NT06

Draw out carbon nanotube from liquid carbon

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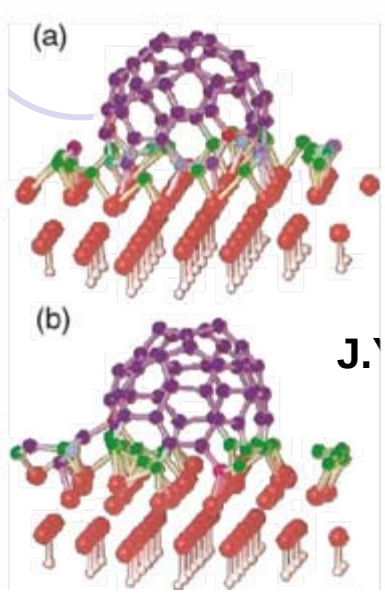
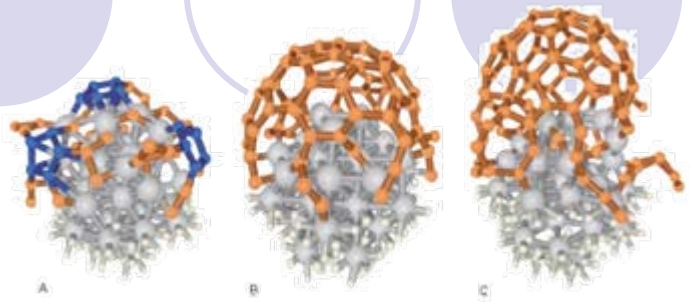
Outline

- Introduction
- Motivation
- Simulation methods
- Results
  - Elongated growth of SWCNT
    - Elementary process
    - Formation of CNT near liquid surface in a cooling process
    - Environment of surface region
    - Electronic states : Formation of π bond in growth process
    - Suitable conditions for elongated growth
  - Defects healing by attached clusters
  - Fabrication of a Y junction from two isolated CNTs
- Discussion and summary

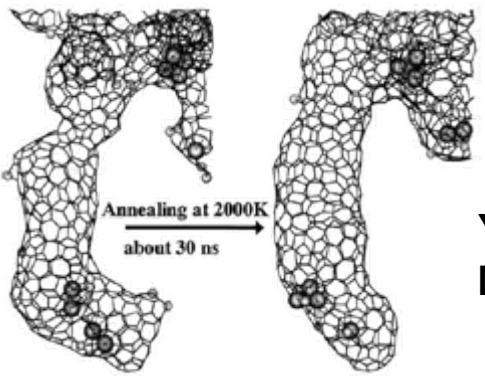
Introduction: Atomistic simulations of nucleation and growth process

J. Gavillet, et. al.
Phys. Rev. Lett.
87, 275504 (2001)

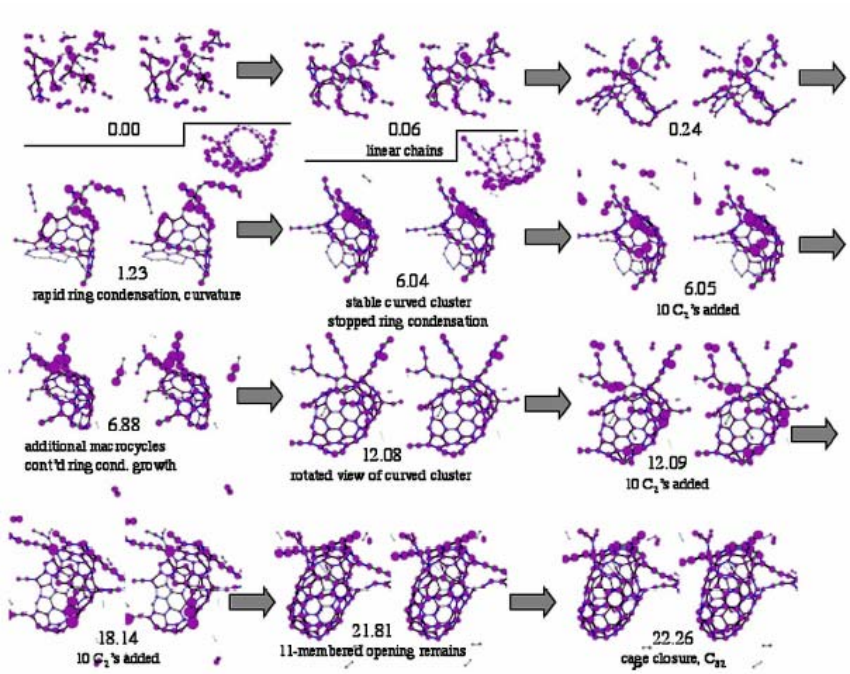


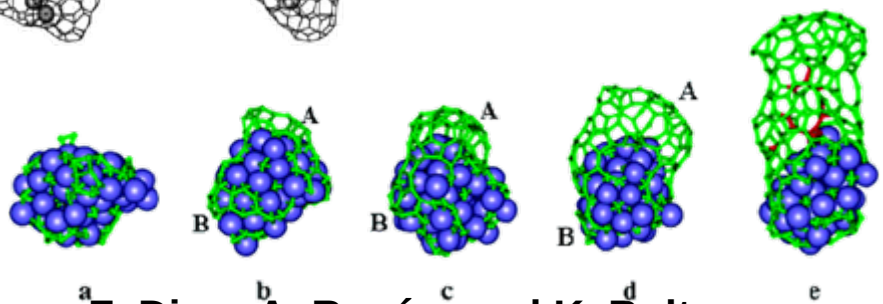


J.Y. Raty, F. Gygi,and G. Galli,PRL 95, 096103 (2005)



Y. Shibuta, S. Maruyama,
Physica D 323, 187 (2002)





F. Ding, A. Rosén, and K. Bolton,
J. Phys. Chem. B, 108, 17369-17377 (2004)

G. Zheng, S. Irle and K. Morokuma,
J. Chem. Phys. 122, 014708 (2005)

Motivation

Nucleation process is crucial to control the structure of CNT, however, controlling nucleation process precisely enough is difficult.

Why not use CNT itself as template ?
And how ? (high-density carbon fluid precursor)

Experimental report :

Liquid carbon, carbon-glass beads, and the crystallization of CNT
i Liquid carbon as precursor of pure carbon-arc–produced MWCNT growth
ii The role of the helium pressure higher than fullerene case: lead to precursor with higher density

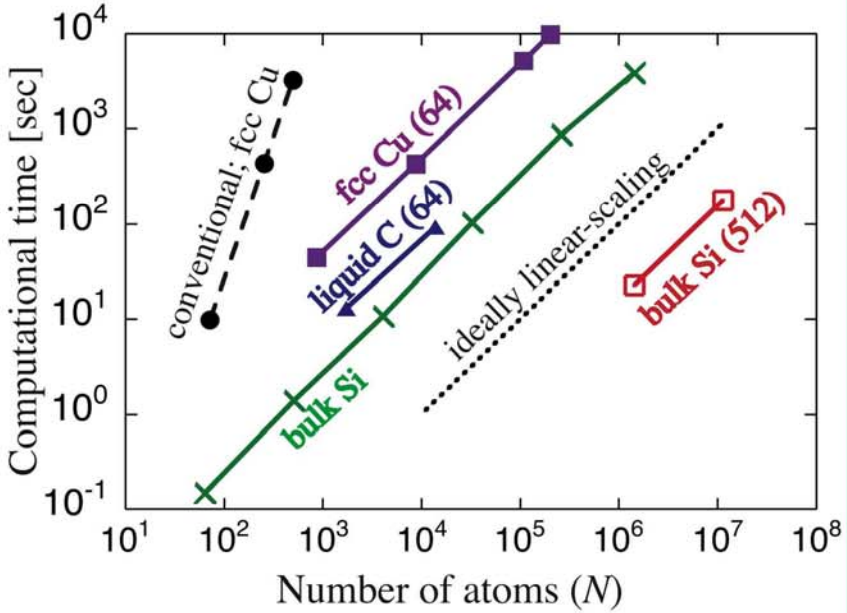
W. A. de Heer, et.al , Science 307, 907 (2005)

Theory: Ultra-large-scale electronic structure calculation

Quantum mechanics *with density matrix or the Green's function (not eigen states)*

Benchmarks: C(liquid), Si(bulk), Cu(bulk)

upto 10^7 atoms using 1~512 CPUs (Intel or SGI)

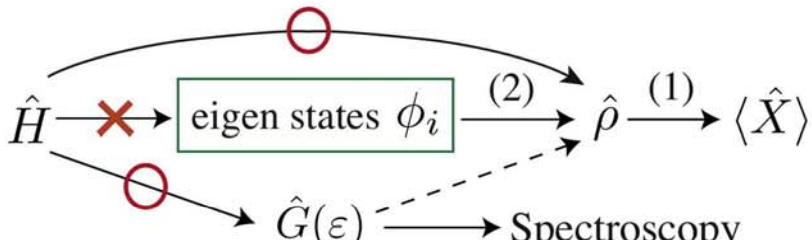


cf. Krylov subspace[1][2] or generalized Wannier state[3].

[1] R. Takayama, T. Hoshi, T. Fujiwara, JPSJ**73**, 1519 (2004).

[2] R. Takayama, T. Hoshi, T. Sogabe, S-L. Zhang, T. Fujiwara, PRB**73**, 165108 (2006).

[3] T. Hoshi, Y. Iguchi, T. Fujiwara, PRB**72,** 075323 (2005).



Calculating a physical quantity $\langle \hat{X} \rangle$

$$\langle \hat{X} \rangle = \sum_i^{\text{occ.}} \langle \phi_i | \hat{X} | \phi_i \rangle = \mathrm{Tr}[\hat{\rho}\hat{X}] \qquad (1)$$

with (one-body) density matrix

$$\hat{\rho} \equiv \sum_i^{\text{occ.}} |\phi_i\rangle\langle\phi_i| \qquad (2)$$

The present calculations are carried out with Slater-Koster- form (tight-binding) Hamiltonians;
C; Xu, *et al.*, J. Phys. Condens. Matter **4**, 6047 (1992).

(Si; Kwon, *et al.*, PRB **49**, 7242 (1994).
Cu; from $H^{(1)}$ in the LMTO theory.)

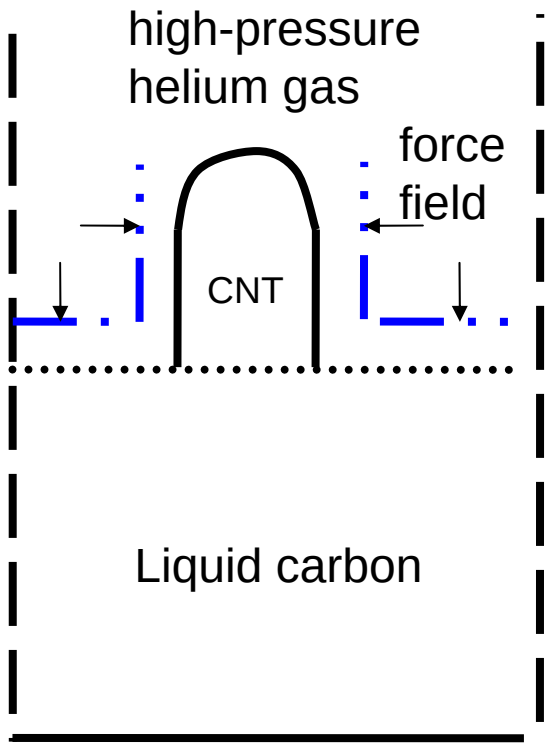
Technical details of the present simulations

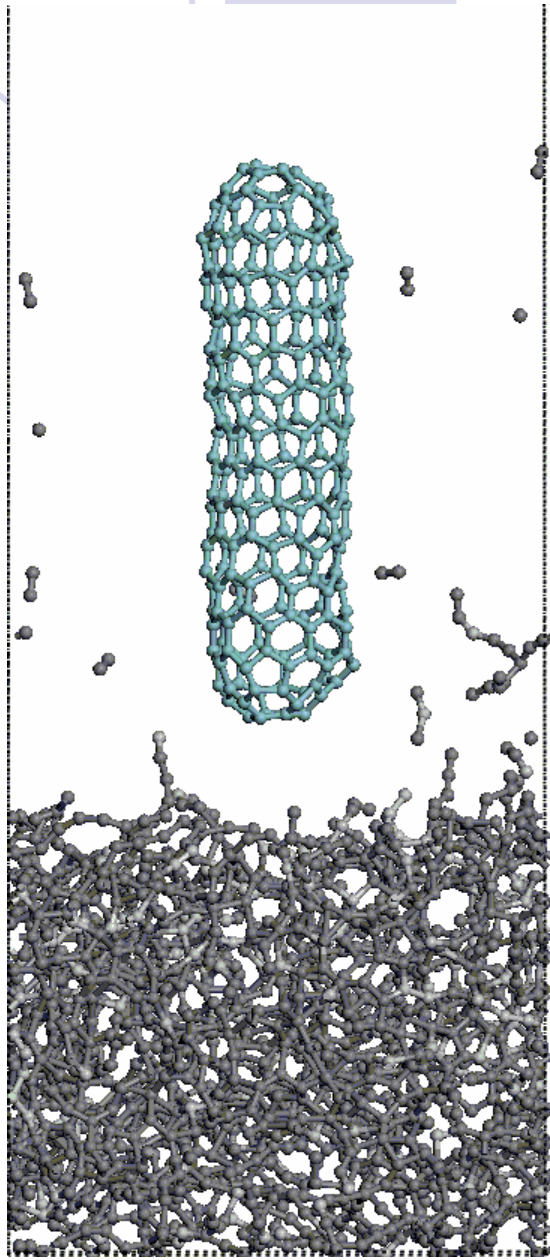
Size: more than 2000 atoms
Simulation time: 10-10^2 ps.
Cell parameter: 3nm × 3nm

Interface model:
Clear interface : Helium gas and liquid carbon tend to separate (*ab initio* simulation)
A stochastic force field acts on carbon atoms within liquid surface region and CNT, which is formulated by the collision model of helium gas. The bottom of liquid is set to rigid wall of perfectly elastic collision.

The evaporated atoms are ‘cut and pasted’ into the liquid region

Time step: 1 fs





Elongated growth process of SWCNT from liquid carbon

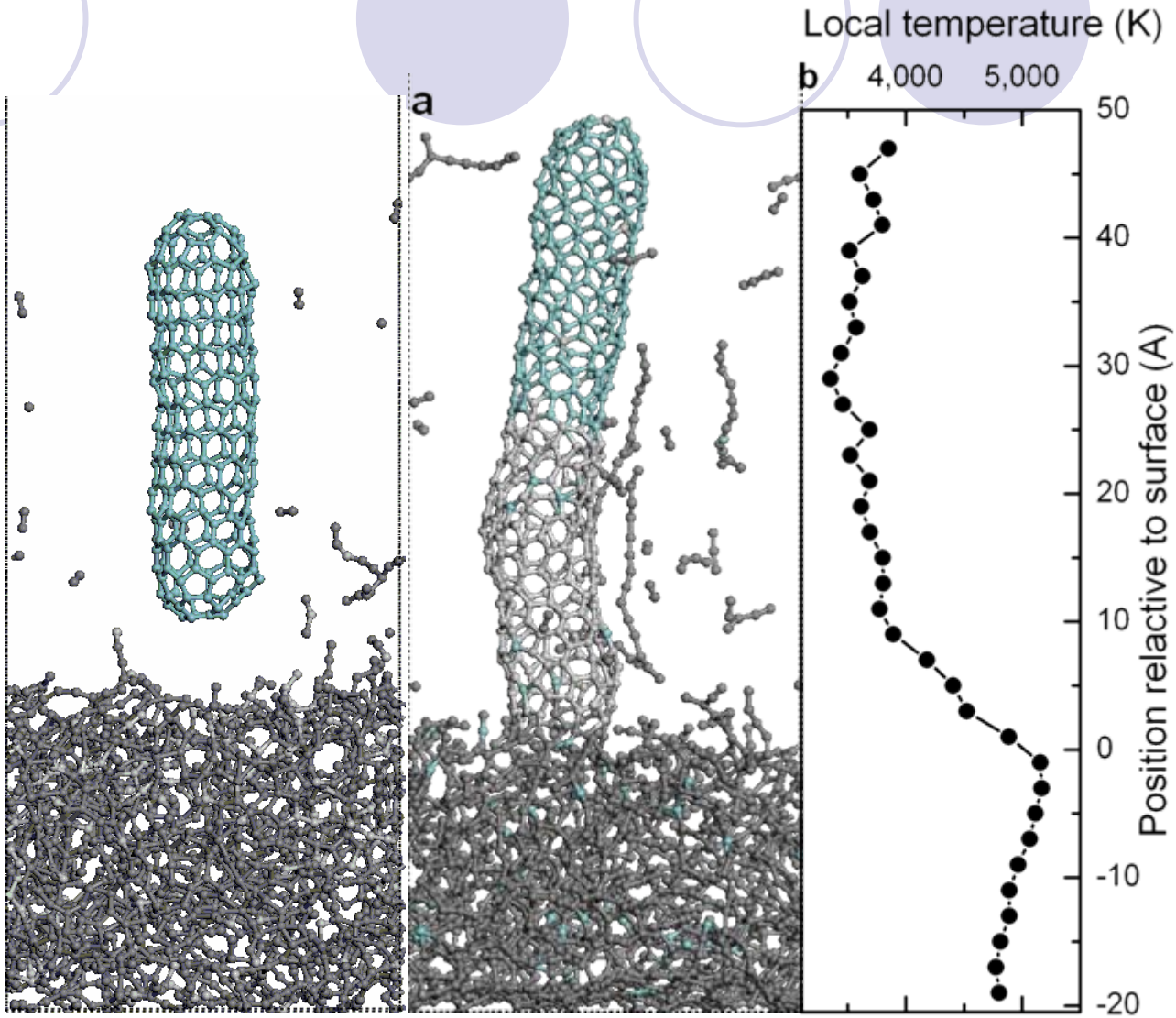
SWCNT : (9,0)
Density : 1.7±0.1 g/cm3
Growth velocity: **30 m/s**
Simulation time : 86 ps

Elongated by more than 2nm
Follow structure of **wall**
Defects

The Nosé-Hoover thermostat is used to control the total kinetic energy of the system. (T=4800 K)

The local temperature of the upper CNT tip is kept to be lower than that of the liquid part. (3800K)
Experiment : pulse heating

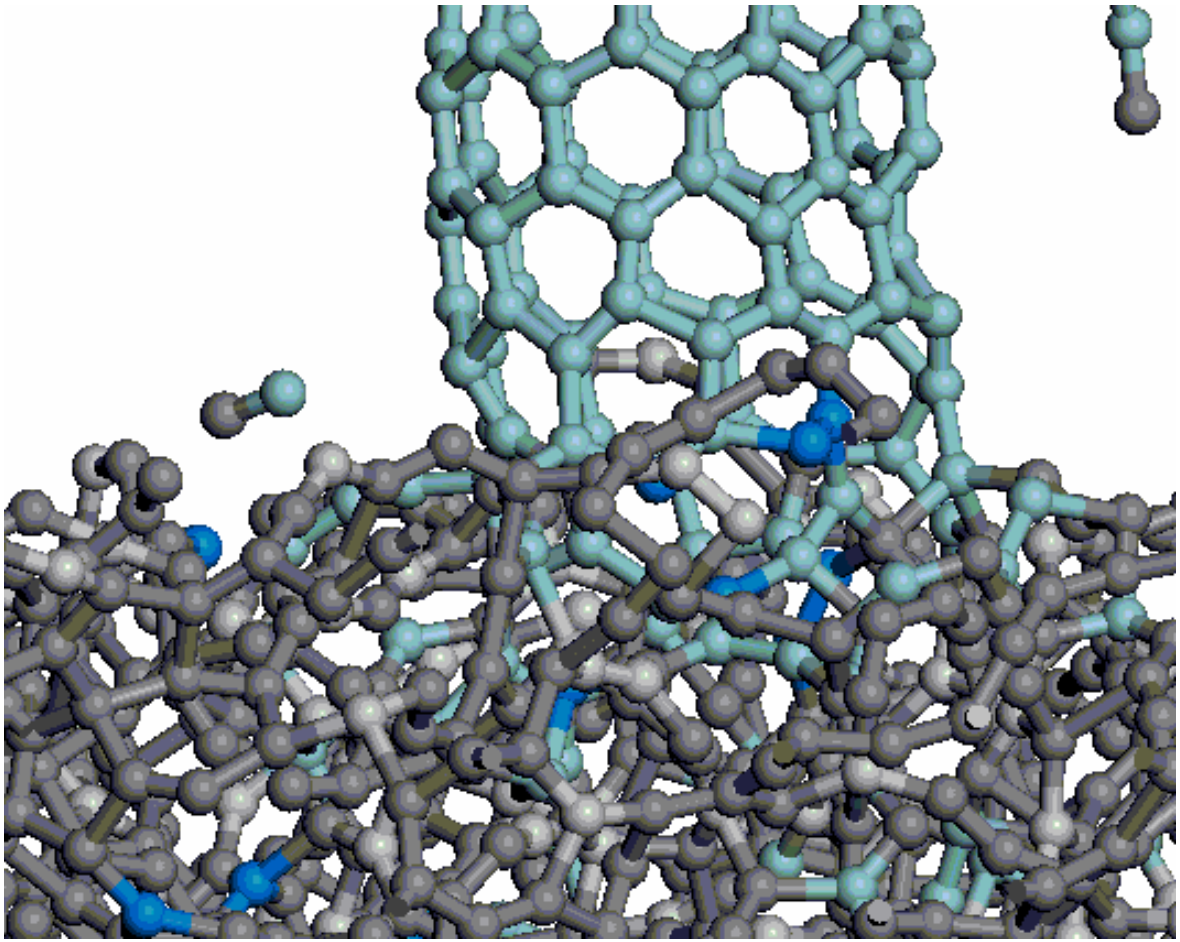
Cooling process



Cap melts

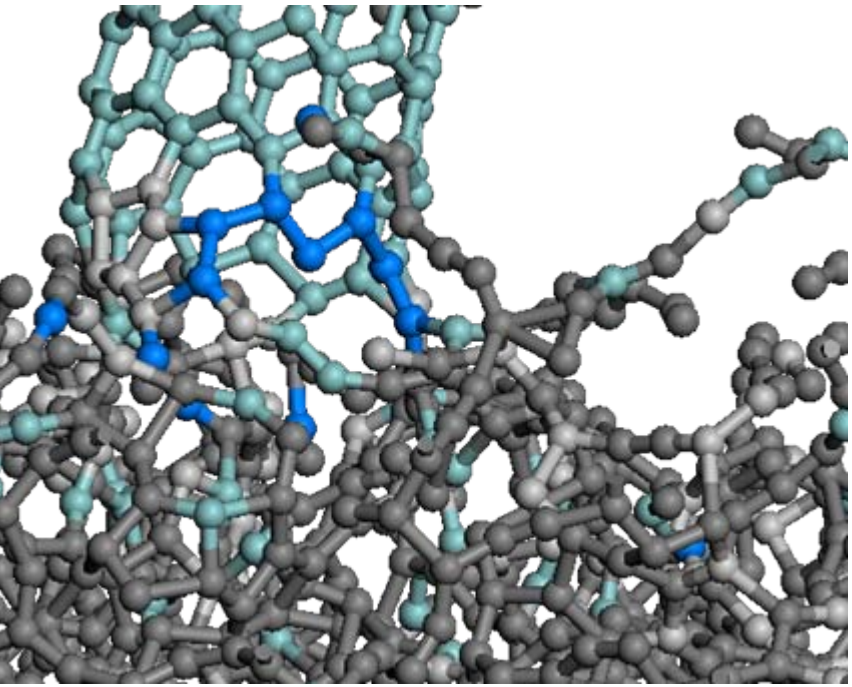
Formation of CNT near liquid surface in a cooling process

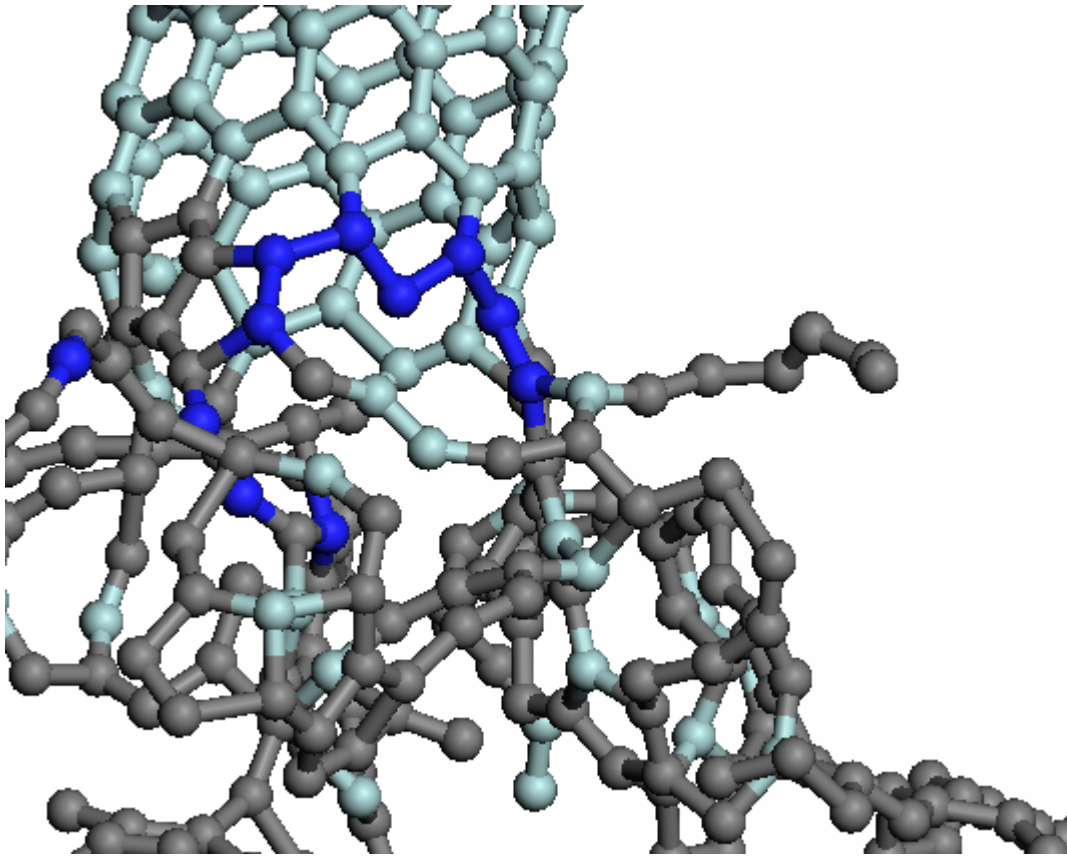
Search for stable configuration in the cooling process



14.5 ps ➔ 26.5 ps

The configuration attached to CNT root

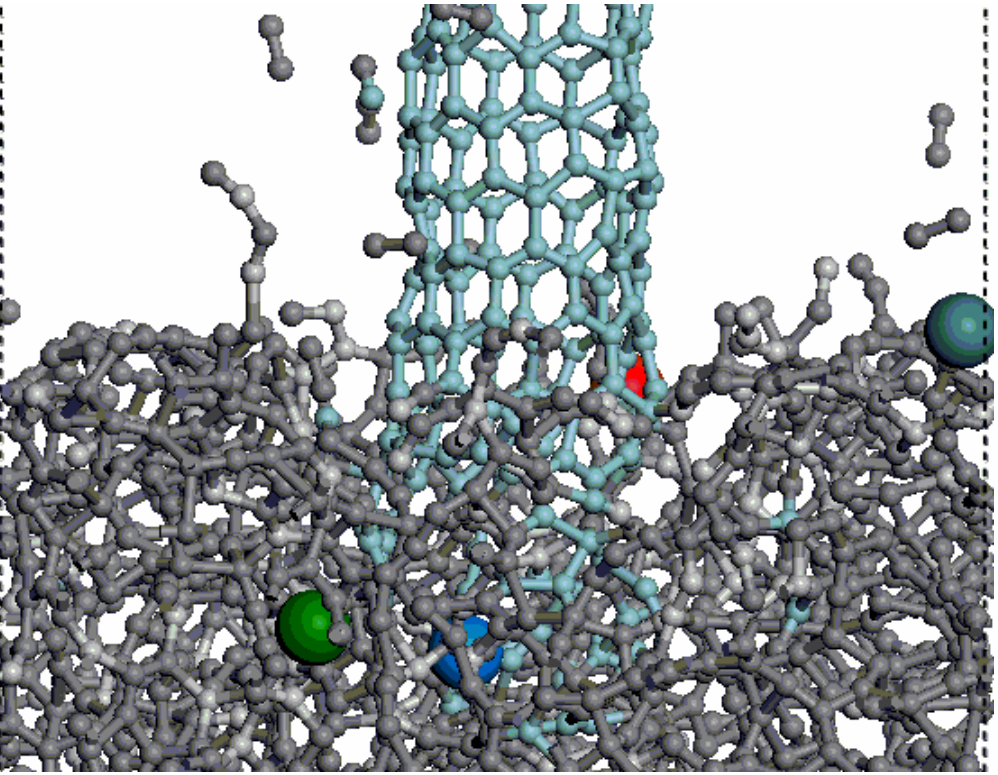




The chain and ring structure attached to CNT root

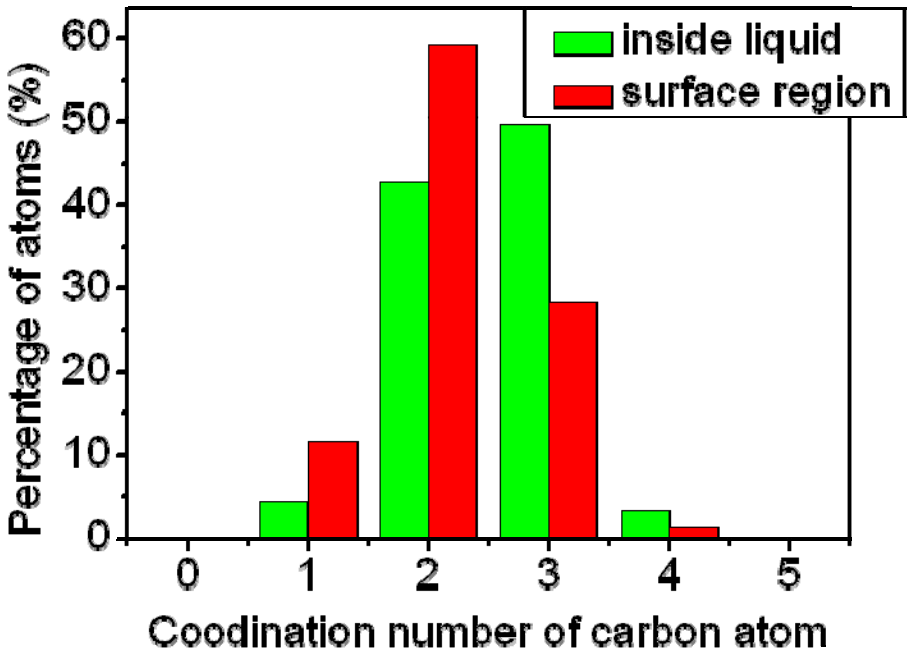
t = 20.5 ps

The atoms come into CNT through surface region



9.0 ps → 20.1 ps

Two-fold carbon atoms are majority in surface region



Electronic states : Formation of π bond in growth process

Local density of states (DOS)
only from π interaction

→ $D_\pi(\varepsilon)$: averaged among the atoms that form the elongated CNT part in the final stage.

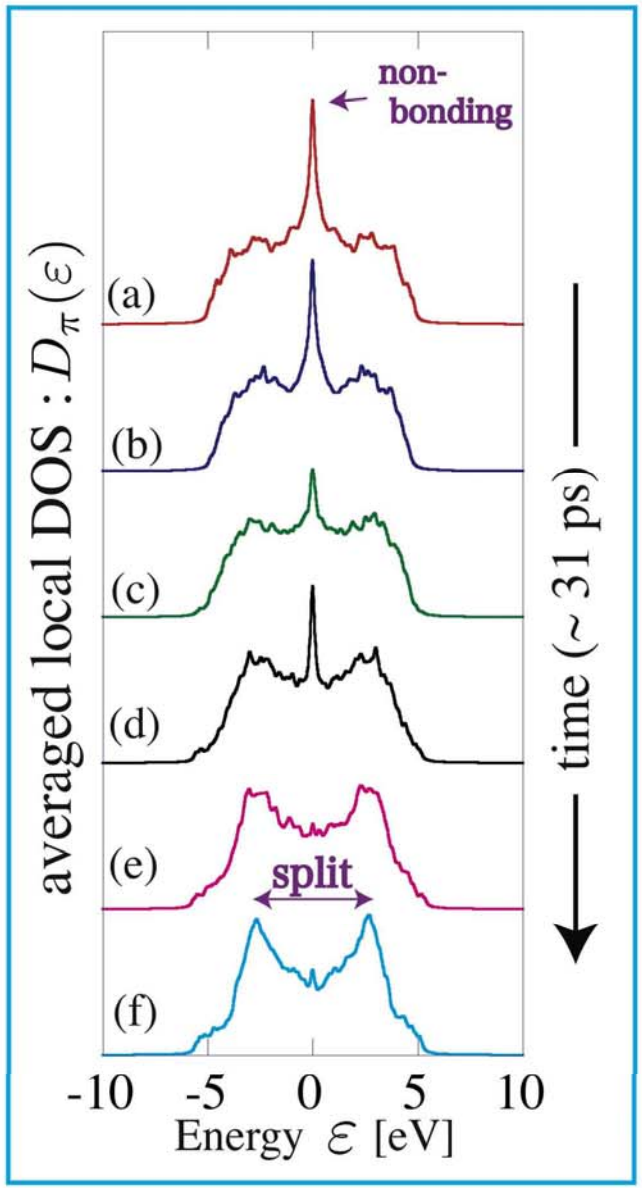
(Atomic p level is located at $\varepsilon = 0$)

liquid region (initial stage)

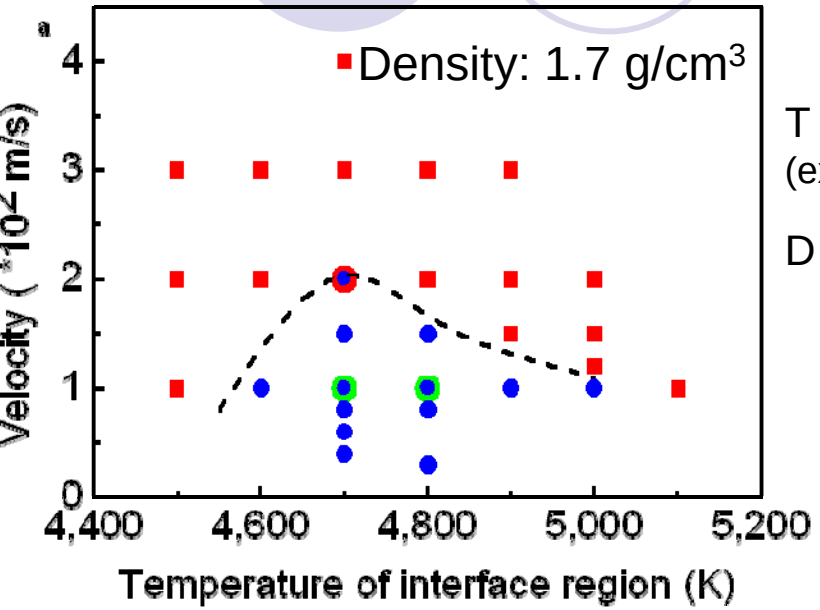
↓ **sharp peak from non-bonding (atomic) *p* state**

elongated CNT part (final stage)

energy splitting into bonding and anti-bonding states



Suitable conditions for elongated growth



Ranges are broad;

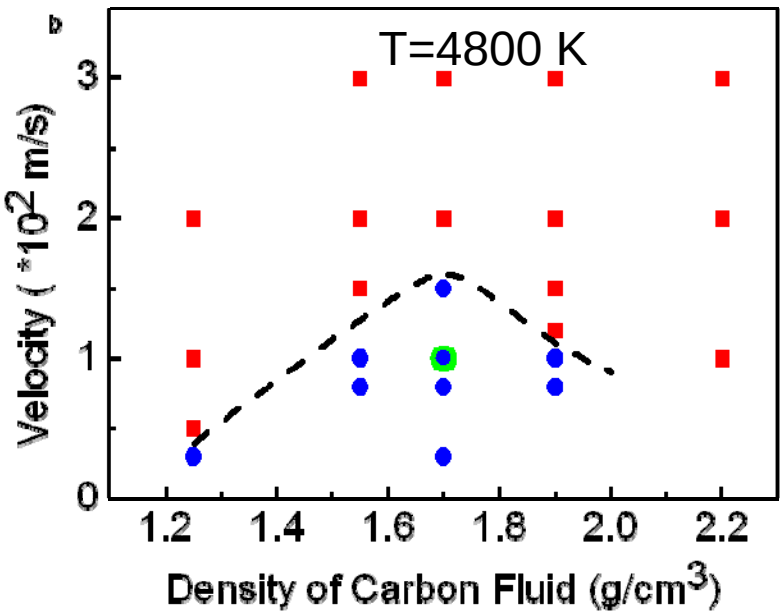
T (graphitization of surface) < Temperature < T (collapse)
(expand the lower limit of temperature by doping ?)

D (self-capping) < Density < D (graphitization of surface)

Low growth velocities are preferred;

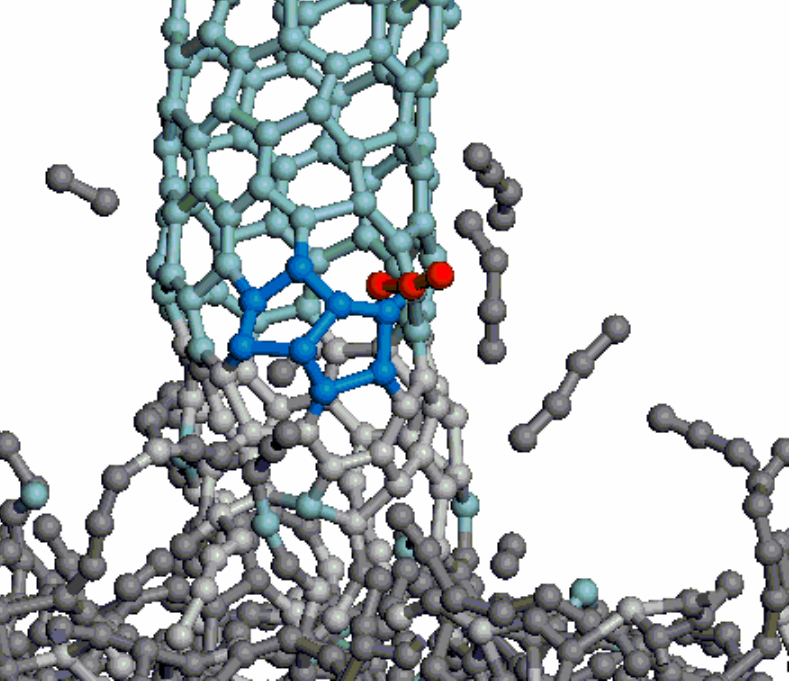
- Elongated by longer than 1.5 nm
- Fail to be elongated by longer than 1.5 nm
- Successful for three times (all trials)
- Success for two times and fail in one time

The dash line indicates the upper limit of growth velocity just for eye guide.



Remarks on the growth mechanism

- CNT is elongated during the cooling process at the liquid surface
- Low-coordination configurations appear in the surface region
- Theπbond formation in elongated CNT part is directly observed from present electronic structure calculation
- Three factors for suitable conditions (drawing velocity, temperature and density of liquid)

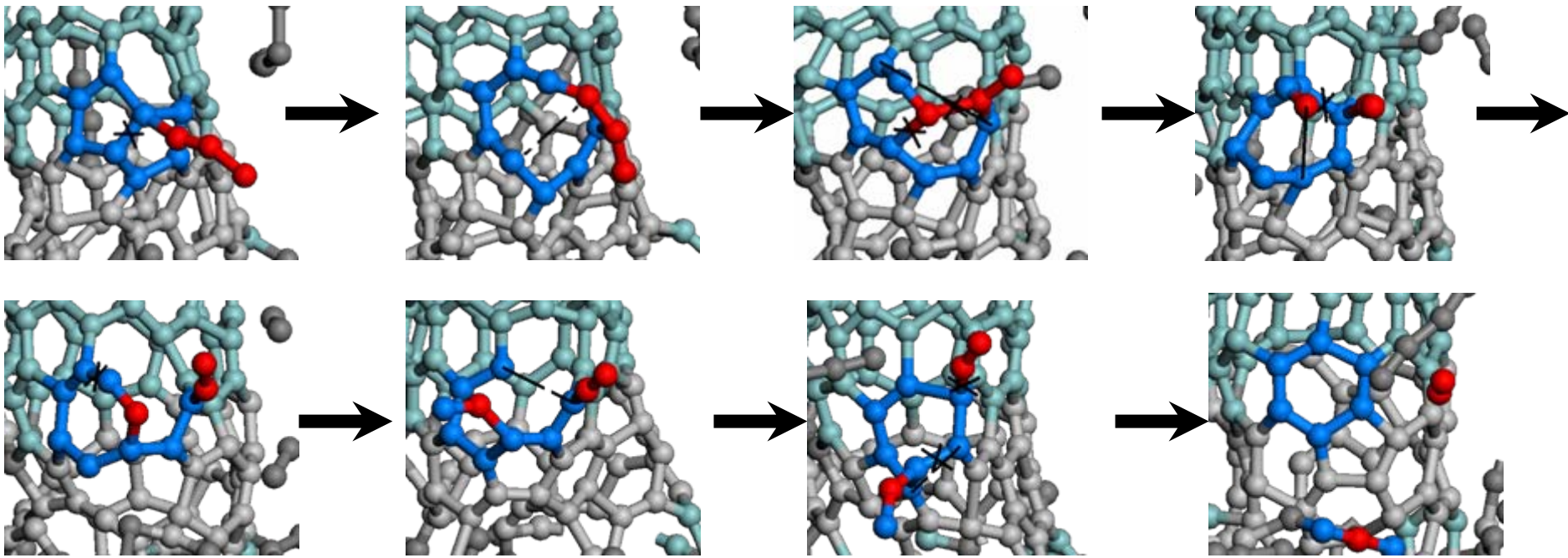


Defects healing by attached clusters

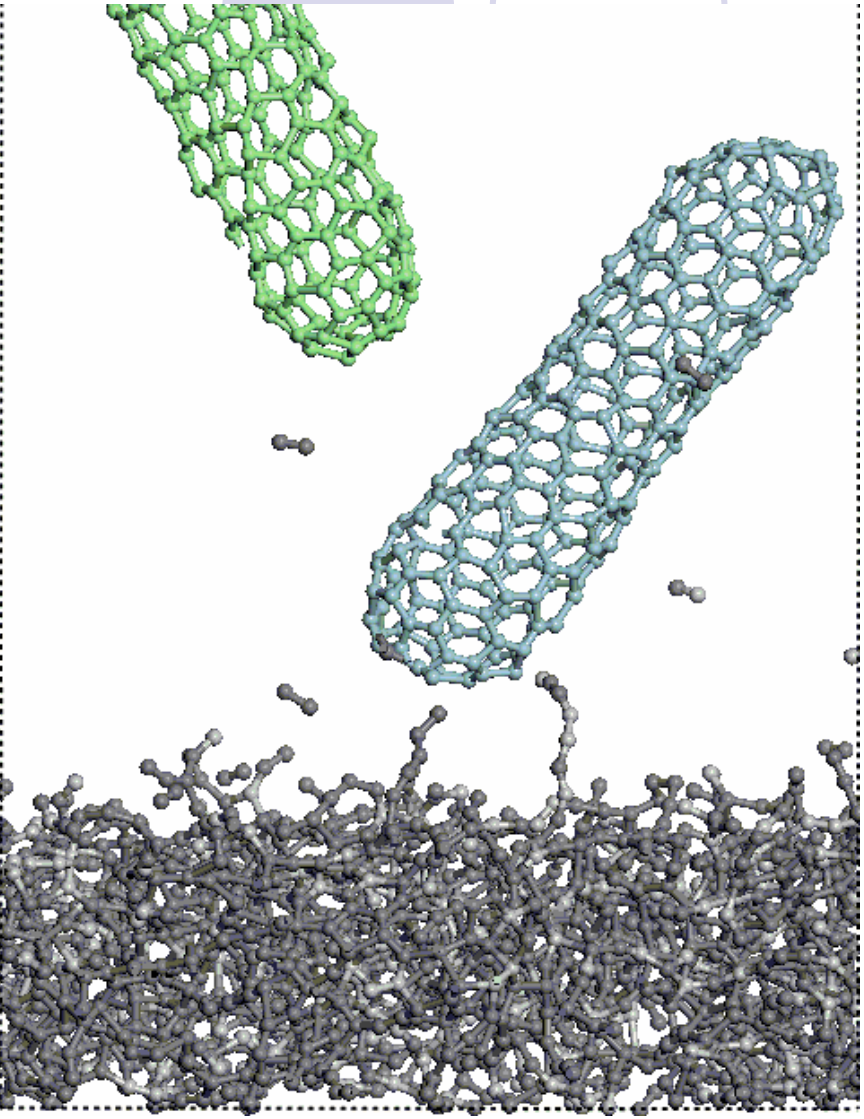
The defect healing in CNT itself
is debarred by high energy barrier.

The clusters close to defects in CNT
can make defect healing easier

33.8 ps – 36.3 ps



Fabrication of a Y junction from two isolated CNTs



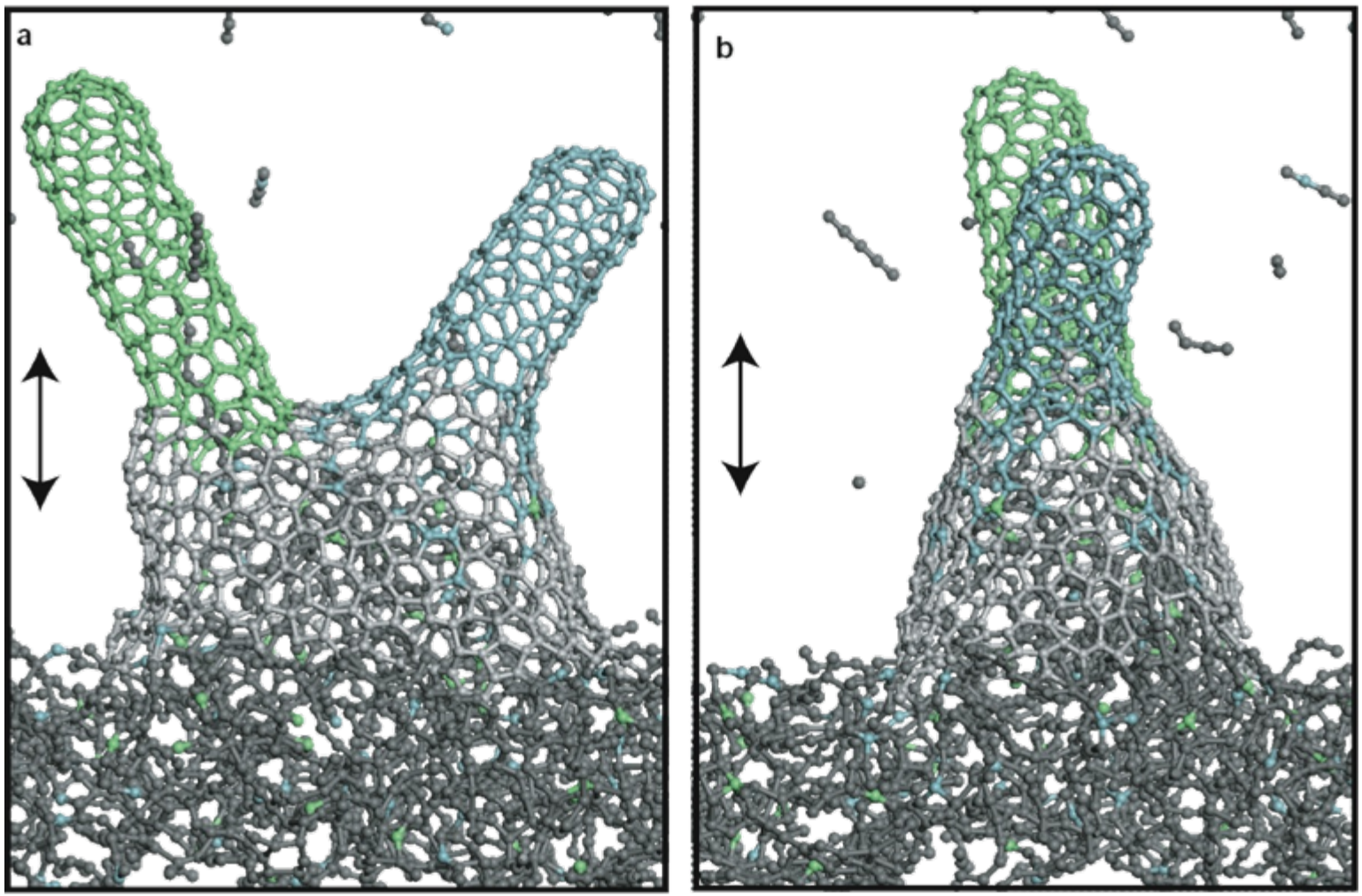
Drawing velocity: 20 m/s; Temperature: 4700 K
Density of liquid: 1.7±0.1 g/cm^3;Simulation time : 74 ps.

The third end is created and elongated

The growth mechanism and optimal conditions are similar to SWCNT growth process

Repeating manipulations could be a possible way to fabricate wirelike **pure CNT curcuits**

The formed Y junction



General discussion

- The conjunction between two viewpoints of CNT
  - The pure carbon elongated growth process show that CNT can be seen actually as elongated fullerene from the point of view of CNT as a molecule.
  - The liquid-precursor growth process is similar to Czochralski process for single crystal growth from the viewpoint of CNT as a kind of crystal.
- If the present growth process were realized,
  - defect-free structure would lead to “clone” of seed CNT
  - the wirelike pure CNT circuit could be directly fabricated

Summary

- Methodology
  - Large-scale quantum mechanical (electronic structure) calculations are realized and crucial to extend research scope for CNT growth
- Simulation results
  - SWCNT can be elongated from liquid carbon steadily
  - Observation of defects healing by attached clusters
  - Fabricate a Y junction from two isolated CNTs
- Prospect
  - The present theory could give an insight for other CNT growth processes from a realistic way (including catalyst and substrate)

Thank you !