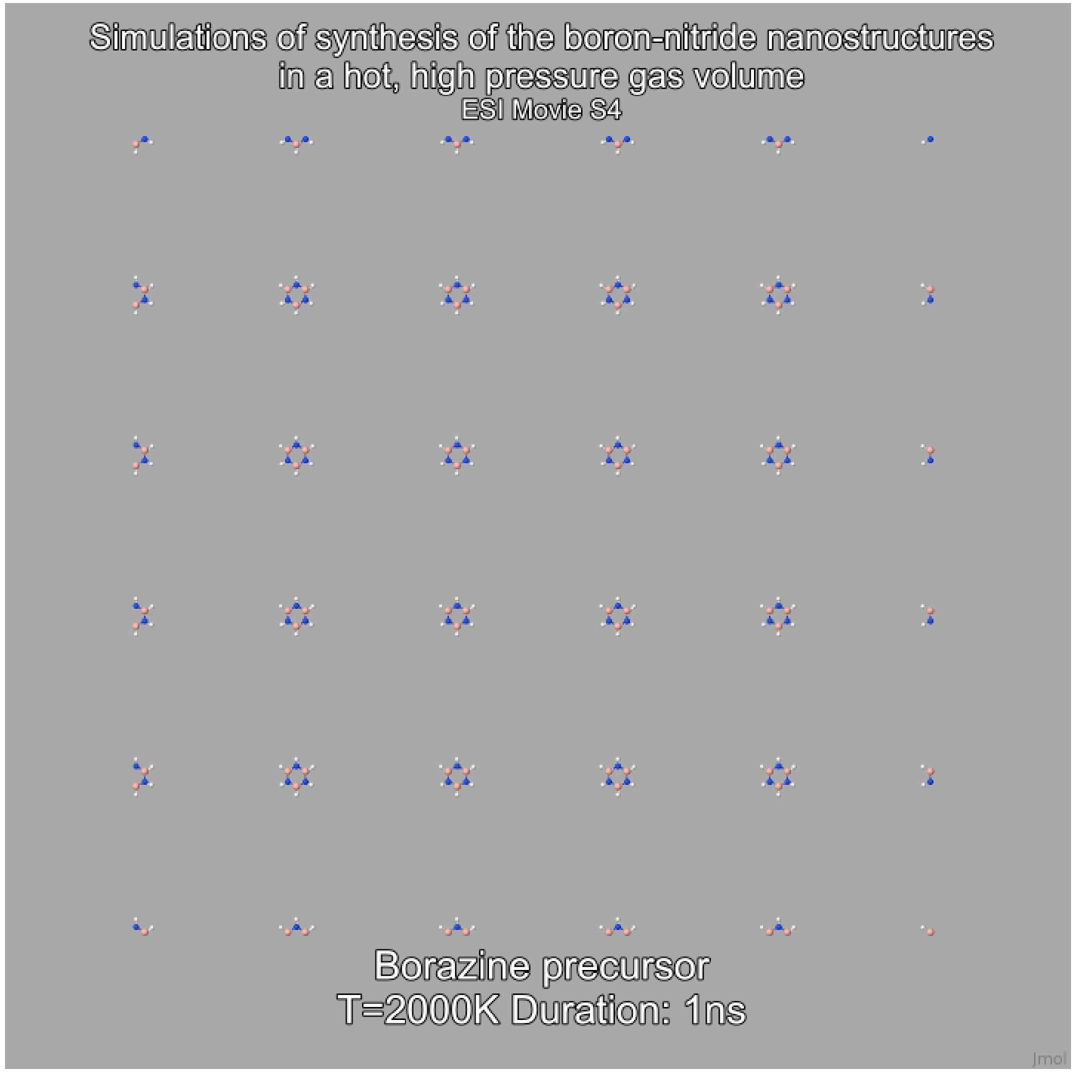
- Gradual increase of sp^2 atoms with decrease of sp atoms

  ➔ chain branching and creation of h-BN structures





Borazine at 2000K



Simulations of synthesis of the boron-nitride nanostructures in a hot, high pressure gas volume

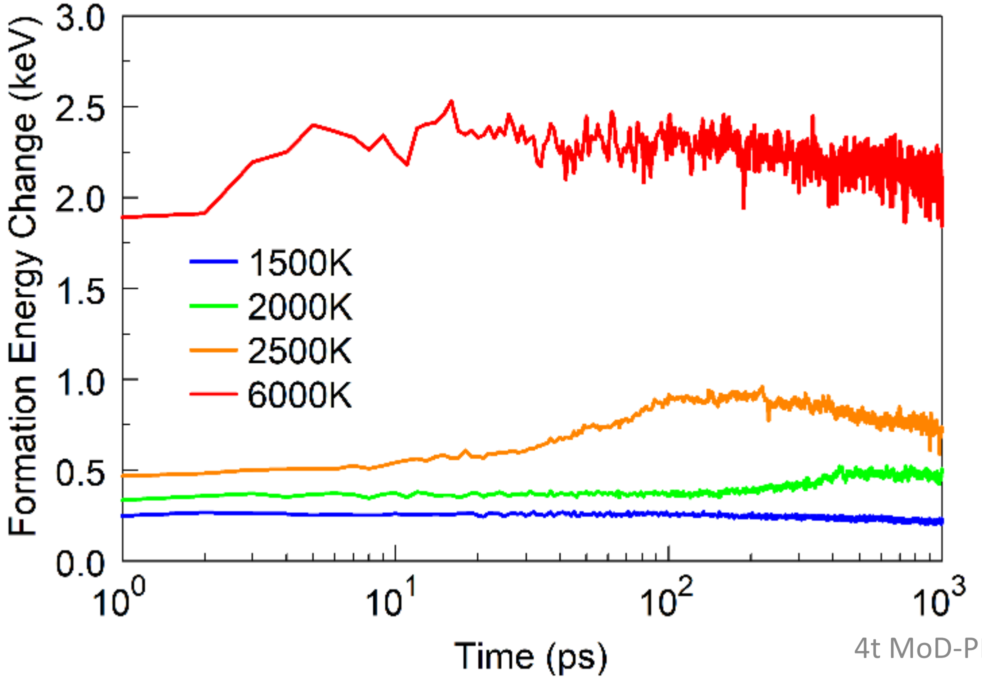
ESI Movie S4

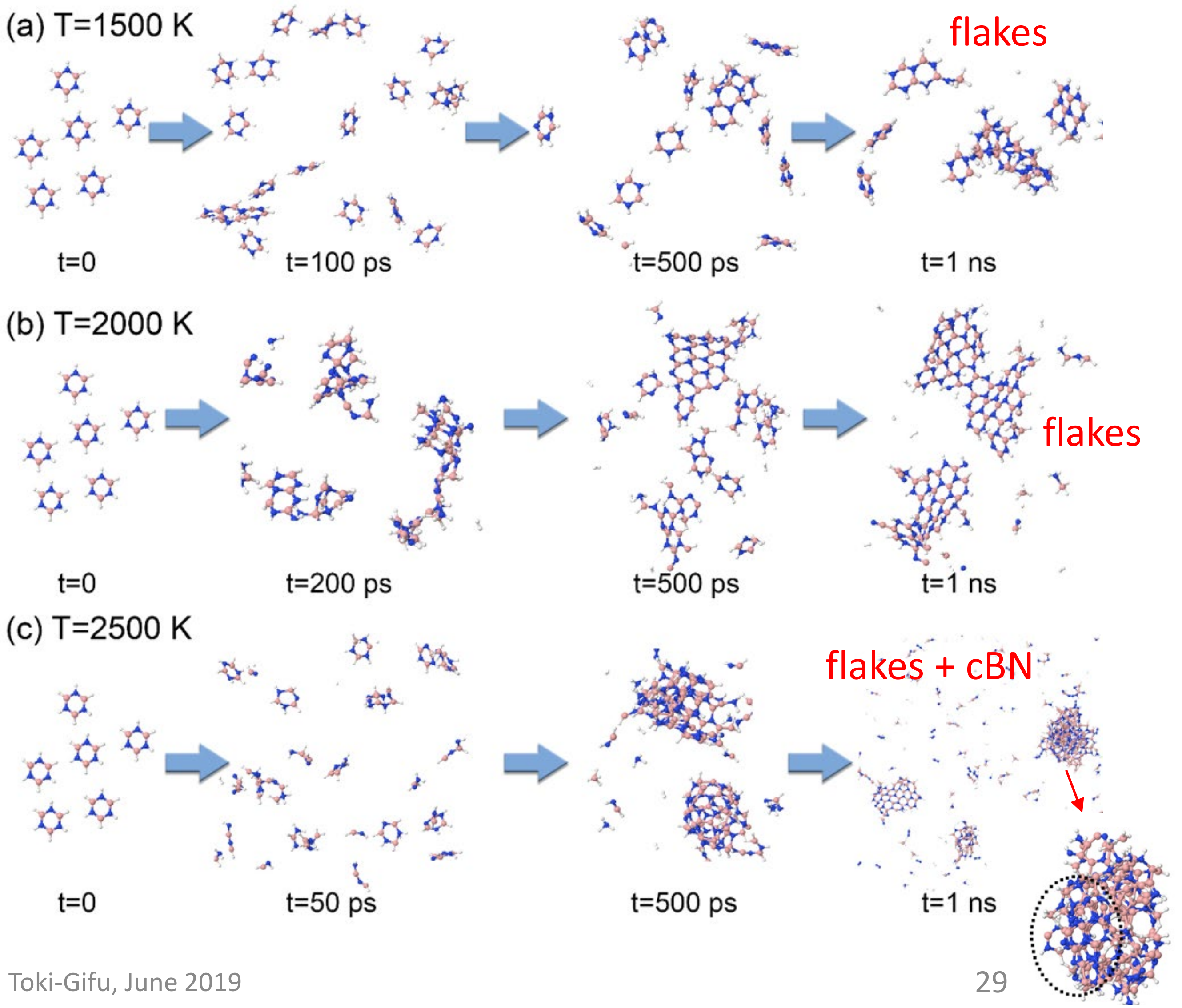
Borazine precursor

T=2000K Duration: 1ns

Stages of structure evolution for **borazine** precursor system

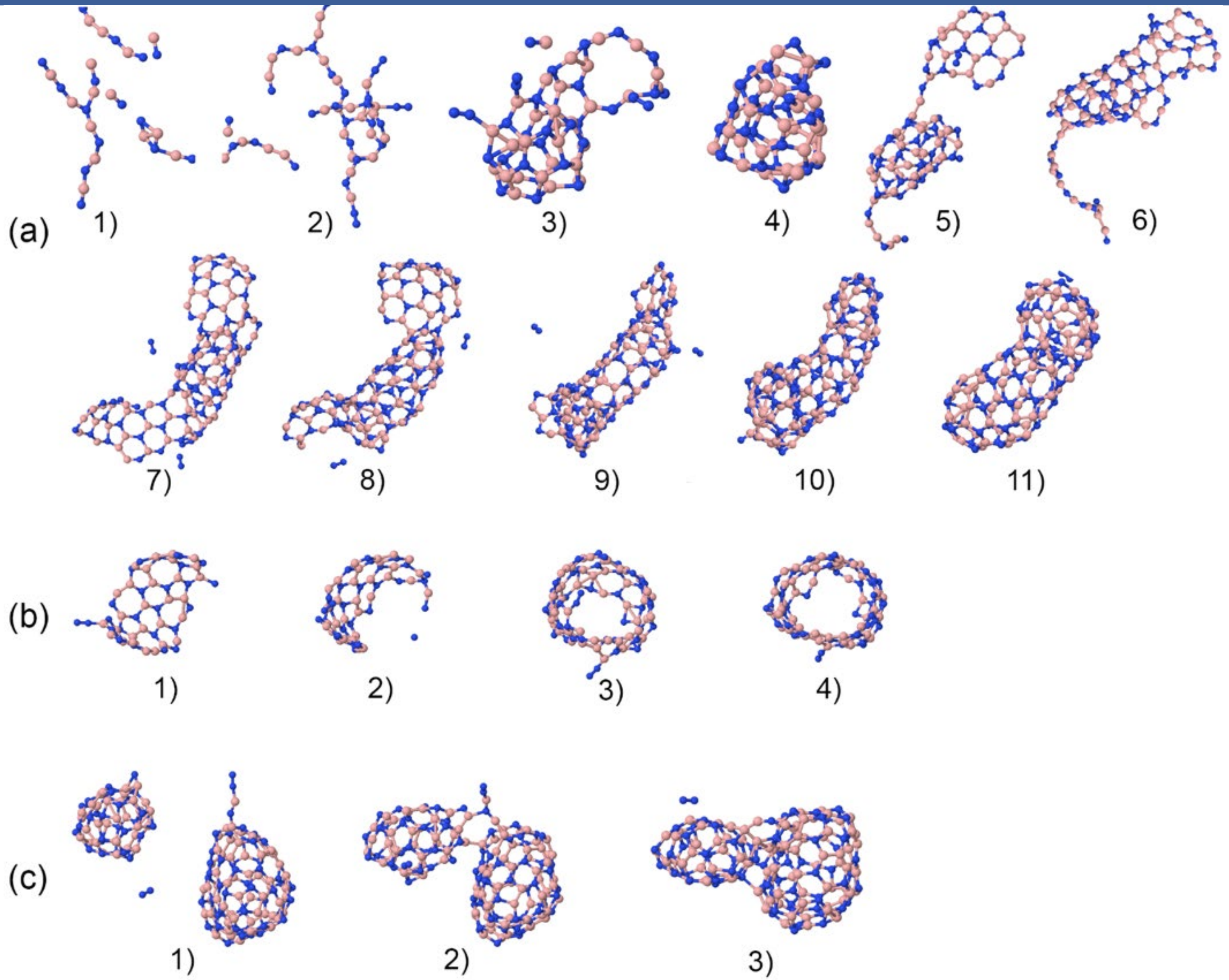
- Borazine molecules needs to release Hs before assembly.
- Higher temperature:
  - Promotes dissociation of borazine and release of H
  - Reduces ratio of H in final





Mechanisms of BNNT self-assembly from gas phase precursors

1. Merge of patches (a)
    - BN chains branch and join
    - BN cluster connects with patches of BN flakes (BNf)
    - Merge and reorganization
2. Self-folding of BNf (b)
3. Coalesce and reorganization of closed BN cages (c)



What novelties have we reported? Summary

- BN-containing molecules are efficient feedstock for building various BN nanostructures at temperatures and pressures provided by electric arc and torch discharge.
- Hydrogen saturates the dangling bonds at the edges and stimulate creation of nanoflakes, and prevents formation of nano-onions
- The atomic hydrogen catalyzes hybridization of B and N atoms from sp2 to sp3, leads to formation of nano-size c-BN at ambient P.
- Compound precursors containing B-N bond (BN, BN-H, Borazine and HBNH) are optimal for synthesis of sp^2 BN structures; optimal temperature is 2000 K.
- Understood some mechanisms of creation of BNNTs in a hot high-P plasma. Self organization of BN diatomic molecules

Details of this talk in:

Han et al, Nanotechnology Lett. (IOP) 28, 07LT01 (2017)
Krstic et al, J. Phys. Chem. C 122, 936 (2018)
Krstic et al, Chem. Sci. 9, 3803 (2018)

Thank you!

How to define the synthesis quality?

Hexagons of alternating B -N bonds basic structural “brick” for all ordered BN nanostructures.

1) Need counting of the hexagons (form the ring counting algorithm, adapted form TINKER package)

This number at time t is $N_{hex}(t)$ – only hexagons with 3B and 3N counted.

2) At any time t, maximum number Nmax of hexagons formed from both trivalent (sp2) and tertravalent (sp3) hybridized B and N atoms, taking only those B and N that are bound to their complement.

$$N_{hex}^{\max} = \frac{B_{sp2} + N_{sp2}}{2} + 2(B_{sp3} + N_{sp3})$$

3) Probability of hexagon formation at time t is $P_{hex} = \frac{N_{hex}}{N_{hex}^{\max}}$

Only hexagons in clusters with more than 10 atoms taken into account (in case of borazine 13, to avoid counting of the borazine hexagons.

4) **We want h-BN based structures**. To obtain probability of h-BN purity in the structures, multiply by probability of formation of B into the sp2 ideal hybrid

$$P_{sp2}^{B} = {B_{sp2}}\Big/{N_B}$$

Finally, **probability of synthesis of h-BN structure form precursor X at T is**

PSQ = parameter of the synthesis quality

➡

$$P(X,T) = P_{hex}(X,T)P_{sp2}^{B}(X,T)$$

Toward root growth mechanism for BNNT

- Our simulations indicate that the root growth mechanism may not valid for BNNT:
  - N atoms at the nanotube root can dissolve by diffusion on boron cluster
  - Incorporation of feedstock happens at the top end of BNNT