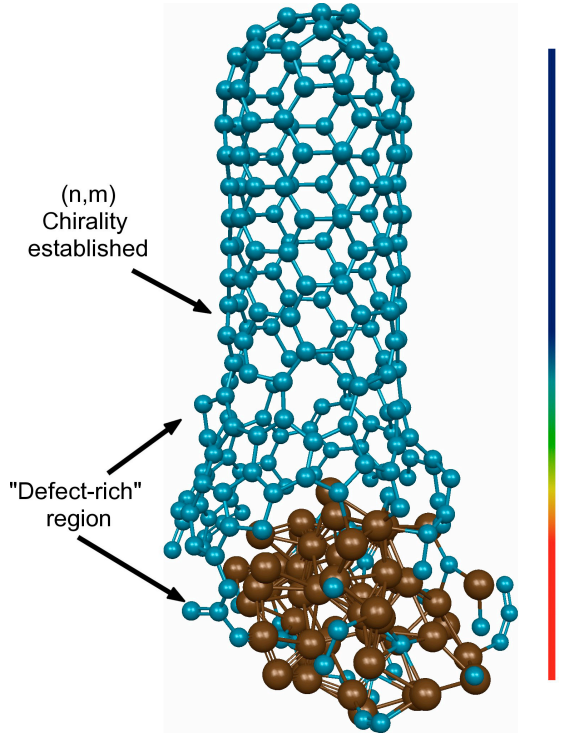
What Can We Learn from Current Molecular Dynamics Simulations of Nanotube Growth?

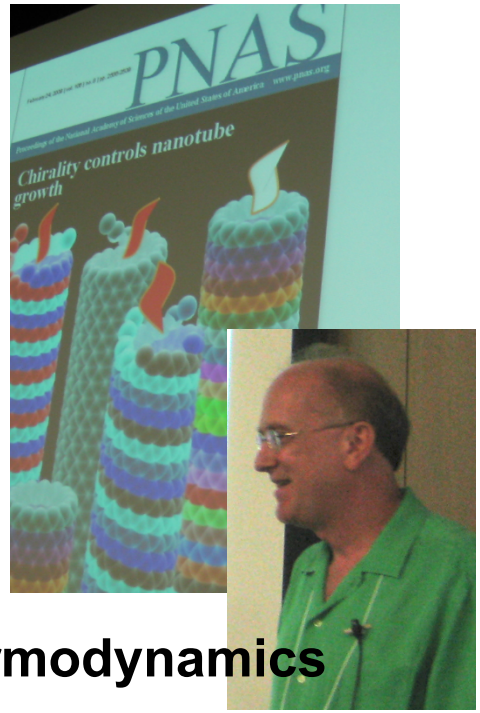


Temperature

Molecular Dynamics

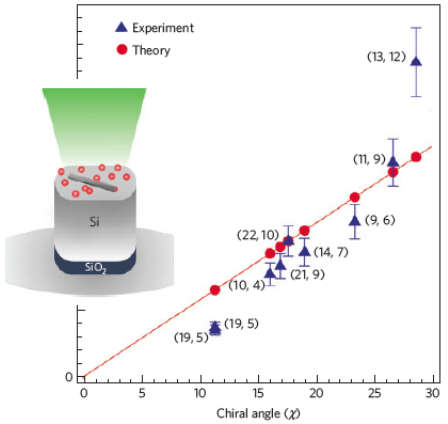
VS

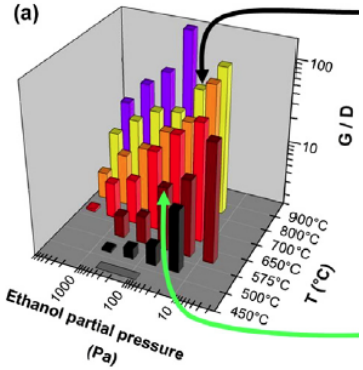
Stephan Irle



Thermodynamics

VS





Experiments

120th GMSI Seminar, Maruyama Lab, The University of Tokyo, November 19, 2012

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Prof. Keiji Morokuma

Dr. Yasuhito Ohta[a]

[a]now: Professor, Nara Women's University

Dr. Hai-Bei Li

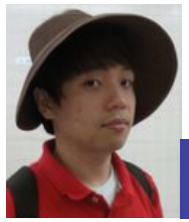
Dr. Yoshiko Okamoto

Dr. Ying Wang[c]

[c]now: Professor, Changchun Institute for Applied Chemistry (CHINA)

Dr. Alister J. Page[b]

[b]now: Lecturer, University of Newcastle (AUS)



Dr. Joonghan Kim

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- Japan Science and Technology Agency CREST grant 2006-2012 (KM, SI) and AFOSR (to KM)

- MEXT Tenure Track program (SI)

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- Research Center for Computational Science (RCCS), Okazaki Research Facilities, National Institutes for Natural Sciences.
- Academic Center for Computing and Media Studies (ACCMS), Kyoto University

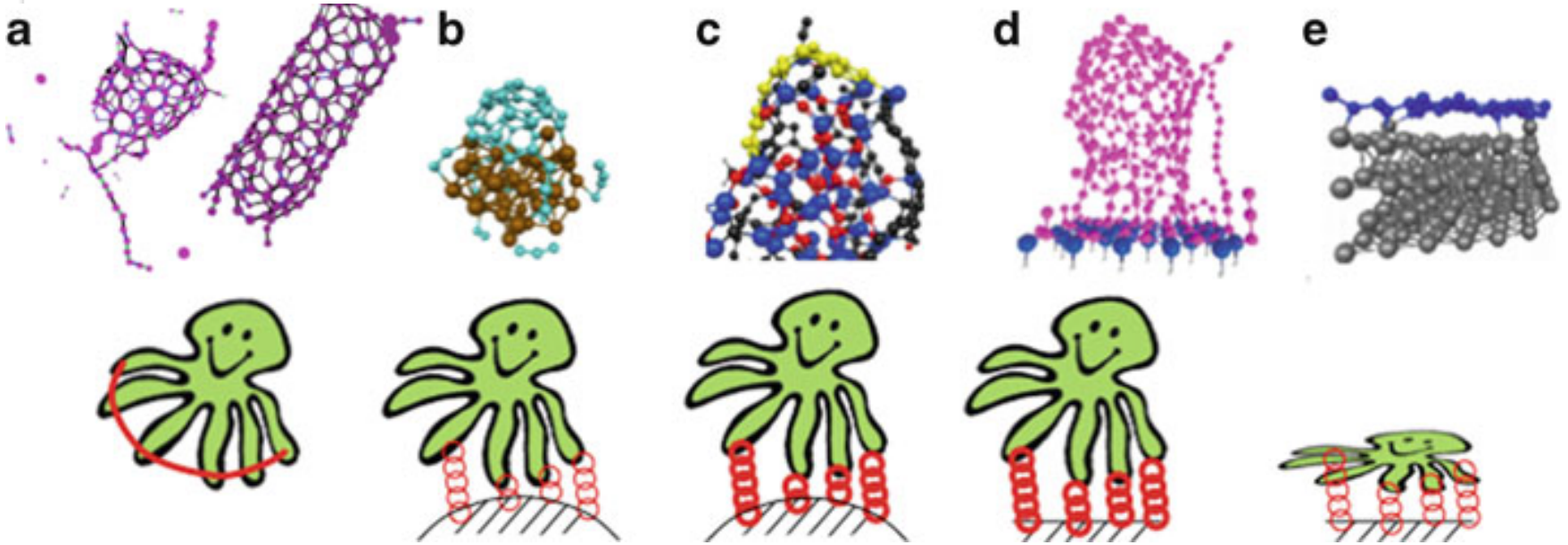
ADVERTISEMENT #1

A contribution to "Practical Aspects of Computational Chemistry II: An Overview of the Last Two Decades and Current Trends", eds. J. Leszczynski and M. K. Shukla, Springer-European Academy of Sciences (publication scheduled for April 2, 2012), http://www.springer.com/chemistry/book/978-94-007-0922-5

Atomistic mechanism of carbon nanostructure self-assembly

as predicted by nonequilibrium QM/MD simulations

Stephan Irle,[1] Alister J. Page,[2] Biswajit Saha,[2] Ying Wang,[1] K. R. S. Chandrakumar,[2] Yoshio Nishimoto,[1] Hu-Jun Qian,[1] and Keiji Morokuma[2,3]



Overview

- Overview: What are MD simulations up against?
- Density-functional tight-binding (DFTB)-based MD
- DFTB/MD Simulations: Acetylene feedstock, carbon-only feedstock, catalytic CVD, catalyst-free CVD
- Key points: What did we learn?
- Comparison with thermodynamics and selected experiments
- What is next?

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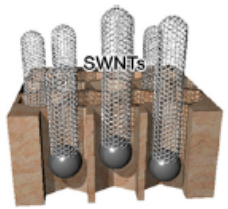
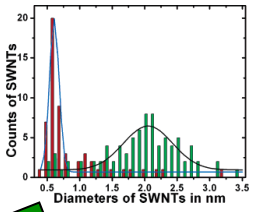
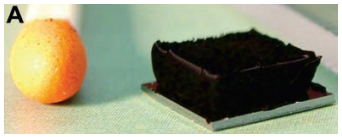
The ultimate goal: (n,m)-specific SWNT Growth

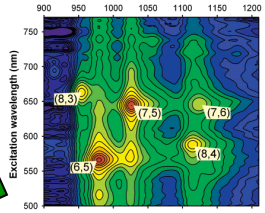


diameter

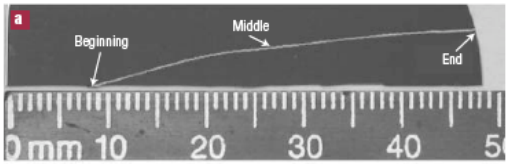




yield



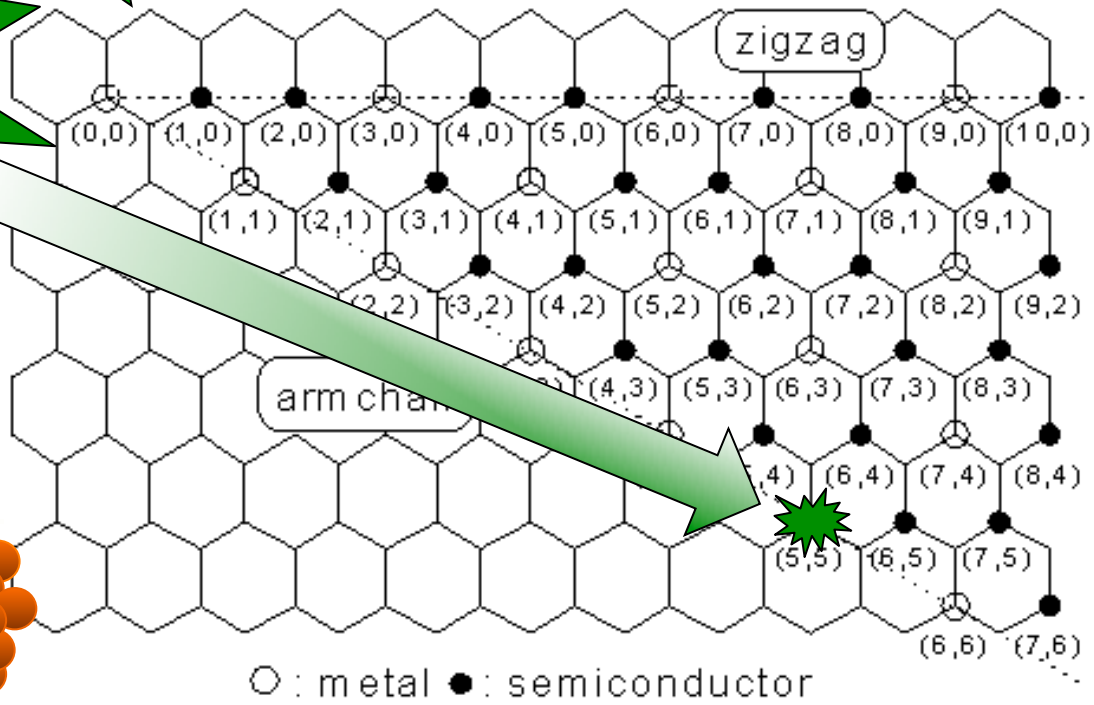
chirality



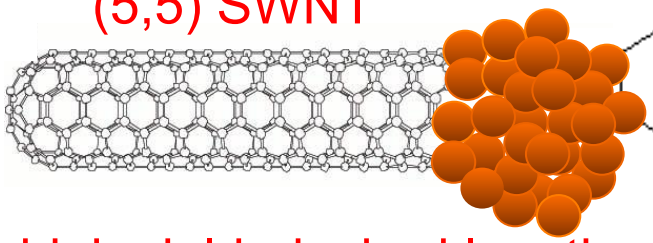
length

ACCVD etc …

Selection of “appropriate” growth conditions



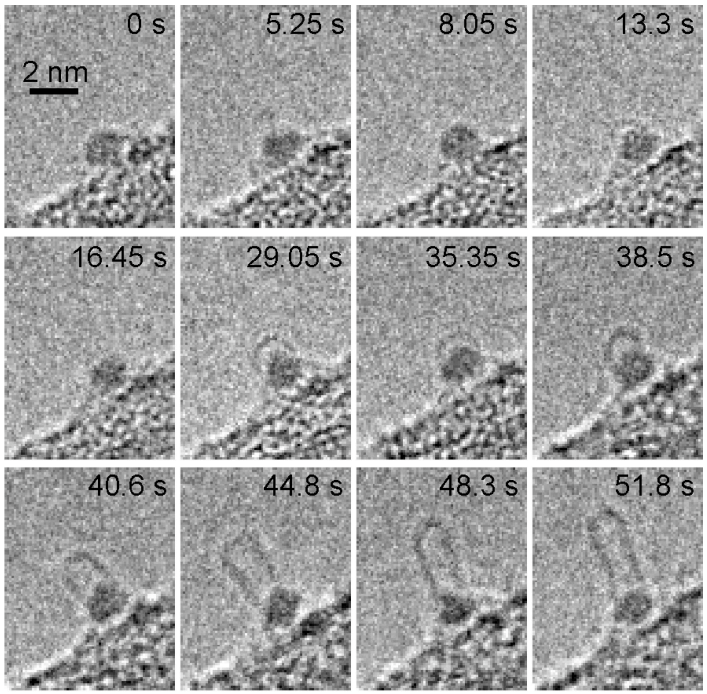
(5,5) SWNT



high yield, desired length, defect-free, eventually catalyst-free

Look here … *in situ* environmental TEM studies of SWNT nucleation and growth

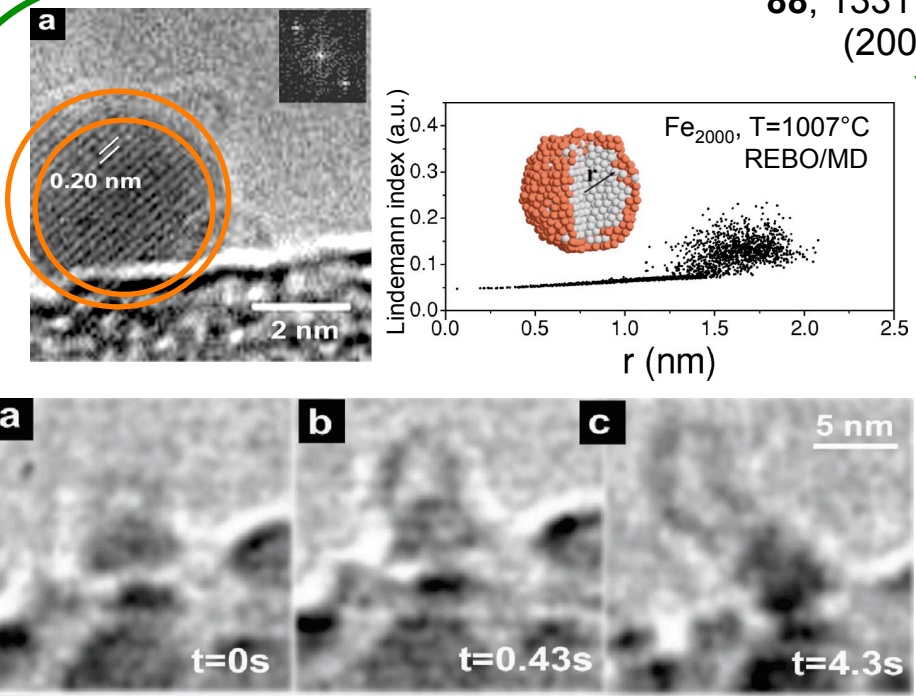
F. Ding, *et al.* *Appl. Phys. Lett.* **88**, 133110 (2006)



Fe/SiO_2 C_2H_2:H_2 T=600°C

Fluctuating solid **Fe_3C**

H. Yoshida, *et al.* Atomic-Scale In-situ Observation of Carbon Nanotube Growth from Solid State Carbide Nanoparticles, *Nano Lett.* **8**, 2082 (2008)

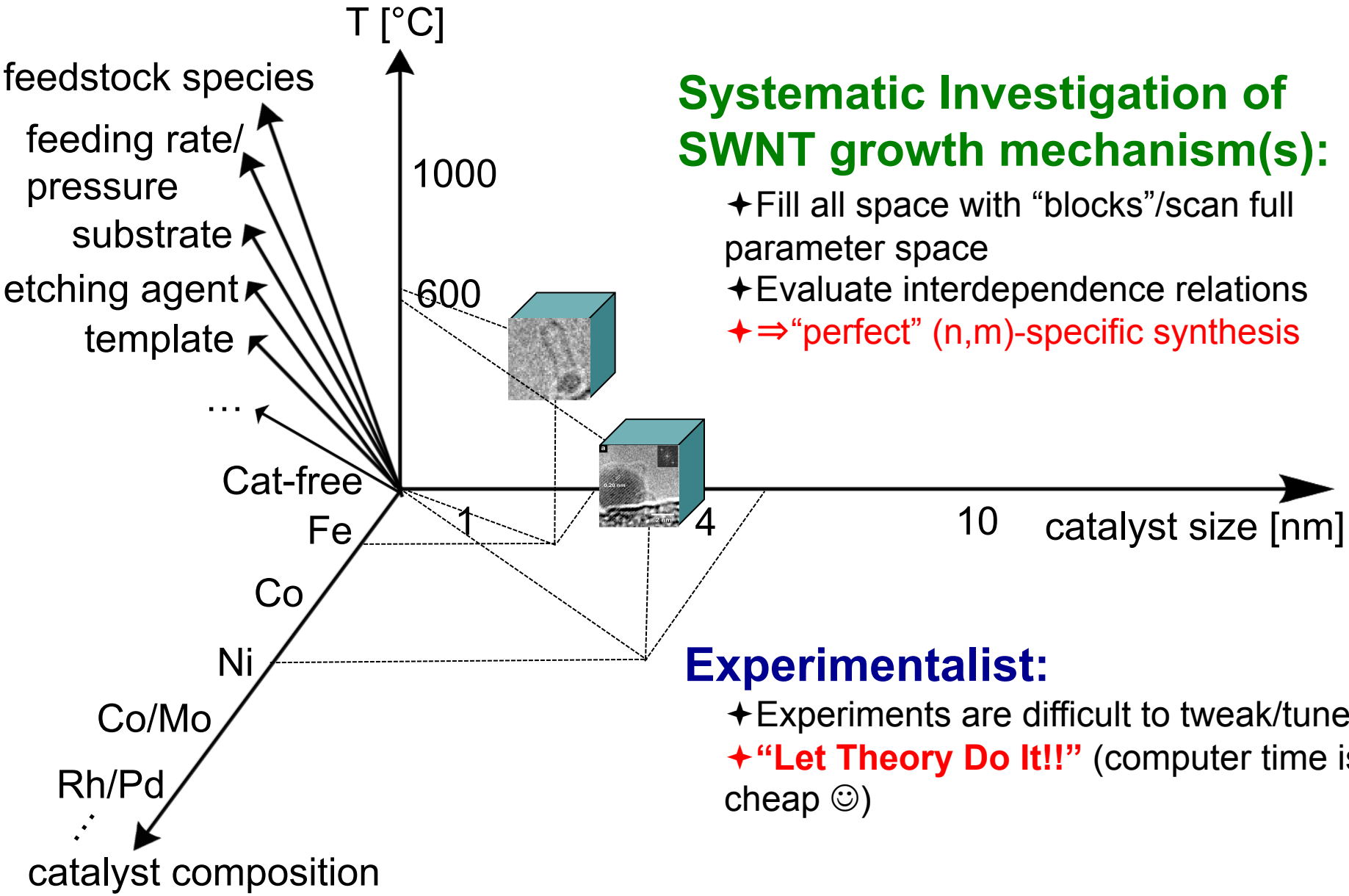


Ni/SiO_2 C_2H_2:NH_3 T=480 to 700°C

Fluctuating solid **pure nickel**

S. Hofmann, *et al.* In-situ Observations of Catalyst Dynamics during Surface-Bound Carbon Nanotube Nucleation, *Nano Lett.* **7**, 602 (2007)

SWNT Growth Hyperdimensional "Parameter Space"



Systematic Investigation of SWNT growth mechanism(s):

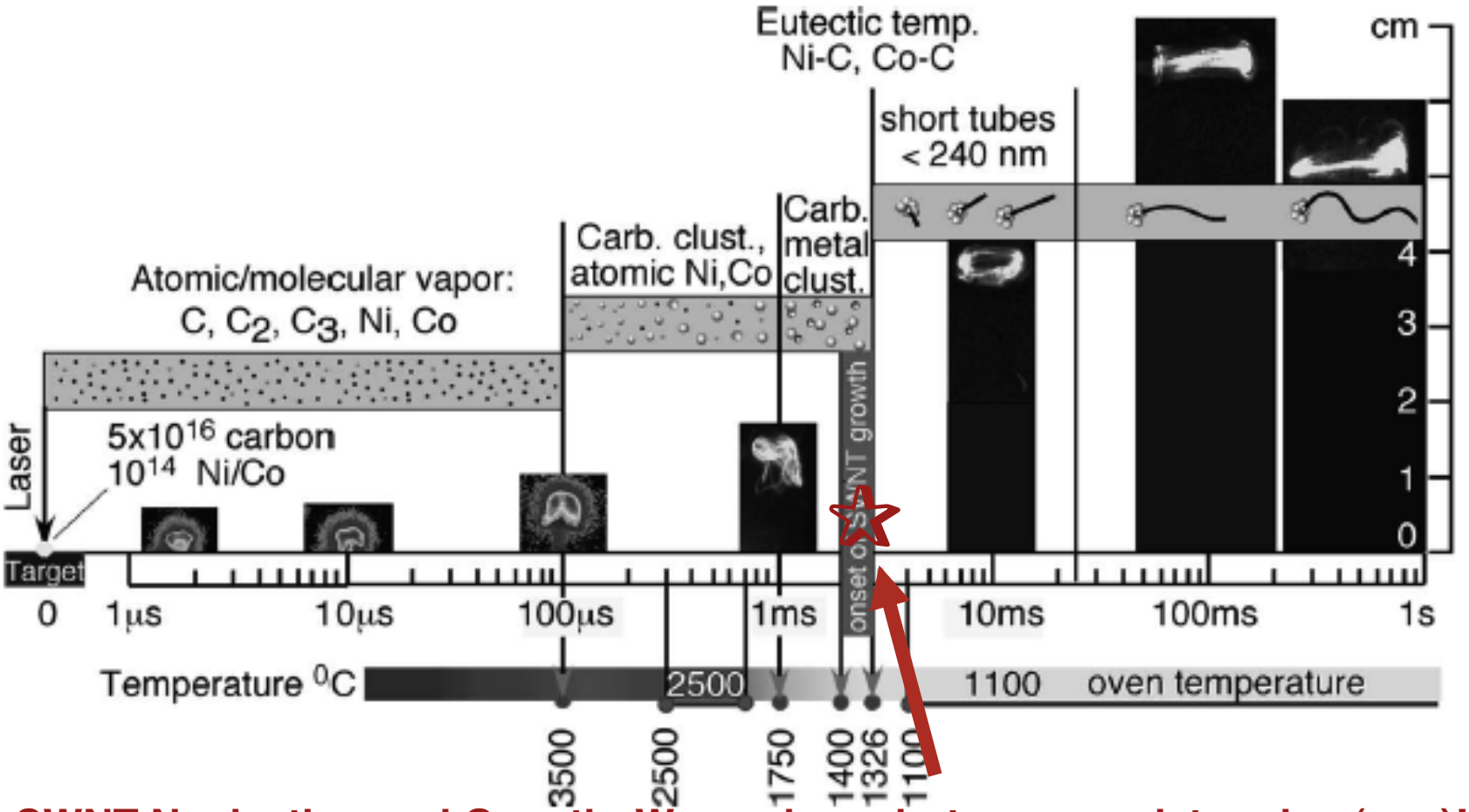
- ✦Fill all space with "blocks"/scan full parameter space
- ✦Evaluate interdependence relations
- ✦⇒"perfect" (n,m)-specific synthesis

Experimentalist:

- ✦Experiments are difficult to tweak/tune
- ✦**"Let Theory Do It!!"** (computer time is cheap ☺)

Long Timescale of SWNT Formation Mechanism! Example: Laser Vaporization Methods

Assumption: Direct correlation between time ~ temperature and growth



SWNT Nucleation and Growth: We are here, but *ms* may determine (n,m)!

A. A. Puretzky, *et al.* Appl. Surf. Sci. **197-198**, 552 (2002)

What MD method should be used?

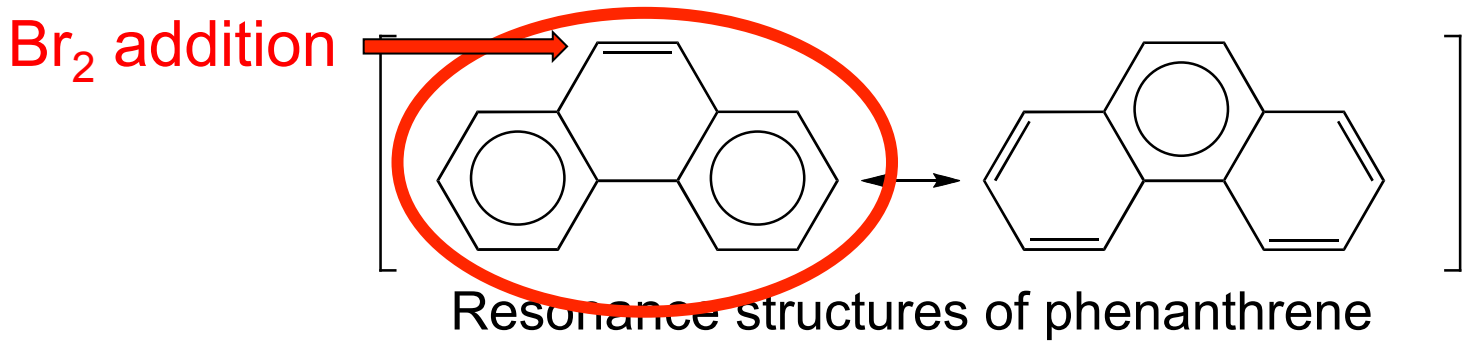
- SiC: sp^3 hybridization, **localized single bonds**
- Graphene: sp^2 hybridization, **delocalized π bonds**

Graphenes and the Clar Rule

E. Clar, *Polycyclic Hydrocarbons,* Academic Press: London (1964)

Polyaromatic hydrocarbons (PAHs): aromatic compounds

Degree of aromaticity can be different for each ring segment!



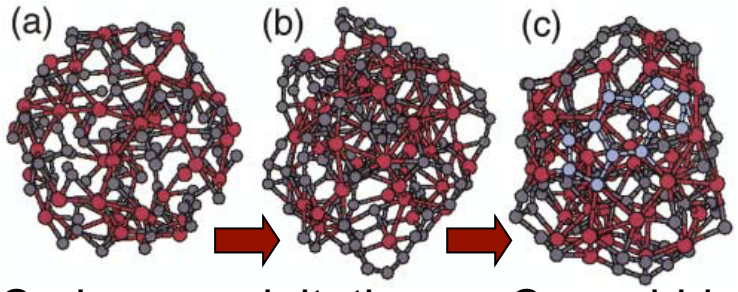
Resonance structures of phenanthrene

Clar's Rule: "Resonance structure with most disjoint aromatic π-sextets is most important for characterization of ring properties"

Previous Car-Parrinello Molecular Dynamics (CPMD)

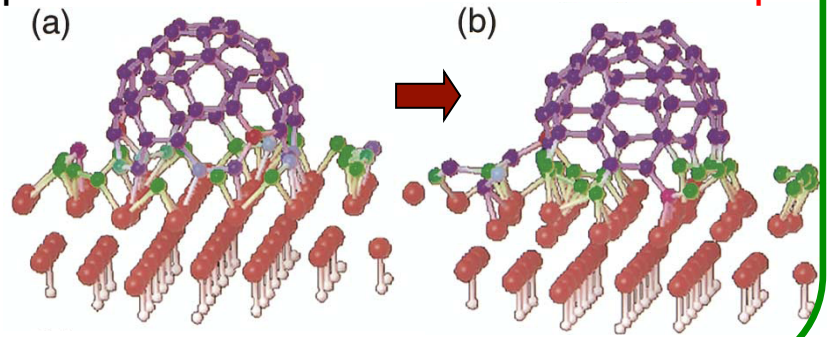
Heroic efforts on supercomputers, one-shot simulations!

J. Gavillet *et al,* Root-Growth Mechanism for SWNTs, *Phys. Rev, Lett.* **87**, 275504 (2001)

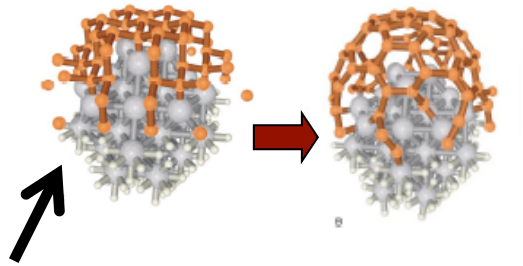


Carbon precipitation on Co carbide particle, 51 Co & 102 C atoms, 25 ps ⇒ 1 hexagon, 2 pentagons

C_{30}+44C on Co surface at 1500 K, 15 ps ⇒ 5 carbon atoms diffused to cap



J.-Y. Raty *et al,* Growth of Carbon Nanotubes on Metal Nanoparticles: A Microscopic Mechanism from *Ab Initio* Molecular Dynamics Simulations, *Phys. Rev, Lett.* **95**, 096103 (2005)



Change from diamond structure (sp^3) to fullerene cap (sp^2) immediately!

simulation time~10 ps
Too short to demonstrate self-assembly

Nano-diamond: Inappropriate model!

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Tight Binding as Approximate DFT Method

Density-Functional Tight-Binding: Method using atomic parame
from DFT (PBE, GGA-type), diatomic repulsive potenti

- Seifert, Eschrig (1980-86): minimum
STO-LCAO; 2-center approximat
- Porezag, Frauenheim
efficient paramete

DFTB

- E
-

1000 X FASTER THAN DFT!

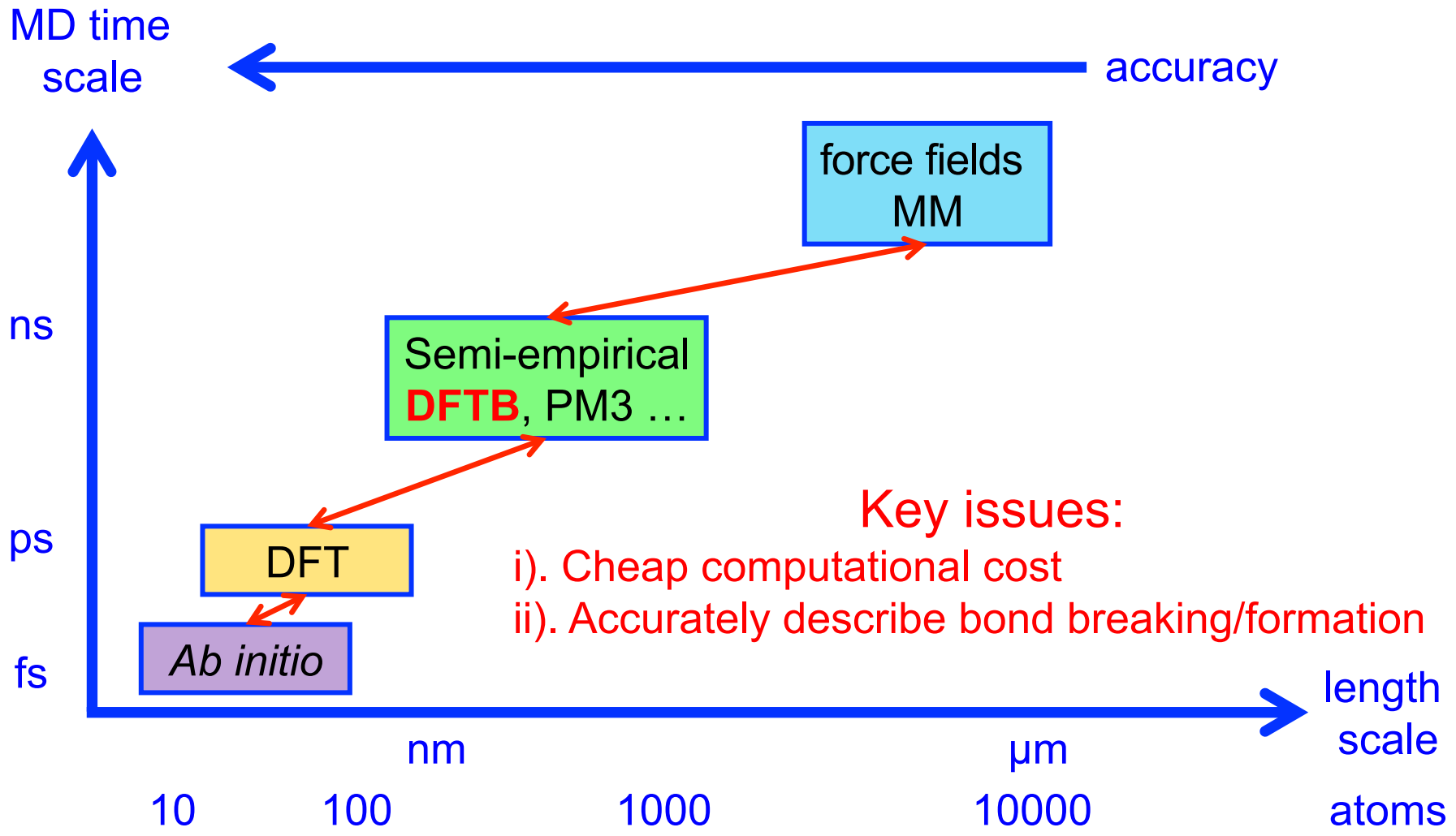
auenheim

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

Marcus Elstner

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

Christof Köhler



➢DFTB (density-functional tight-binding) is a well established **approximate DFT method,** but diatomic *parameters* are required. Therefore, we started to develop X-Y parameters for all elements.

Optimized elemental electronic DFTB parameters now available for Z=1-109!

Chien-Pin Chou

Yoshifumi Nishimura, Chien-Pin Chou
Henryk A. Witek, Stephan Irle

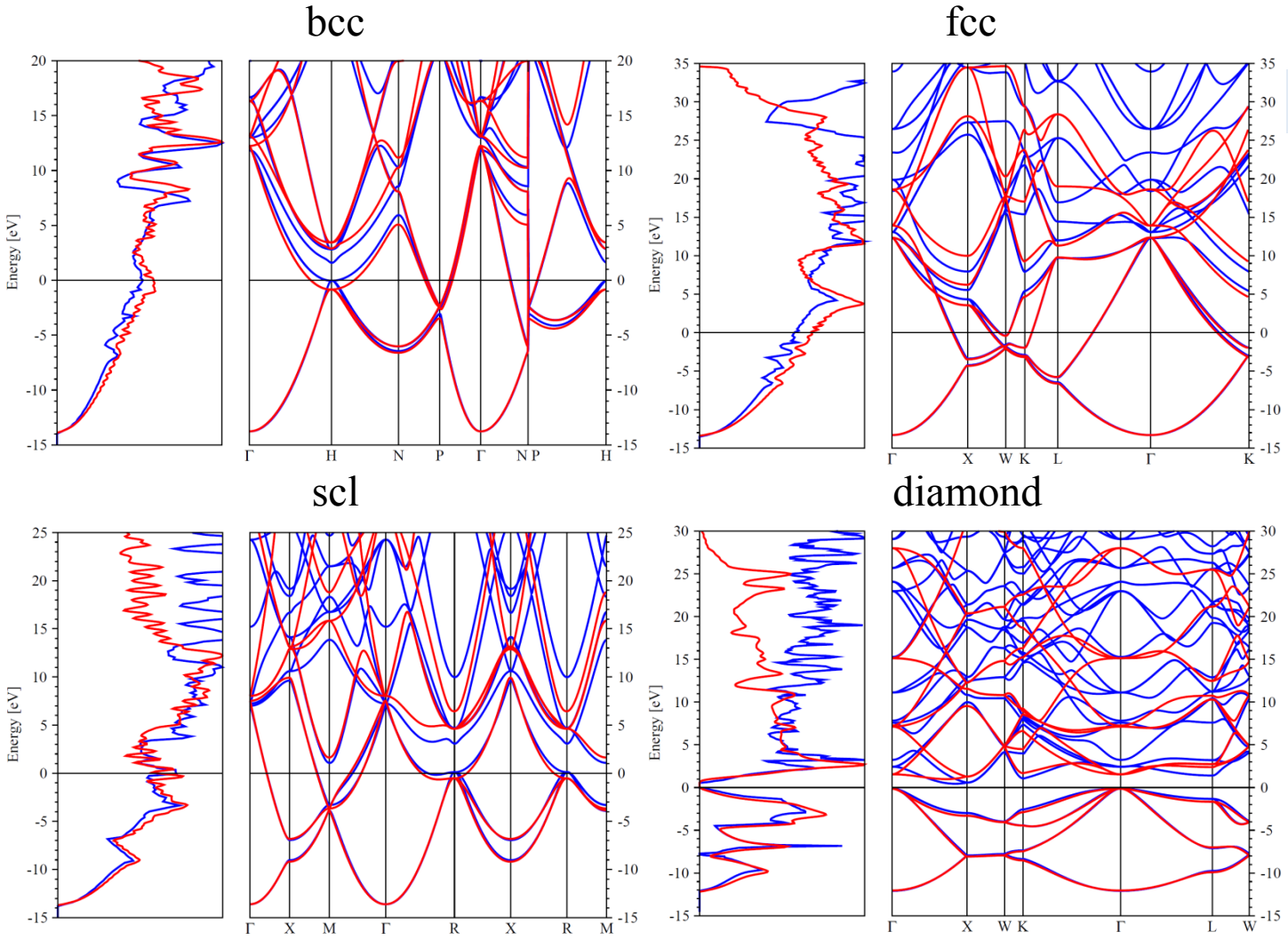
Yoshifumi Nishimura

Nagoya University

National Chiao Tung University, Taiwan

Henryk A. Witek

Example: DFTB Si bandstructures, parameters optimized @ bcc only



$3s^2 3p^2 3d^0$

Lattice constants:

Expt	
· bcc	3.081
fcc	3.868
scl	2.532
diamond	5.431

Parameter sets:

W (orb)	3.33938
a (orb)	4.52314
r (orb)	4.22512
W (dens)	1.68162
a (dens)	2.55174
r (dens)	9.96376
ε_s	-0.39735
ε_p	-0.14998
ε_d	0.21210

➢Artificial crystal structures can be reproduced well

SCC-DFTB: general comparison with experiment

Performance for small organic molecules
(mean absolut deviations)

- Reaction energies: ~ 5 kcal/mol
- Bond lengths: ~ 0.014 A°
- Bond angles: ~ 2°
- Vibrational frequencies: ~6-7 %

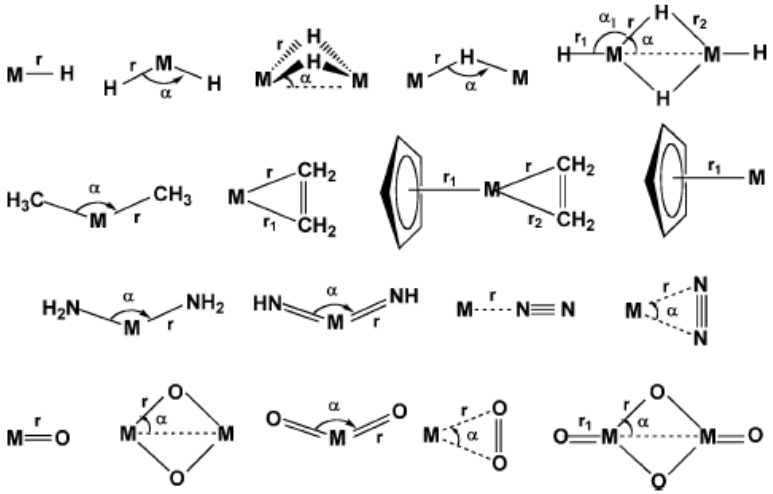
SCC-DFTB: Transition metals

G. Zheng *et al.J. Chem. Theor. Comput.* **3** 1349 (2007)

Table 2. List of Molecules and Their Spin States Used in the Parametrization Procedure[a]

	M–M	M–H	M–C	M–N	M–O
			M = Sc		
tier 1	$^1Sc_2$	$^1ScH_3$	$^1HScCH_2$	^1ScN	^1HScO
			$^1H_2ScCH_3$	$^1H_2ScN_2$	$^1H_2ScOH$
			M = Ti		
tier 1	$^1Ti_2$	$^1TiH2$	^1HTiCH	^1HTiN	^1H_2TiO
			$^1H_2TiCH_2$	$^1H_2TiNH$	$^1H_3TiOH$
			$^1H_3TiCH_3$	$^1H_3TiNH_2$	
tier 2			$^1Ti(CO)_2^{+4}$	$^1Ti(NH_3)_2^{+4}$	$^1Ti(H_2O)_2^{+4}$
			$^1Ti(CO)_3^{+4}$	$^1Ti(NH_3)_3^{+4}$	$^1Ti(H_2O)_3^{+4}$
			$^1Ti(CO)_4^{+4}$	$^1Ti(NH_3)_4^{+4}$	$^1Ti(H_2O)_4^{+4}$
			$^1Ti(CO)_5^{+4}$	$^1Ti(NH_3)_5^{+4}$	$^1Ti(H_2O)_5^{+4}$
			$^1Ti(CO)_6^{+4}$	$^1Ti(NH_3)_6^{+4}$	$^1Ti(H_2O)_6^{+4}$
			M = Fe		
tier 1	$^1Fe_2$	$^1FeH_2$	$^1FeCH_2$	^1FeNH	^1FeO
			$^1FeCH_3^+$	$^1HFeNH_2$	^1HFeOH
			^1HFeCO	$^1FeNH_3^{+2}$	$^1FeOH_2^{+2}$
tier 2			$^6Fe(CO)_2^{+3}$	$^6Fe(NH_3)_2^{+3}$	$^6Fe(H_2O)_2^{+3}$
			$^6Fe(CO)_3^{+3}$	$^6Fe(NH_3)_3^{+3}$	$^6Fe(H_2O)_3^{+3}$
			$^6Fe(CO)_4^{+3}$	$^6Fe(NH_3)_4^{+3}$	$^6Fe(H_2O)_4^{+3}$
			$^6Fe(CO)_5^{+3}$	$^6Fe(NH_3)_5^{+3}$	$^6Fe(H_2O)_5^{+3}$
			$^6Fe(CO)_6^{+3}$	$^6Fe(NH_3)_6^{+3}$	$^6Fe(H_2O)_6^{+3}$

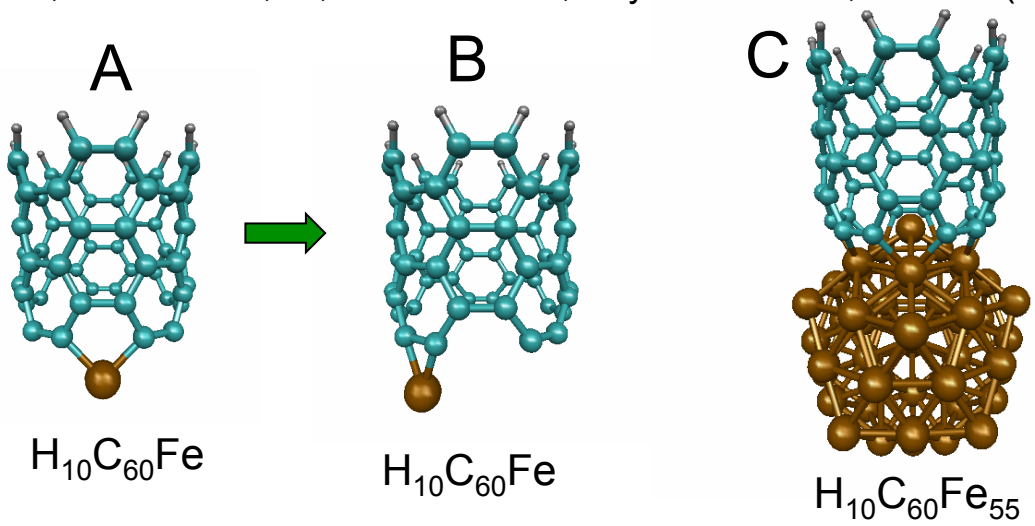
Scheme 1. Schematic Representation of the Geometrical Parameters of the Set of Tier 3 Molecules for M = Ti, Fe, Co, and Ni[a]



Bond lengths: ~0.1 Å
Bond angles: ~10°
Relative energies: ~20 kcal/mol

(5,5) armchair SWNT ($H_{10}C_{60}$) + Fe / Fe_{55}

Y. Ohta, Y. Okamoto, SI, K. Morokuma, Phys. Rev. B **79**, 195415 (2009)



Fe_{55} icosahedron,

P. Larsson *et al.* Phys. Rev. B **75**, 115419 (2007)

Adhesion energies (eV/atom)

	A	B	C
DFT:PW91[1]	-6.24	-5.63	-1.82
SCC-DFTB[2]	-5.17	-4.68	-1.86

Relative energies often OK!

[1] Phys. Rev. B **75**, 115419 (2007) [2] Fermi broadening=0.13 eV

[1]: PW91: An ultrasoft pseudopotential with a plane-wave cutoff of 290 eV for the single metal and the projector augmented wave method with a plane-wave cutoff of 400 eV for the metal cluster 20

{2} Fe-Fe and Fe-C DFTB parameters from: G. Zheng *et al., J. Chem. Theor. Comput.* **3**, 1349 (2007)

MD for Chemical Reactions

Newton's equations of motion for the *N*-particle system:

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i$$

E is a potential energy function
In our case: DFTB total electronic energy

$\mathbf{F}_i$ can be calculated as $-\partial E / \partial r_i$. There are several approximate methods to solve this system of equations. Some commonly used methods are:

Verlet's algorithm

Beeman's algorithm

Velocity Verlet algorithm:

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + (\delta t)^2 \frac{\mathbf{F}_i(t)}{2m_i}$$

$$\mathbf{v}_i(t+\delta t) = \mathbf{v}_i(t) + \delta t \frac{\mathbf{F}_i(t+\delta t) + \mathbf{F}_i(t)}{2m_i}$$

Practical implementation requires discrete Δt

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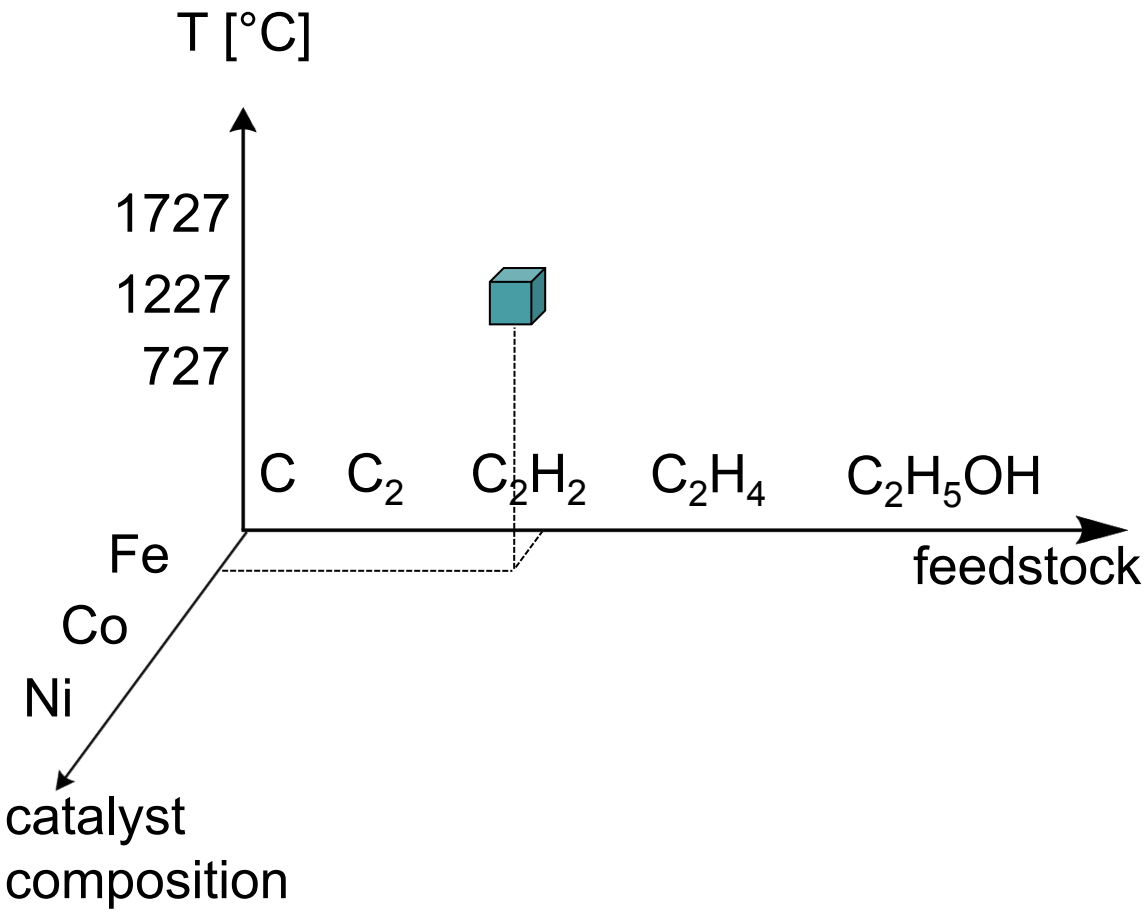
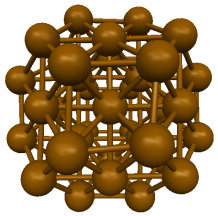

T [°C]
1727
1227
727
C
C_2
C_2H_2
C_2H_4
C_2H_5OH
feedstock
Fe
Co
Ni
catalyst
composition

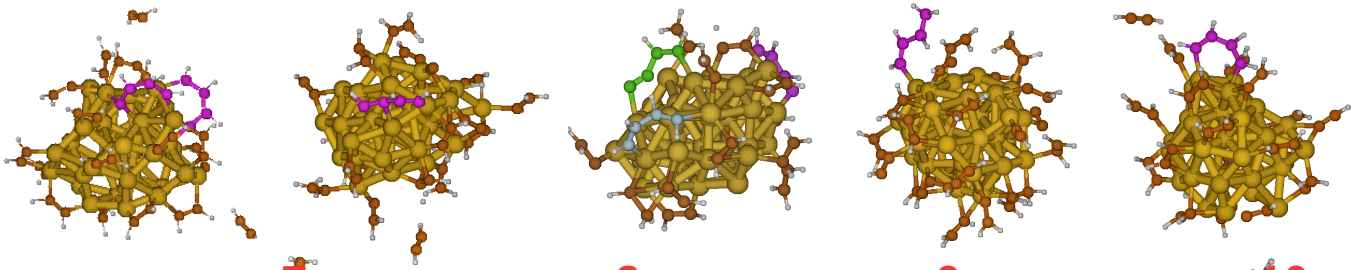
Dr. Ying Wang

DFTB/MD Studies — Acetylene Decomposition

Initial model: Fe_{38}

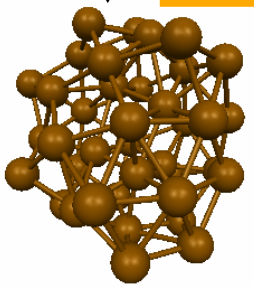


t = 0 ps



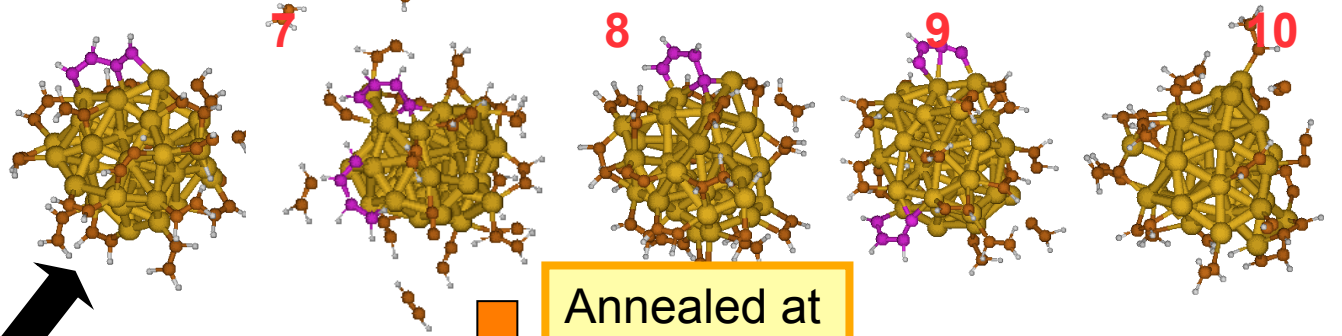
10 ps

Annealed at 1500 K



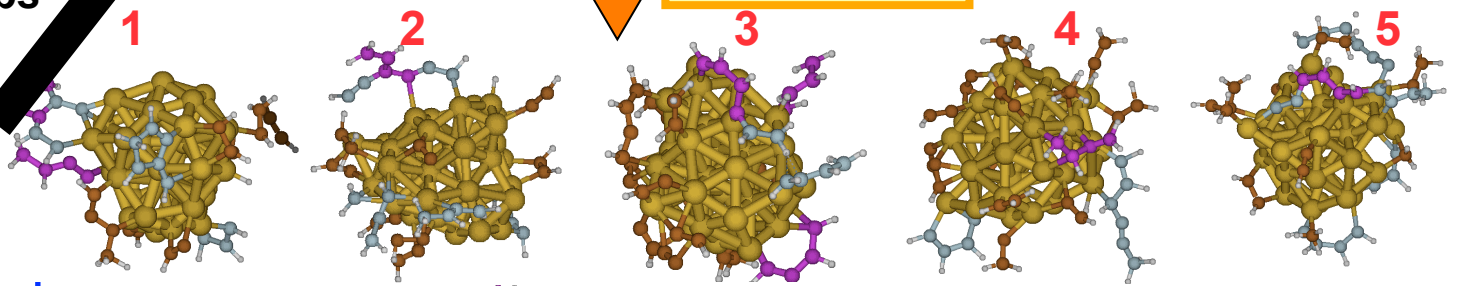
30 C_2H_2's

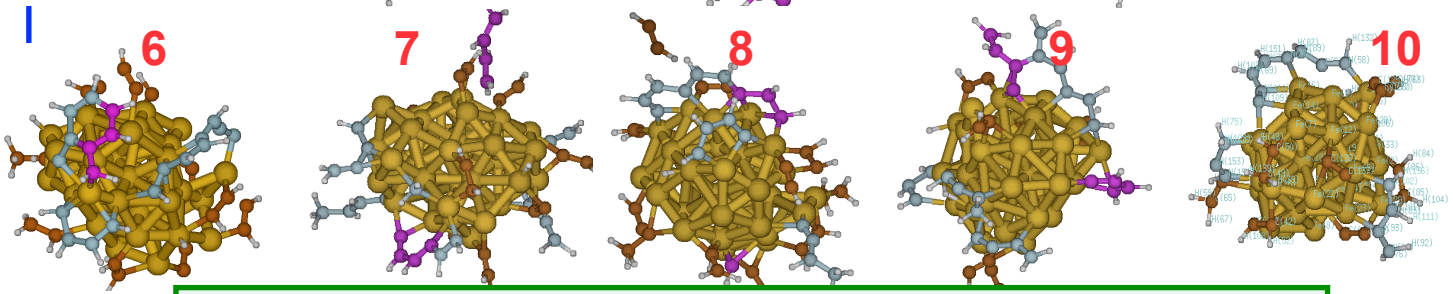
30 ps



50 to 65 ps

Annealed at 1500 K





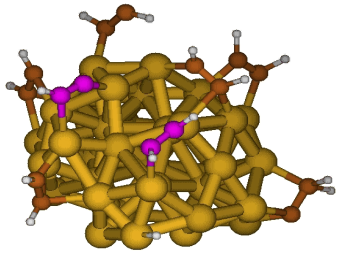
10 geometries are randomly sampled between 5 and 10 ps for ten trajectories.

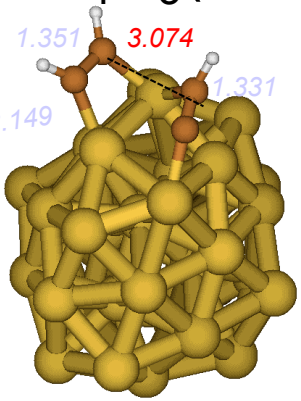
Polyacetylene formation, largest carbon cluster: $C_{10}H_x$

C-C Bond formation:

$C_2H_2(ads)+C_2H(ads) \rightarrow C_4H_3(ads)$

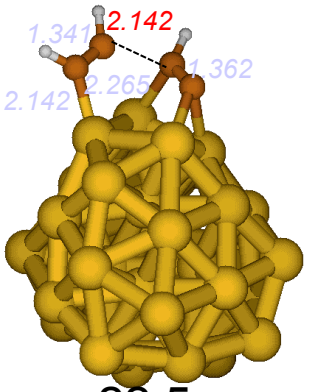
Relative energies in [kcal/mol]
including ZPE
IRC verified





0.0

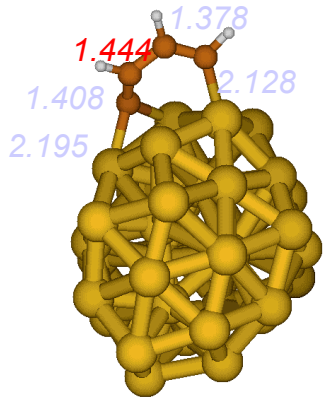
NImag=0



22.5

NImag=1

ν_{imag}= 455i cm^{-1}

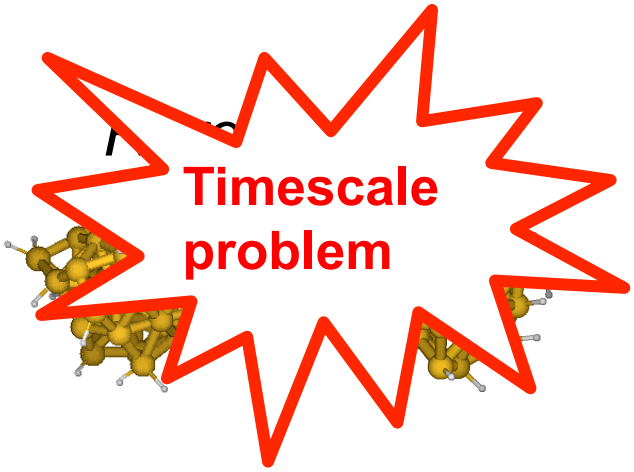


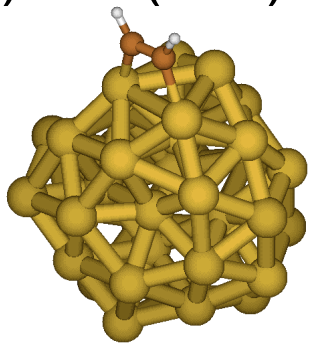
-11.8

NImag=0

H abstraction:

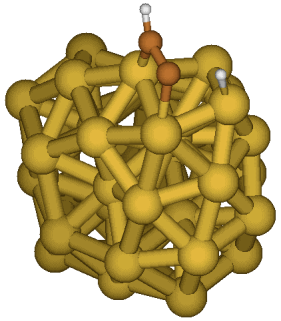
$C_2H_2(ads) \rightarrow C_2H\,(ads) + H(ads)$





0.0

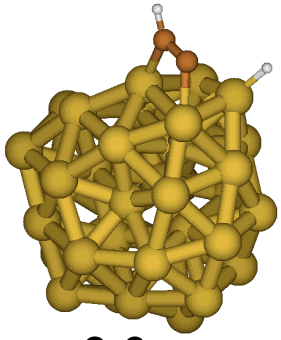
NImag=0



36.5

NImag=1

ν_{imag}= 1377i cm^{-1}

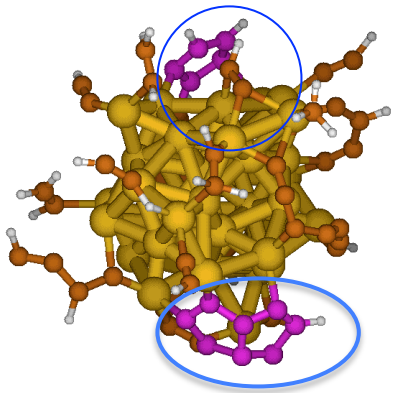


8.0

NImag=0

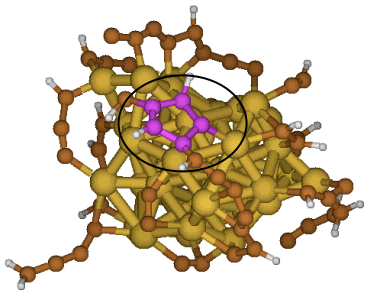
C_2H_2 **supply**/2H **removal** (every 5 ps until 60 carbon atoms attached)

A



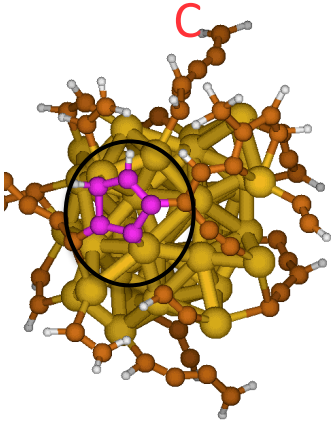
55ps

B



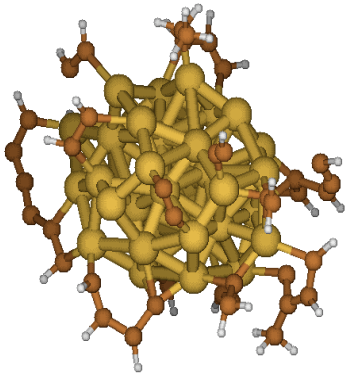
60ps

C



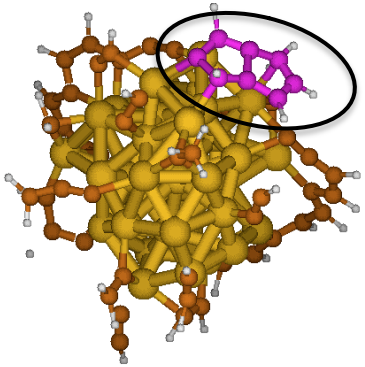
45ps

D



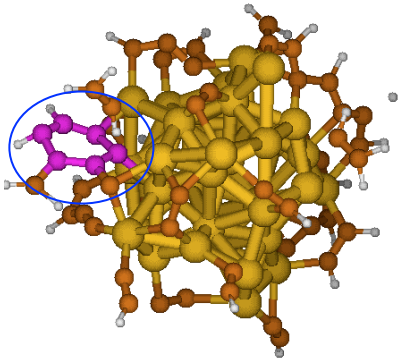
40ps

E



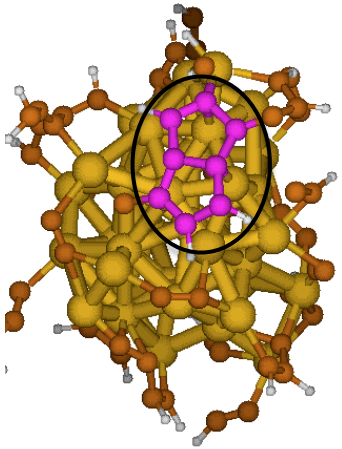
40ps

F



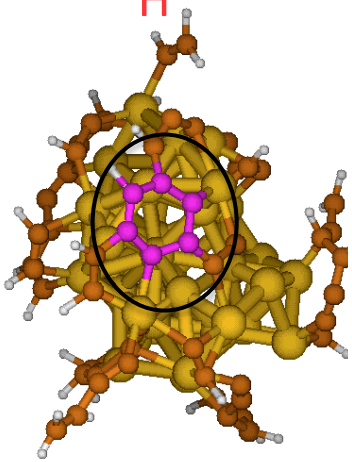
55ps

G



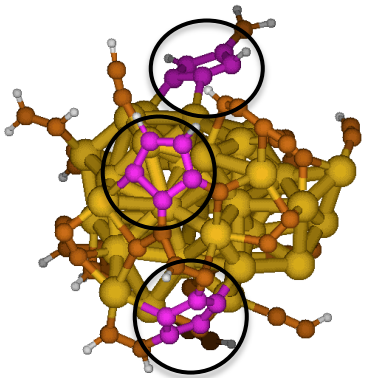
60ps (61 C)

H



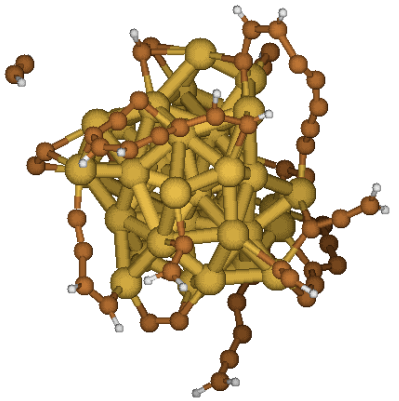
55ps

I



65ps

J

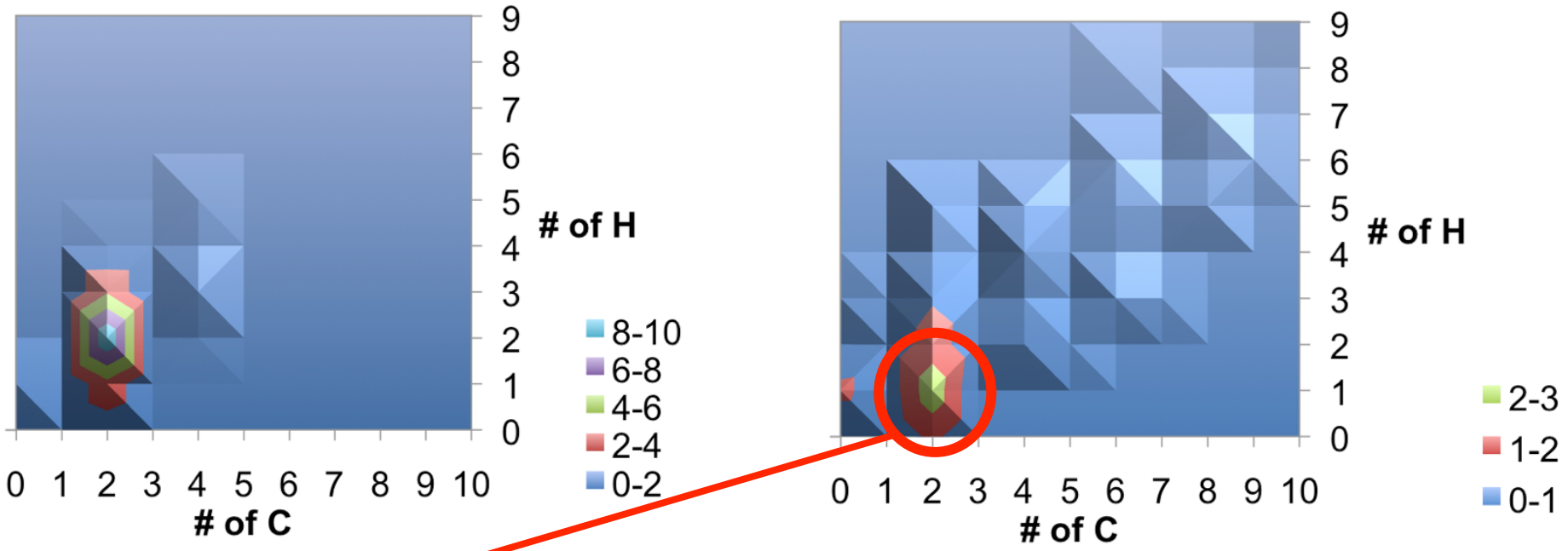


75ps
(61 C)

C_xH_y composition on Fe_{38} cluster

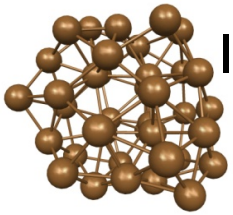
BEFORE **AFTER**

C_2H_2 **supply**/2H **removal** (every 5 ps until 60 carbon atoms attached)



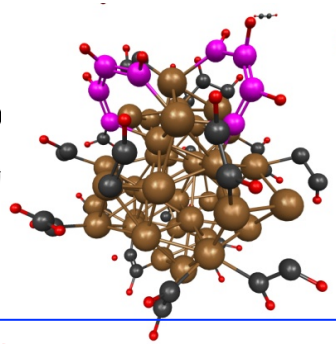
·C_2H radicals are consumed/re-generated!

"dissipative small molecule organocatalyst"



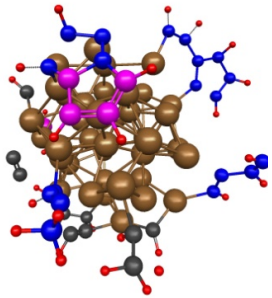
Initial C_2H_2 supply

30 ps



Initial annealing

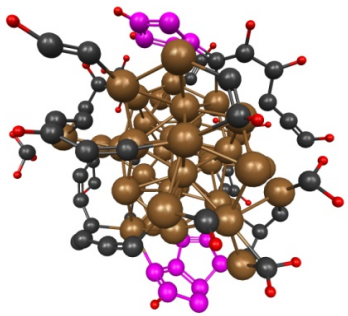
80 ps



Remove floating hydrocarbons, decrease box size to (20 Å)[3]

Secondary C_2H_2 supply/2H removal→60 carbon on cluster

45-75 ps

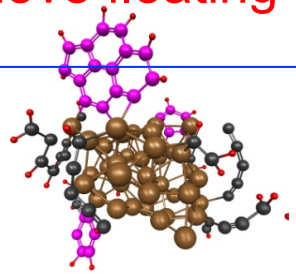


Secondary annealing 350ps

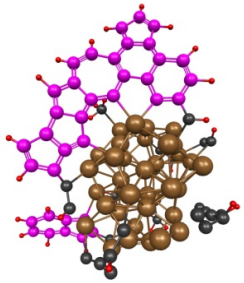
Secondary annealing 350ps

Secondary annealing 350ps

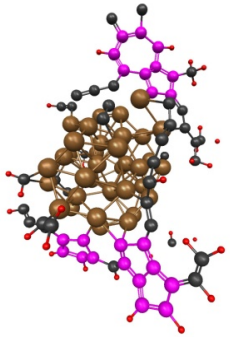
A1



A2



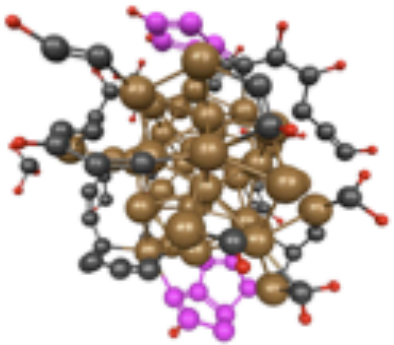
A3



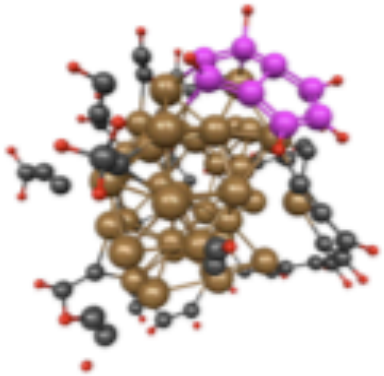
"Final results" after secondary annealing

a)

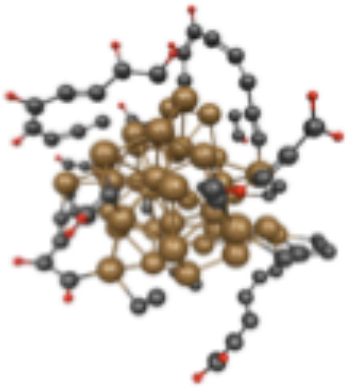
A
$Fe_{38}C_{60}H_{33}$/55ps



E
$Fe_{38}C_{60}H_{42}$/40ps



J
$Fe_{38}C_{61}H_{19}$/75ps



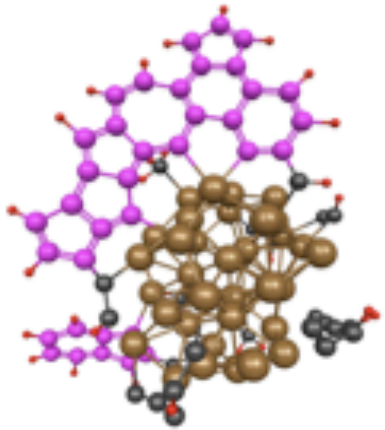
Annealed at 1500 K

A2
$Fe_{38}C_{60}H_{33}$/515ps

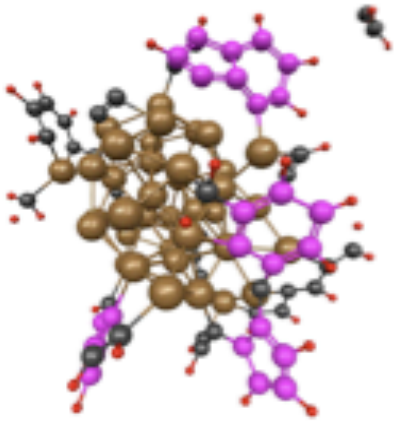
E2
$Fe_{38}C_{60}H_{42}$/500ps

J1
$Fe_{38}C_{61}H_{19}$/535ps

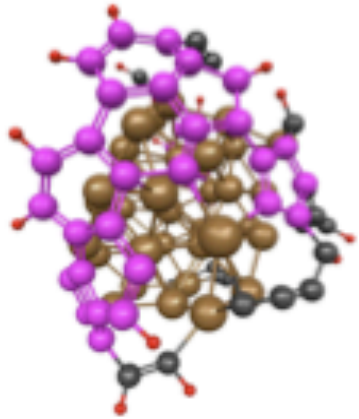
b)



"standing wall"



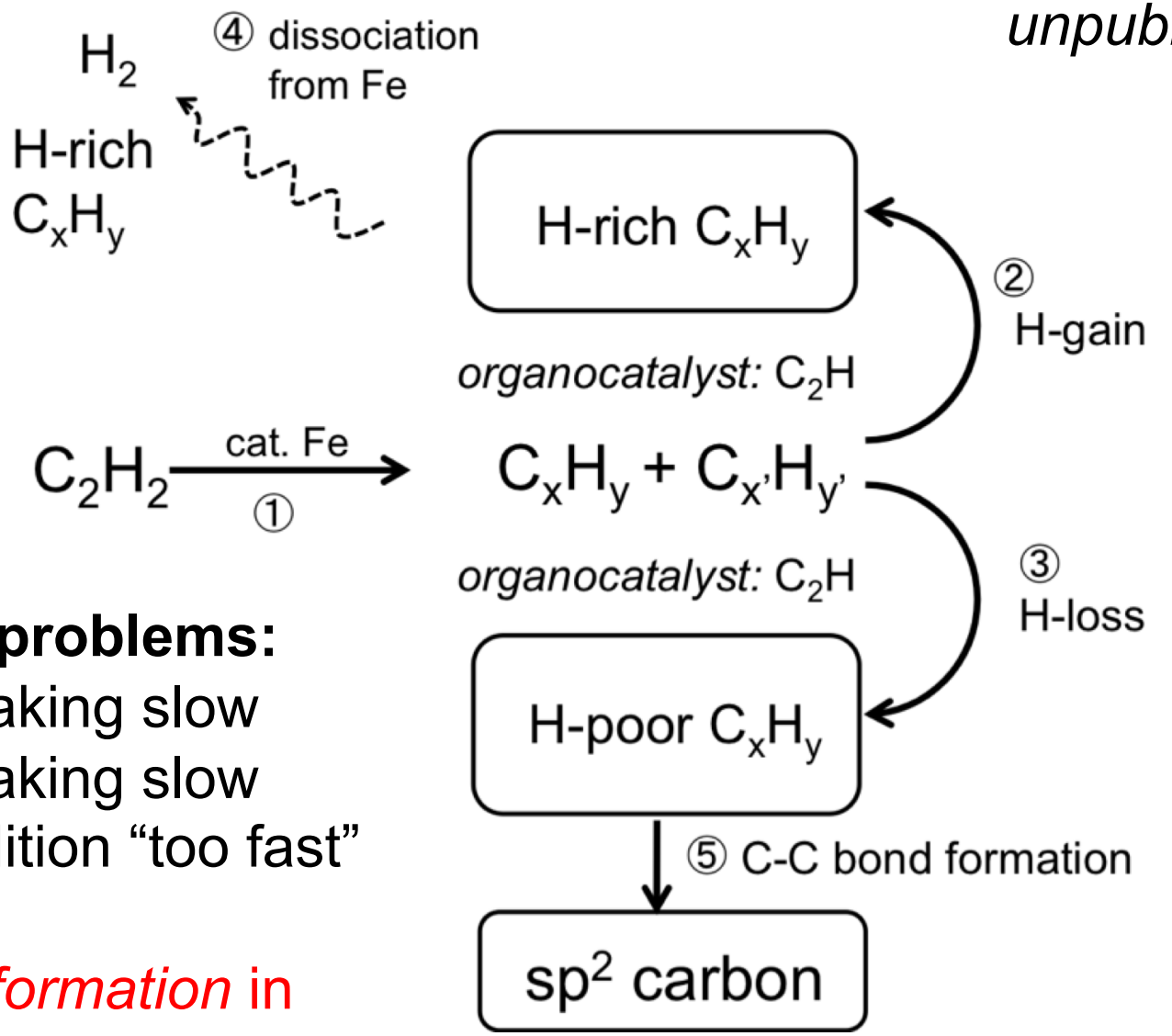
"PAHs"



"cap"

"Disproportionation Mechanism" of Acetylene Decomposition

unpublished



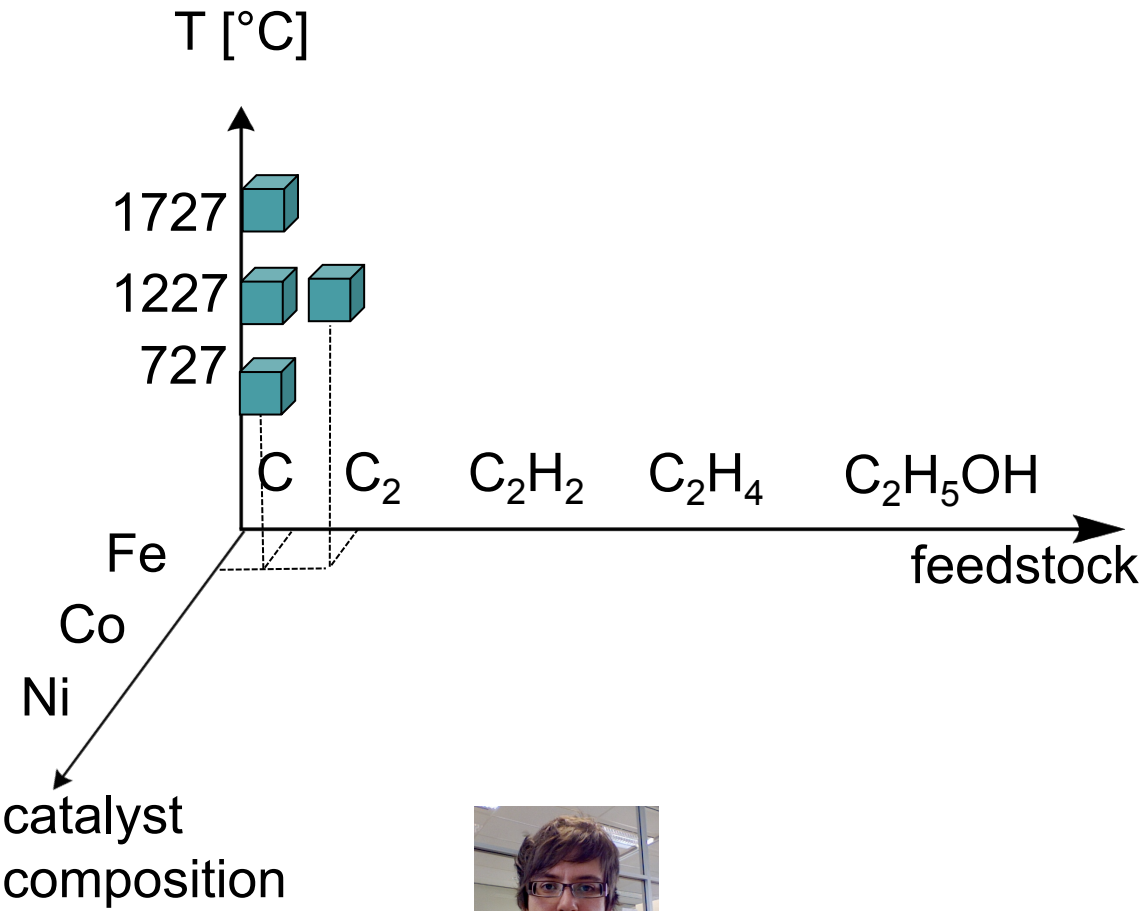
Fundamental problems:

-C-C bond breaking slow

-C-H bond breaking slow

-Acetylene addition "too fast"

→ *No carbide formation* in simulations



Dr. Yasuhito Ohta

Dr. Alister J. Page

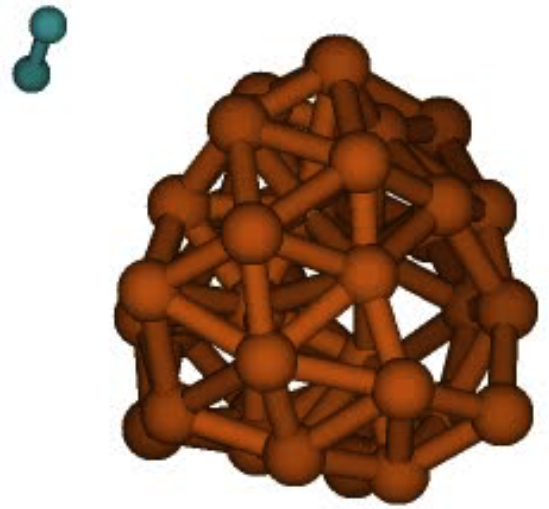
Dr. Yoshiko Okamoto

Dr. Joonghan Kim

C_2 shooting and annealing on Fe_{38} particle

Y. Ohta, Y. Okamoto, A. J. Page, SI, K. Morokuma, ACS Nano **3**, 3413 (2009)

- SCC-DFTB; T_e = 10,000 K.
- MD; Δt=1 fs.
- NVT ensemble; T_n= 1,500 K.
- Nosé-Hoover-Chain thermostat.

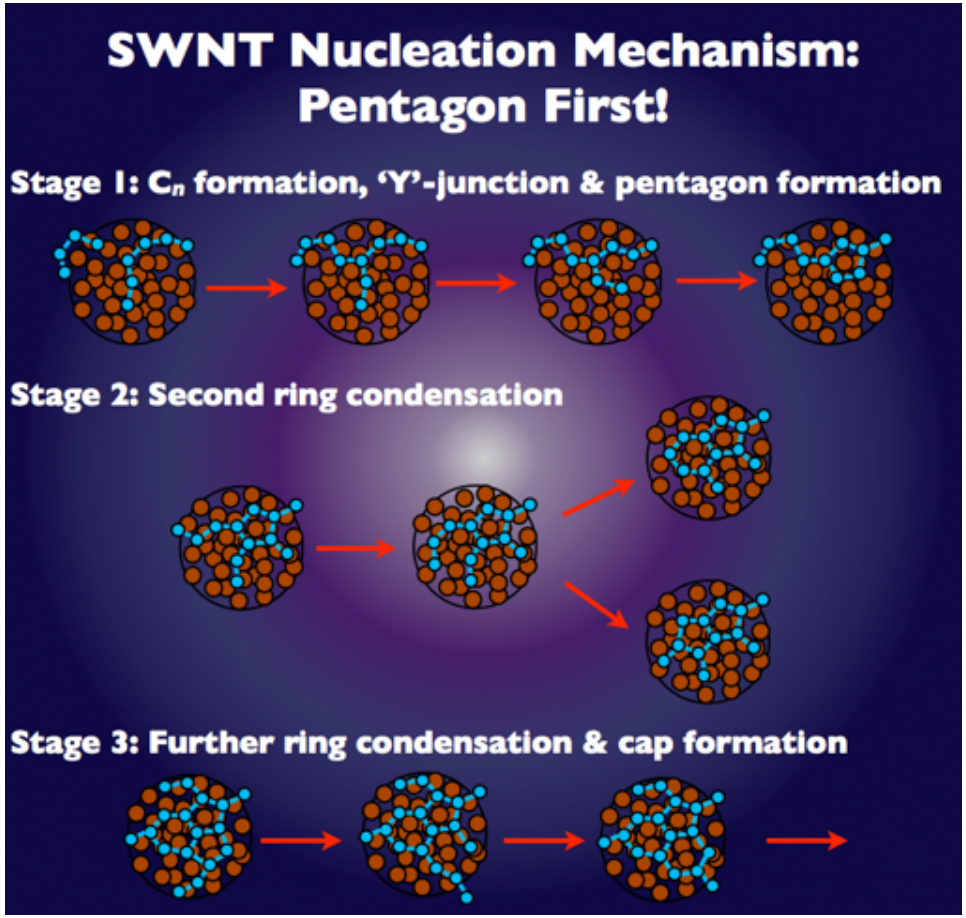


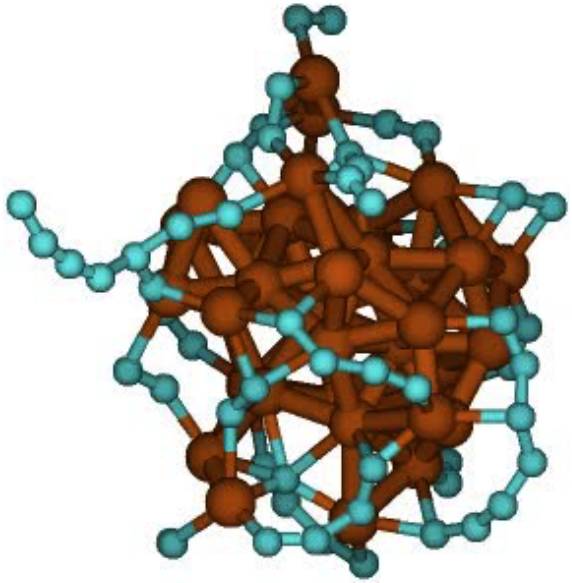
- 30 C_2 deposited onto fcc-Fe_{38} surface (1/ps).
- NVT thermal annealing for 400 ps.

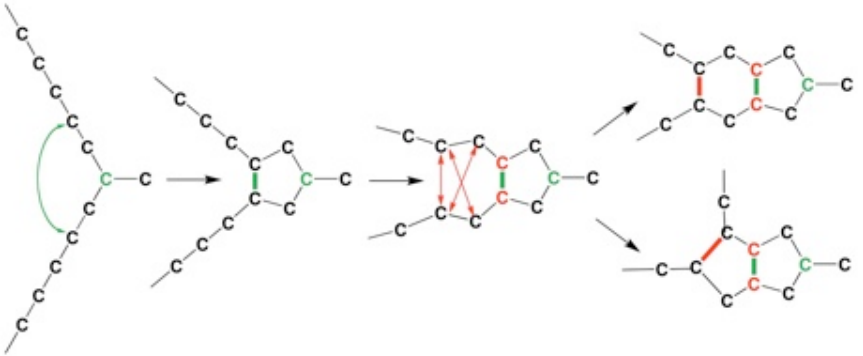
Yasuhito Ohta

C_2 shooting and annealing on Fe_{38} particle

Y. Ohta, Y. Okamoto, A. J. Page, SI, K. Morokuma, ACS Nano **3**, 3413 (2009)



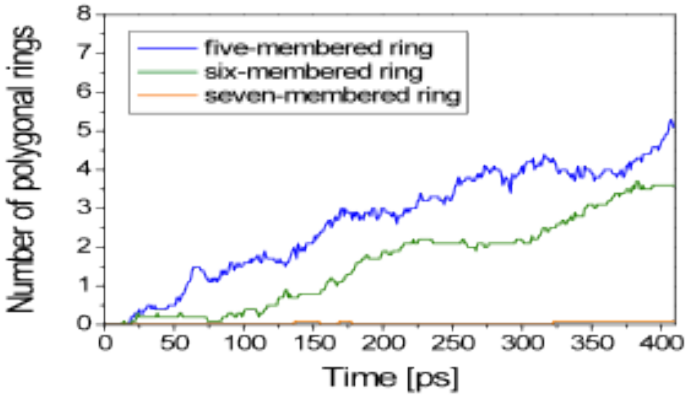


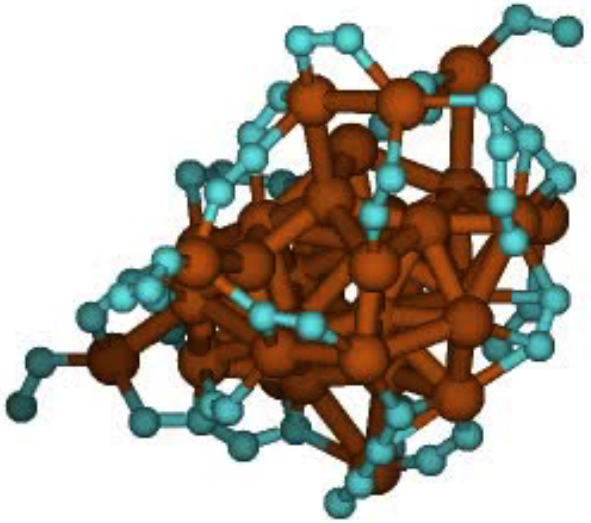


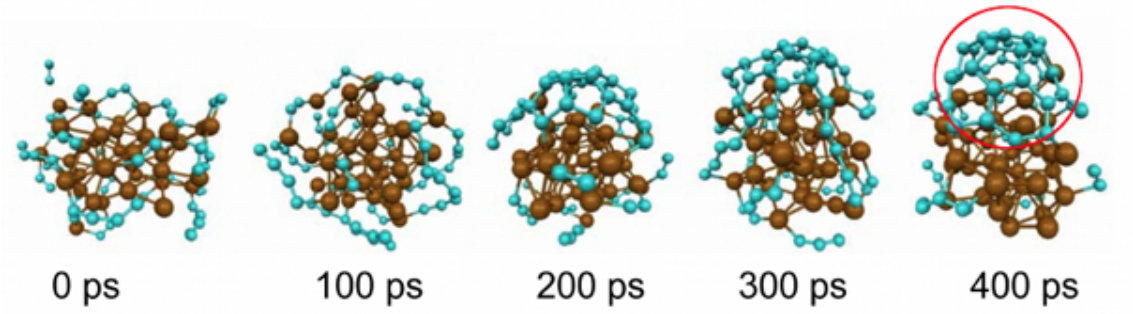
C_2 shooting and annealing on Fe_{38} particle

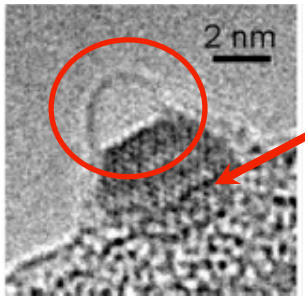
Y. Ohta, Y. Okamoto, A. J. Page, SI, K. Morokuma, ACS Nano **3**, 3413 (2009)

SWNT nucleation:
driven by 5-/6-membered ring formation







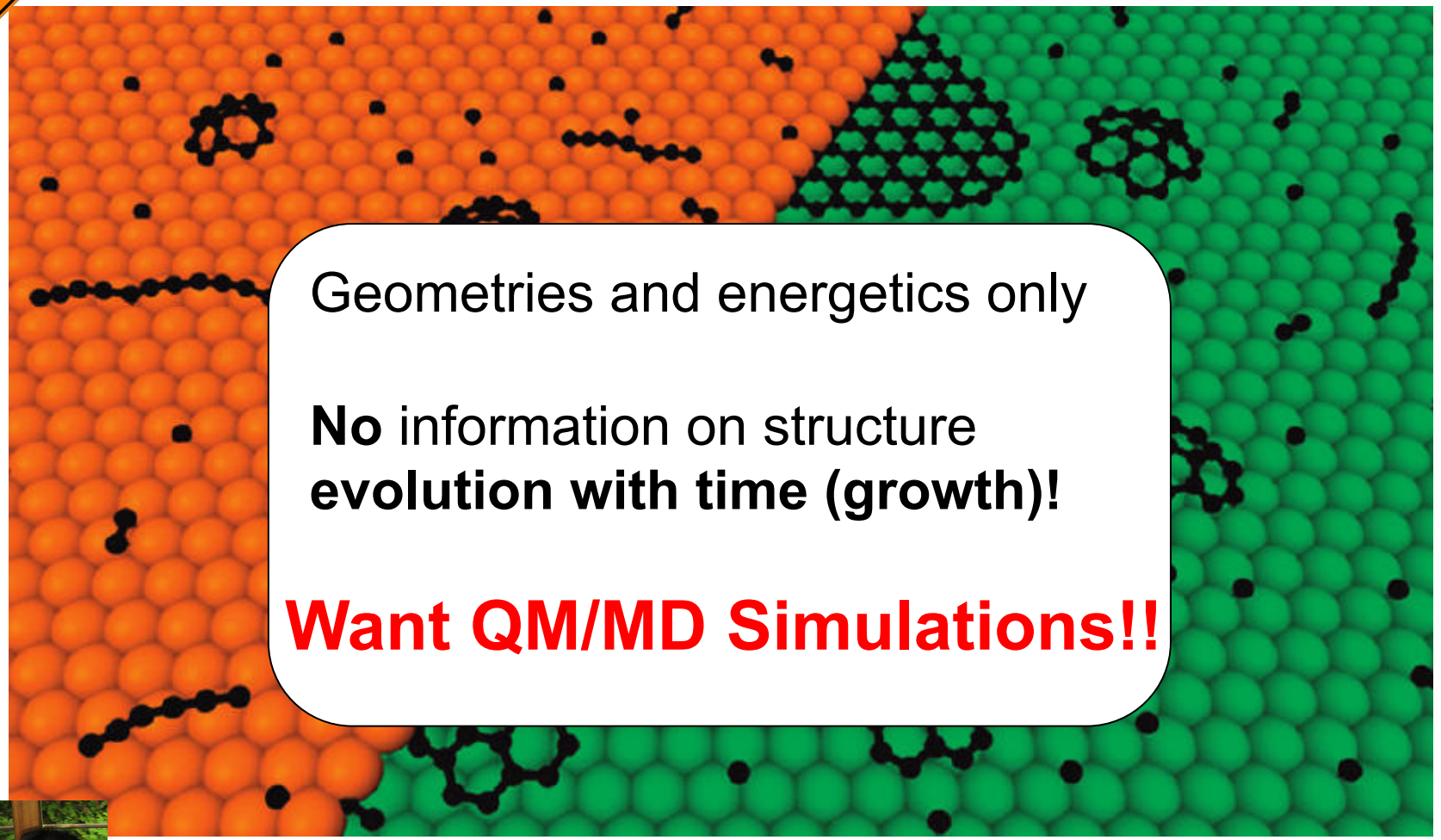


Fe_3C nanoparticle

Yoshida *et al.*, *Nano. Lett.* (2008)

SWNT 'cap' formed without carbide phase... (again!)

Detour: How Does Graphene Form on Ni(111)?



Geometries and energetics only

No information on structure **evolution with time (growth)!**

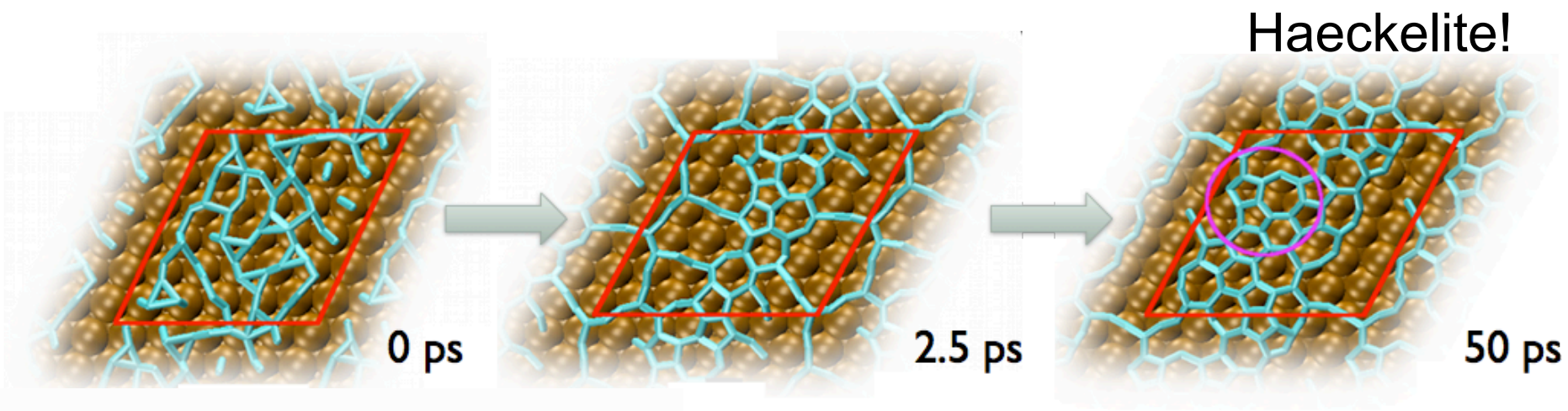
Want QM/MD Simulations!!

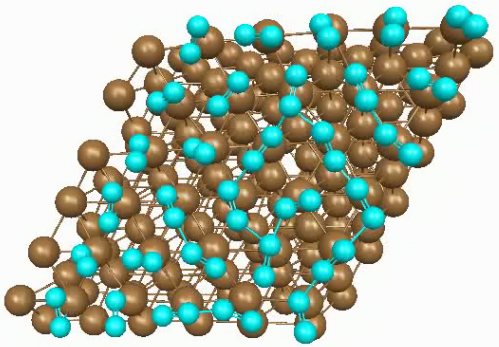
Image source:
Gao *et al.* J. Am. Chem. Soc. **133**, 5009 (2011), static DFT calculations

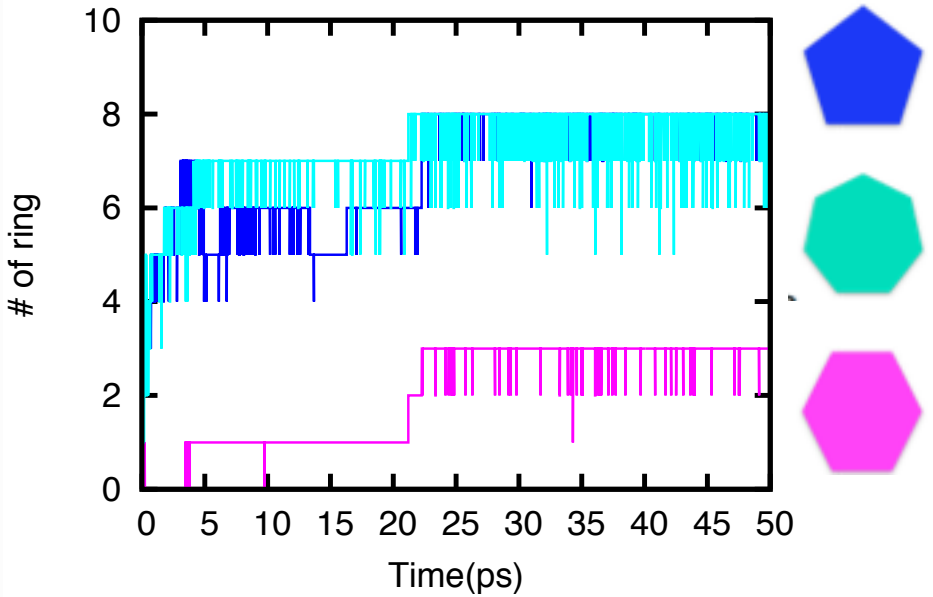
Dr. Ying Wang

QM/MD of 30 C_2 on Ni(111), 1180 K

Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, SI, K. Morokuma, *J. Am. Chem. Soc.* **133**, 18837 (2011)







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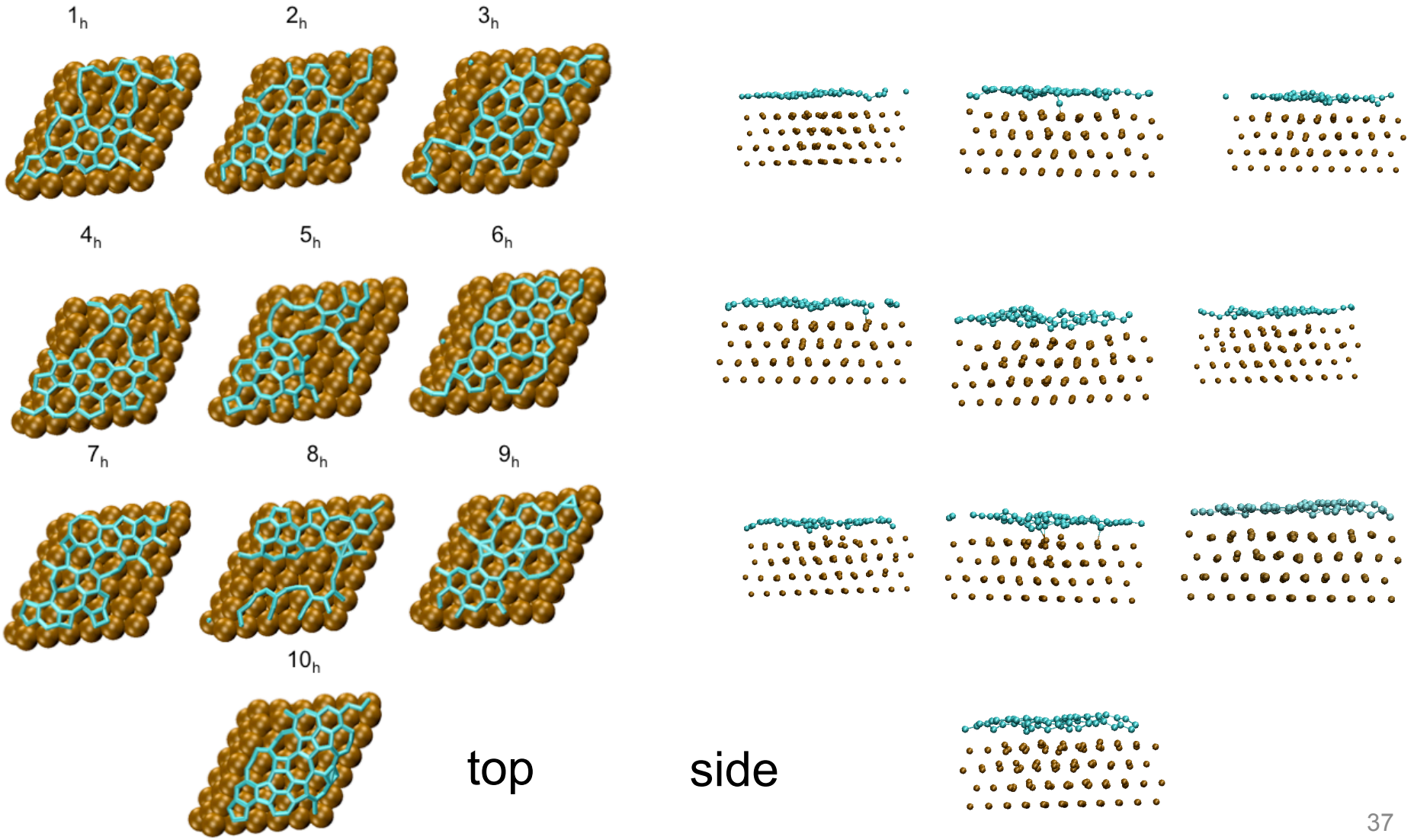
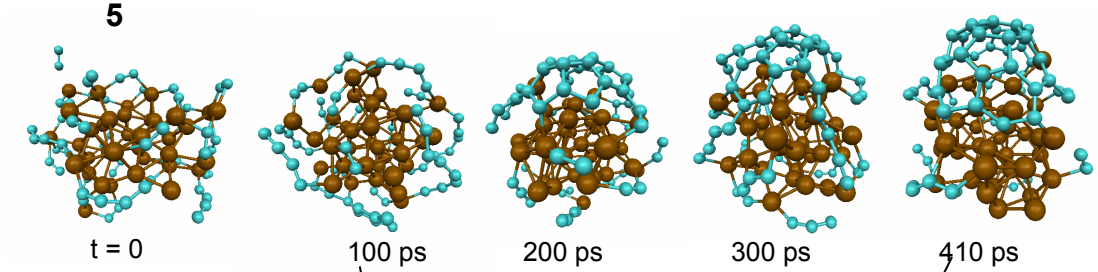
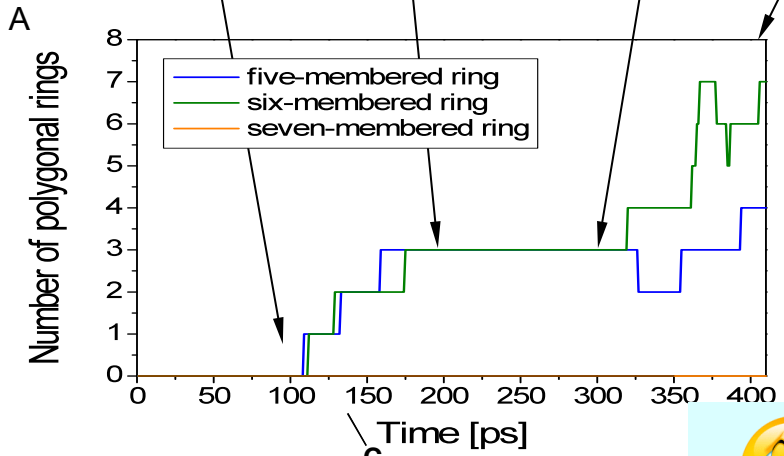
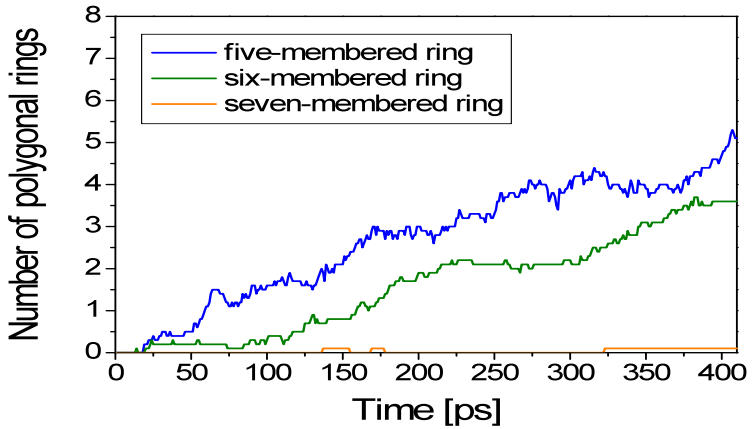


Y. Ohta, Y. Okamoto, A. J. Page, SI, K. Morokuma, ACS Nano **3**, 3413 (2009)



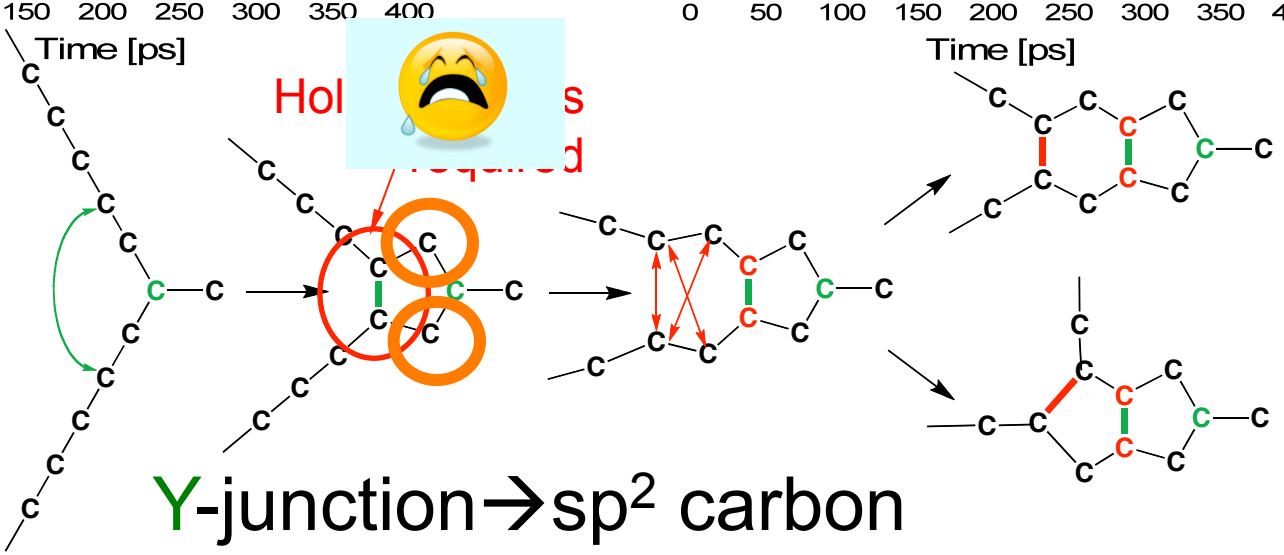


Average 5- and 6-ring counts over 10 annealing trajectories



Formation of first condensed 2-ring system (5/5 or 5/6)

Always pentagon first!

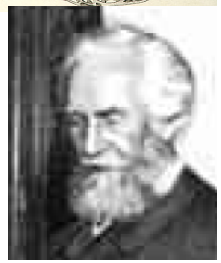


Y-junction→sp^2 carbon

Radiolara

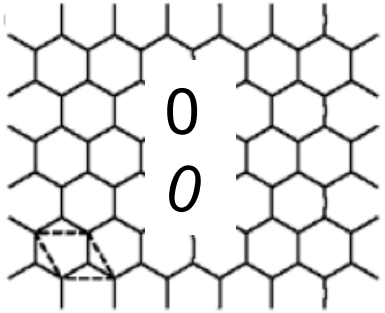
Haeckelite

Crespi *et al.* Phys. Rev. B **53**, R13303 (1996); Terrones *et al.* Phys. Rev. Lett. **84**, 1716 (2000); Rocquefelte *et al.* Nano Lett. **4**, 805 (2004)

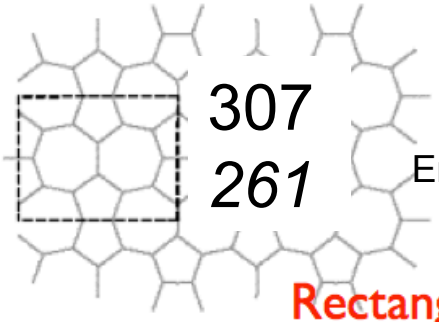


Ernst Haeckel
(1834-1919)

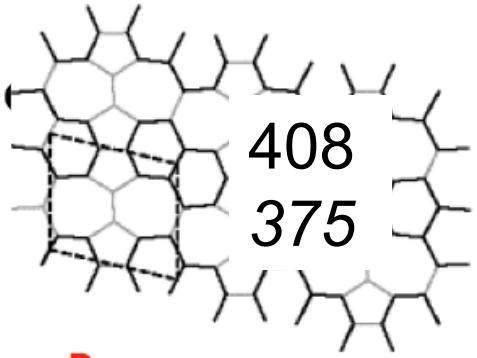
Thrower-Stone-Wales Transformation



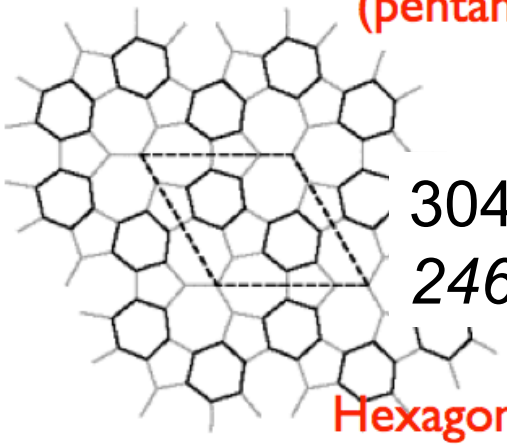
Graphene



Rectangular, $R_{5,7}$
(pentaheptite)



Oblique, $R_{5,6,7}$



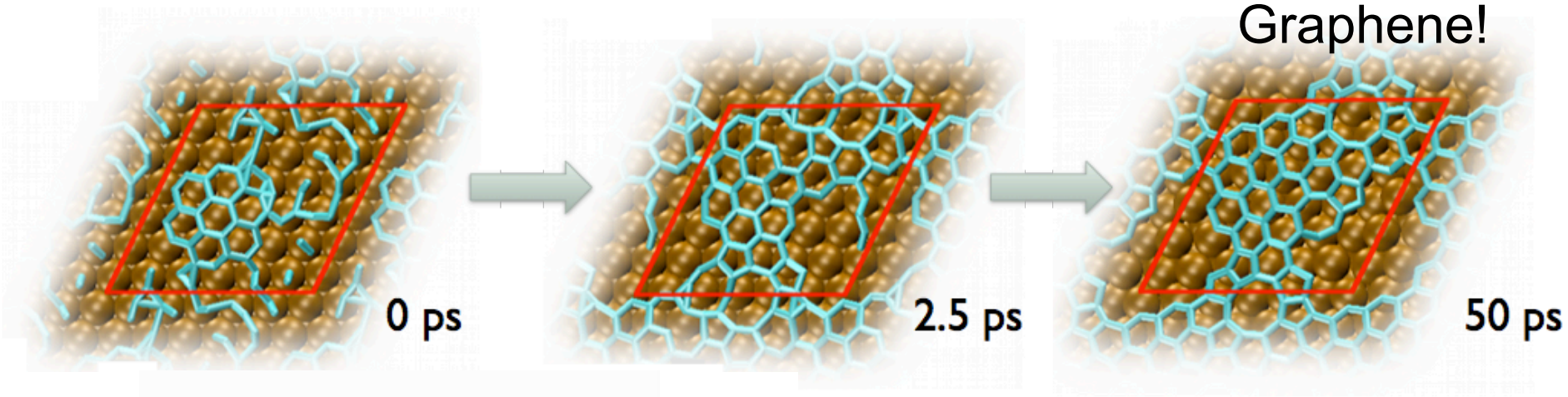
Hexagonal, $H_{5,6,7}$

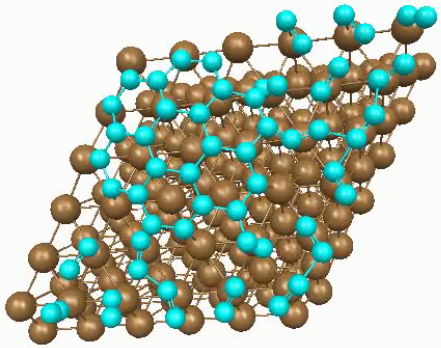
$\Delta E(TB)$ (meV/C atom)
$\Delta E(PBE)$ (meV/C atom)

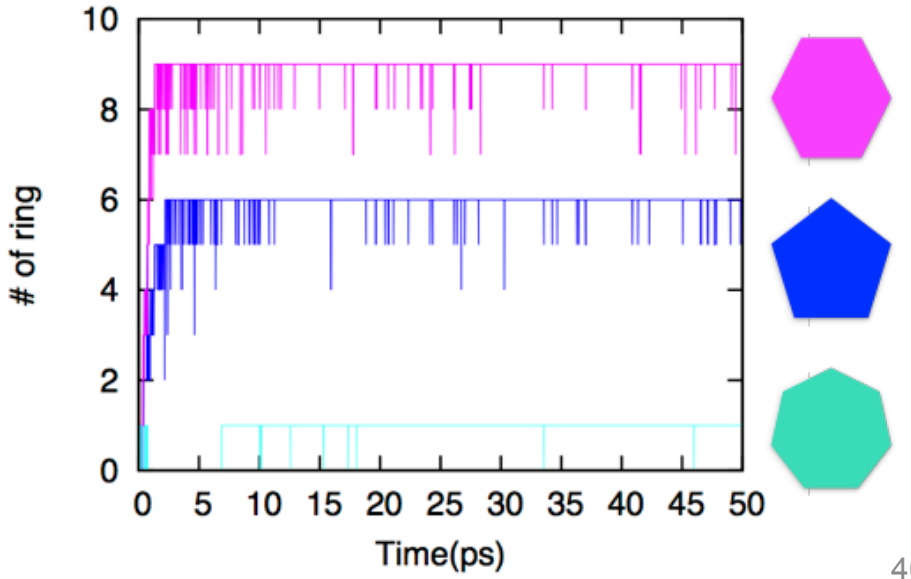
C_{60}: 419
380

QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, SI, K. Morokuma, *J. Am. Chem. Soc.* **133**, 18837 (2011)

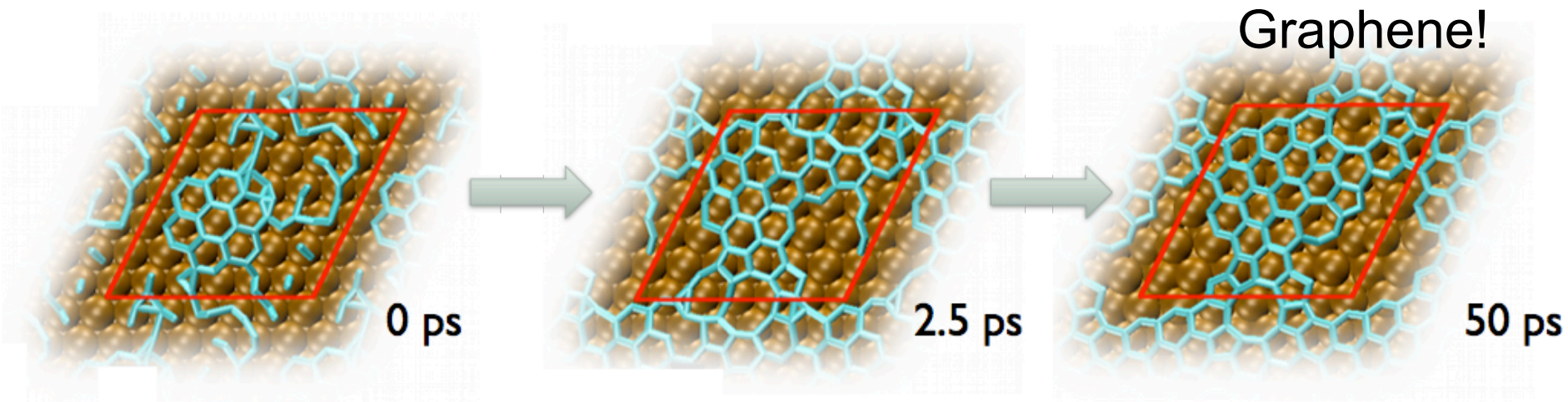




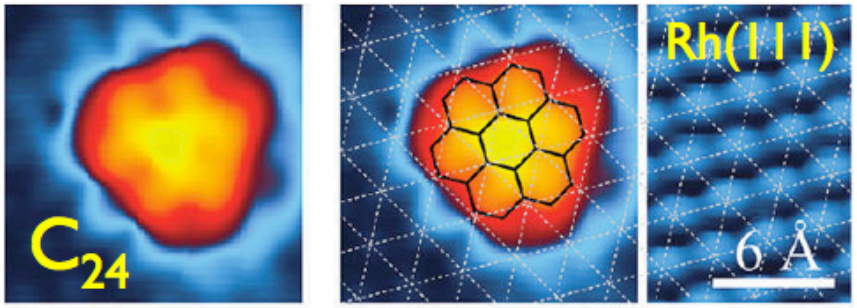


QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

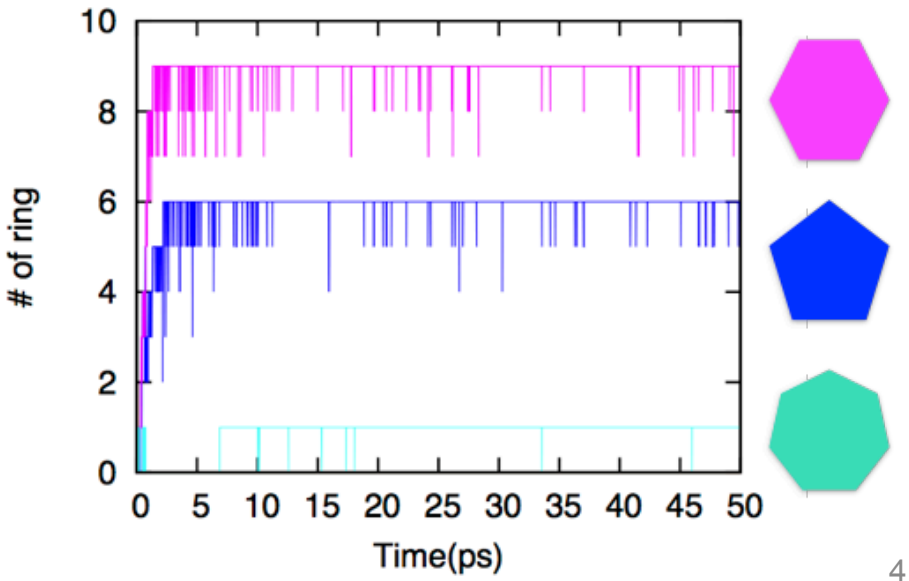
Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, SI, K. Morokuma, *J. Am. Chem. Soc.* **133**, 18837 (2011)



- Pentagon-first vs. **template effect**.
- Suppression of heptagons and pentagons

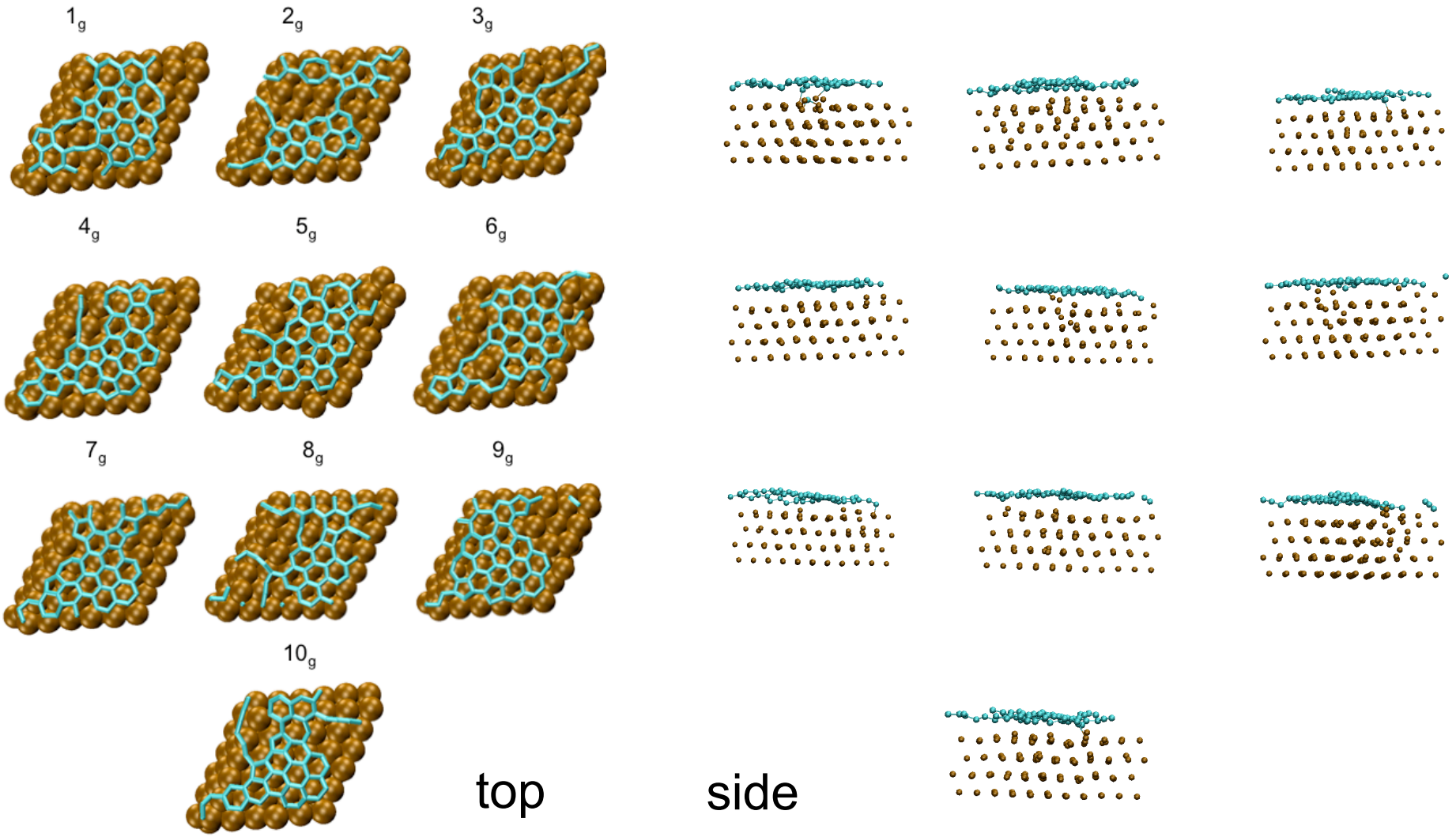


Wang *et al., Nano Lett., (2011)*

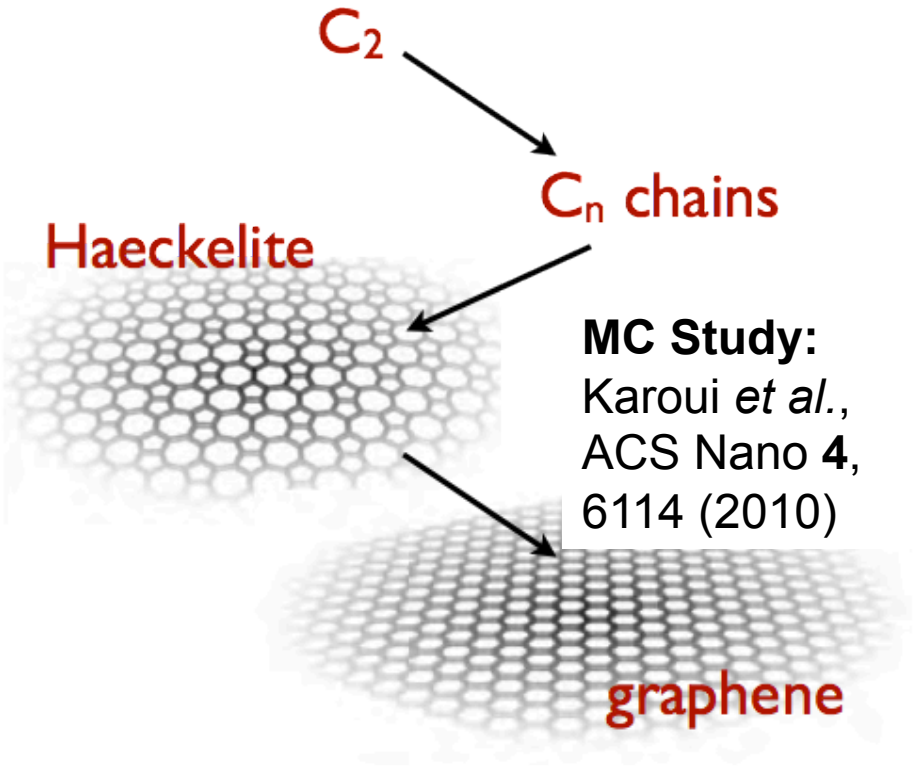


QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

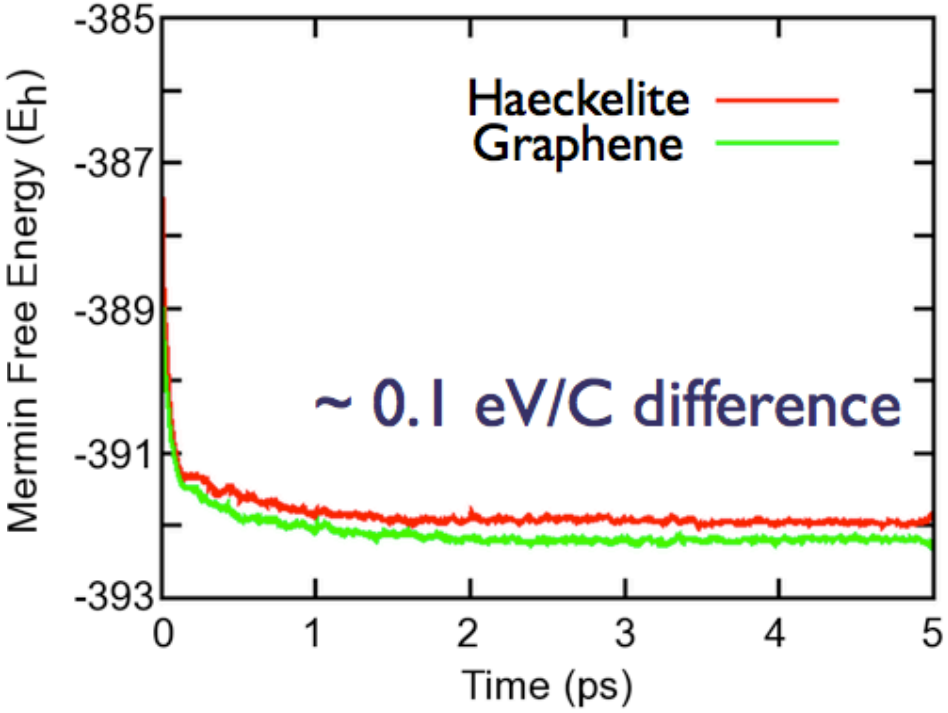
Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, SI, K. Morokuma, *J. Am. Chem. Soc.* **133**, 18837 (2011)



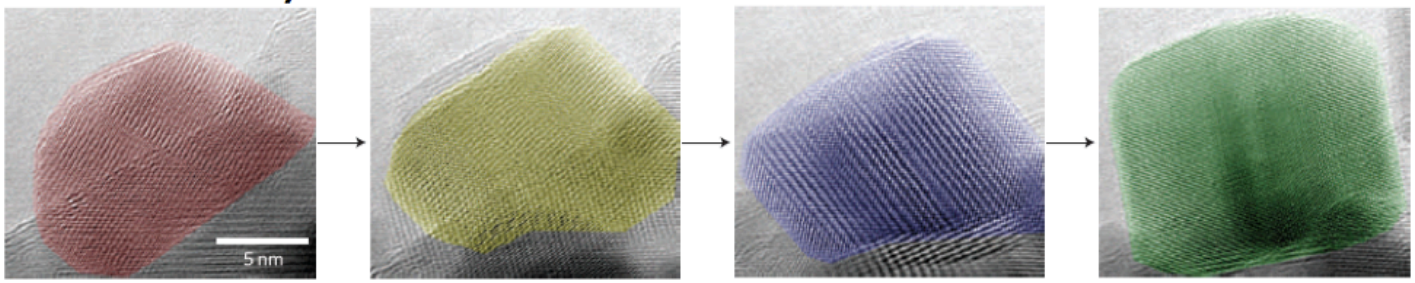
DFTB/MD: Haeckelite is a Metastable Phase



MC Study:
Karoui *et al.*,
ACS Nano **4**,
6114 (2010)



$LiFePO_4$ nanocrystal, 450 °C



Chung *et al.*, Nature Phys. (2008)

Ostwald's 'rule of stages'

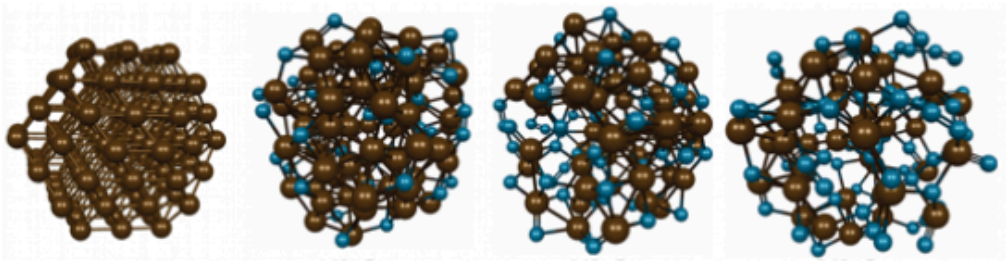
F. W. Ostwald,
Z. Phys. Chem.
22, 289 (1897)

Fe-Carbide Nanoparticle Precursor

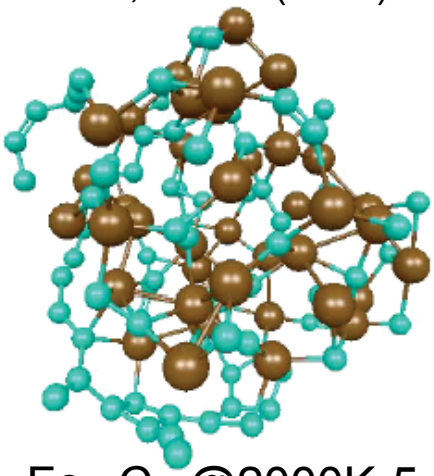
A. J. Page, H. Yamane, Y. Ohta, SI, K. Morokuma, *J. Am. Chem. Soc.* **132**, 15699 (2010)

- SCC-DFTB; T_e = 10,000 K.
- MD; Δt=1 fs.
- NVT ensemble; T_n= 800, 1,400 & 2,000 K.
- Nosé-Hoover-Chain thermostat.

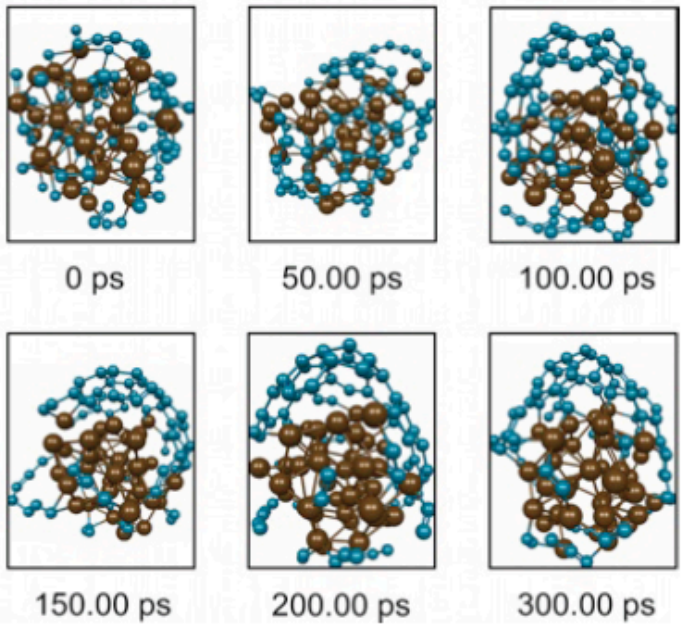
- fcc-Fe_{116} nanoparticles.
- 'Random replacement' of 33, 50 and 66% Fe atoms.
- NVT thermal annealing for 300 ps.



Fe_{116} $Fe_{77}C_{39}$ $Fe_{58}C_{58}$ $Fe_{39}C_{77}$



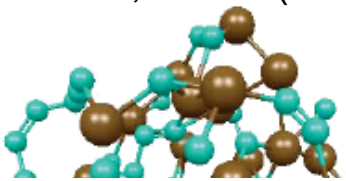
$Fe_{58}C_{58}$@2000K-5



$Fe_{39}C_{77}$@1400K-9

Fe-Carbide Nanoparticle Precursor

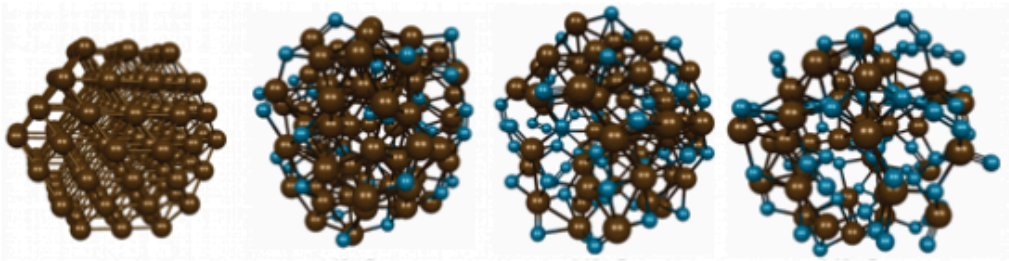
A. J. Page, H. Yamane, Y. Ohta, SI, K. Morokuma, *J. Am. Chem. Soc.* **132**, 15699 (2010)

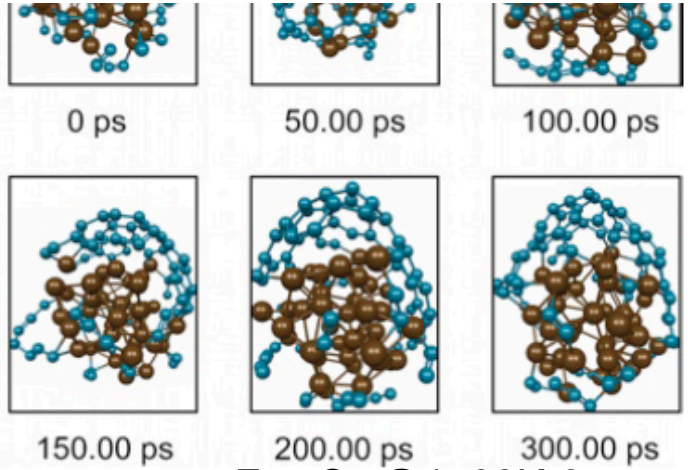


PRL **100,** 195502 (2008) PHYSICAL REVIEW LETTERS week ending 16 MAY 2008

Reduced Carbon Solubility in Fe Nanoclusters and Implications for the Growth of Single-Walled Carbon Nanotubes

A. R. Harutyunyan,[1,*,†] N. Awasthi,[2] A. Jiang,[2] W. Setyawan,[2] E. Mora,[1] T. Tokune,[1] K. Bolton,[3] and S. Curtarolo[2,*,‡]
[1]*Honda Research Institute USA, Inc., 1381 Kinnear Road, Columbus, Ohio 43212, USA*
[2]*Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA*
[3]*University College of Borås, SE-501 90 Borås and Physics Department, Göteborg University, SE-412 96 Göteborg, Sweden*
(Received 26 October 2007; published 14 May 2008)



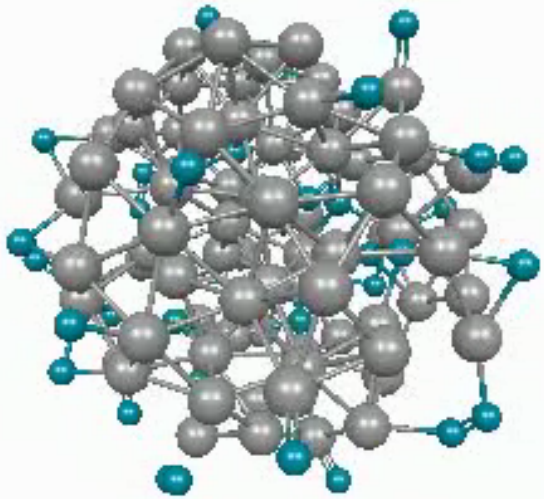


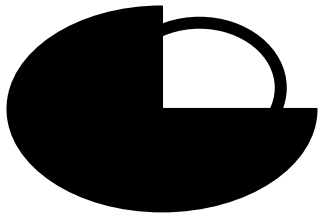
$Fe_{39}C_{77}$@1400K-9

Ni-Carbide Nanoparticle Precursor

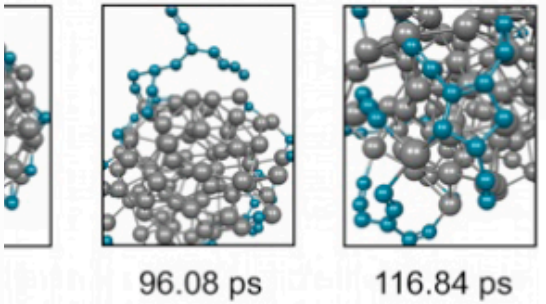
A. J. Page, H. Yamane, Y. Ohta, SI, K. Morokuma, *J. Am. Chem. Soc.* **132**, 15699 (2010)

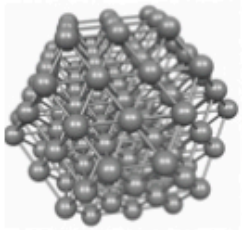
Metal-car
Precipitatio
S



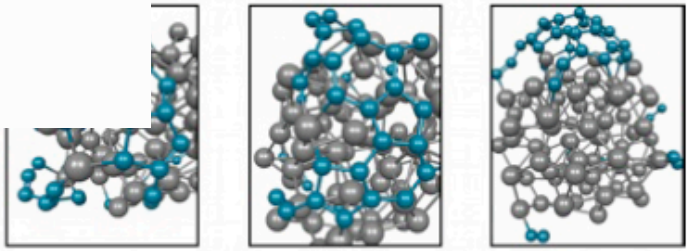


$Ni_{77}C_{39}$@1400K-5





Ni_{116} $Ni_{77}C_{39}$ $Ni_{58}C_{58}$ $Ni_{39}C_{77}$



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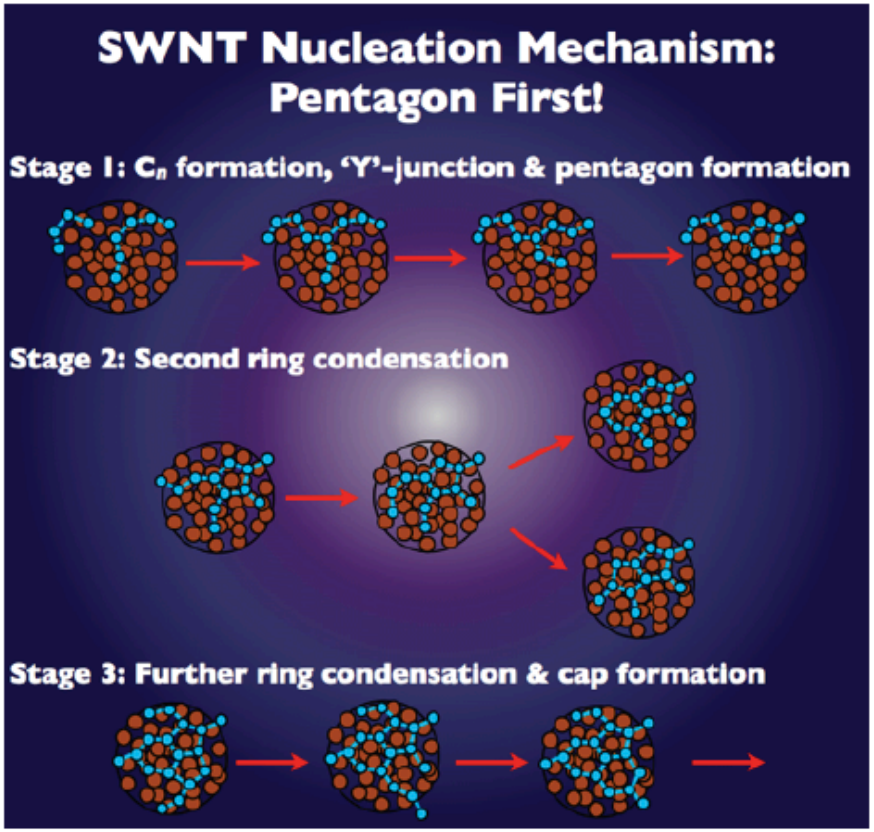
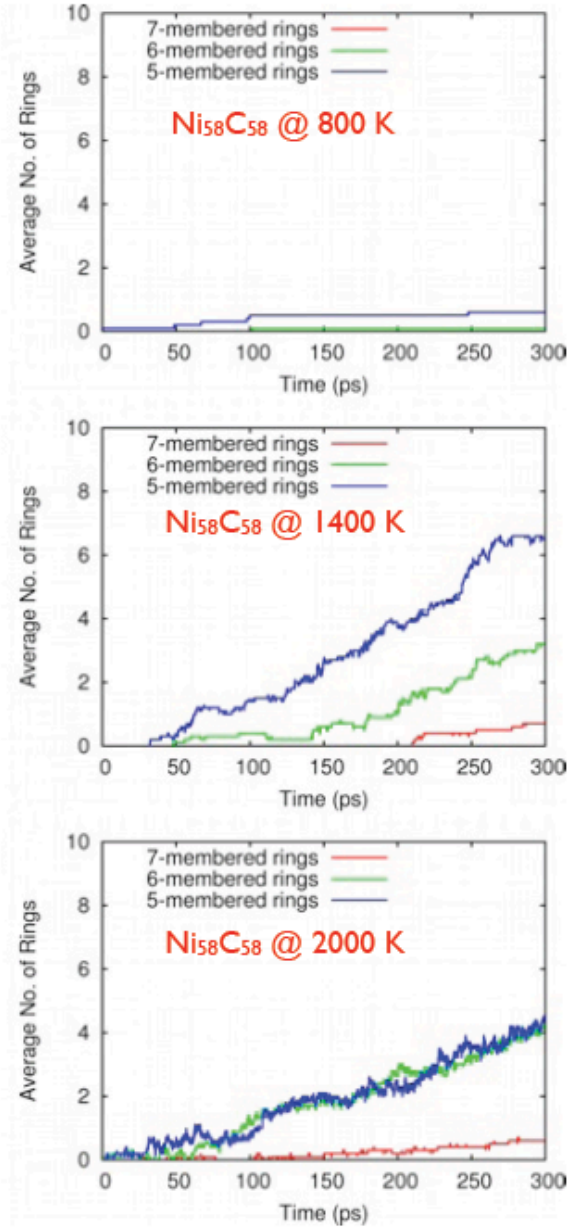


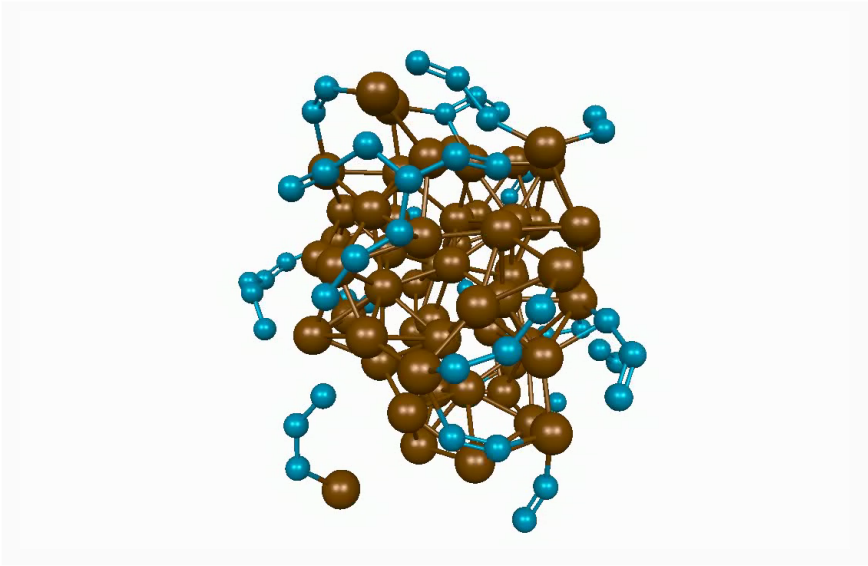


Carbide phase ➛ Catalyst/Cap structure in < 300 ps!

Fe/Ni-carbide nanoparticles thermodynamically unstable at these conditions.

A. J. Page, H. Yamane, Y. Ohta, SI, K. Morokuma, *J. Am. Chem. Soc.* **132**, 15699 (2010)

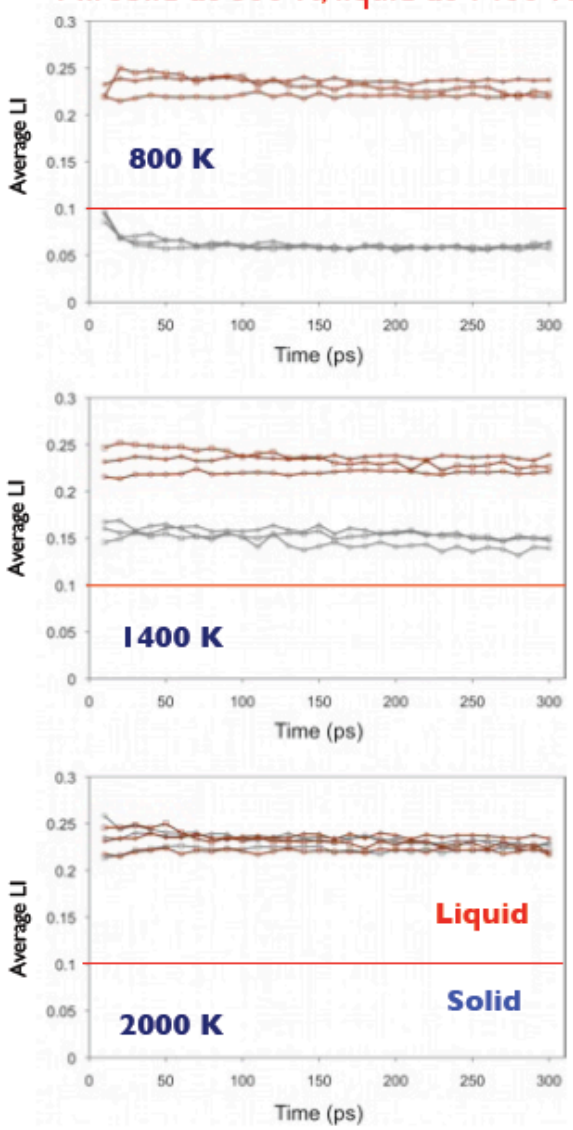
- SWNT nucleation dynamics:
  - Driven by 'catalyst-carbon' interaction strength.
  - Catalyst-carbon interactions: Ni-C=1.06 eV; Fe-C=1.78 eV.
  - Fe-carbide: SWNT nucleation impeded (destruction of C-C bonds).
- Carbon precipitation dynamics:
  - Determined by catalyst-carbon interaction & phase of catalyst.



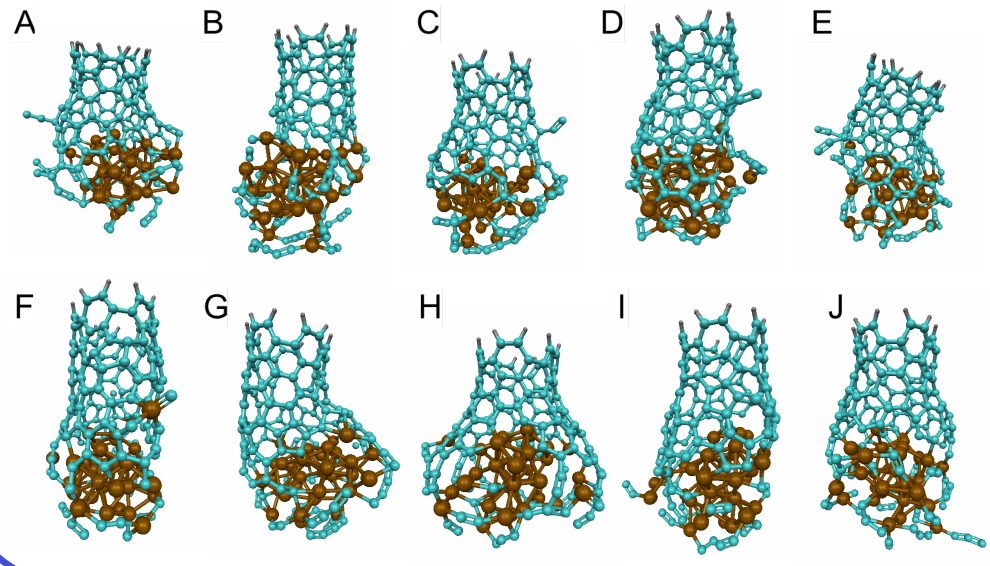
Repeated formation and destruction of first pentagon
($Fe_{58}C_{58}$ @ 2000 K)

Phase of Catalyst during Nucleation:

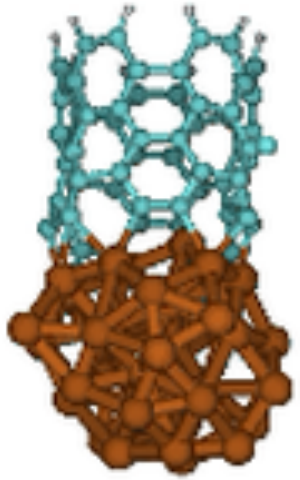
Fe: liquid > 800 K;
Ni: solid at 800 K, liquid at 1400 K.



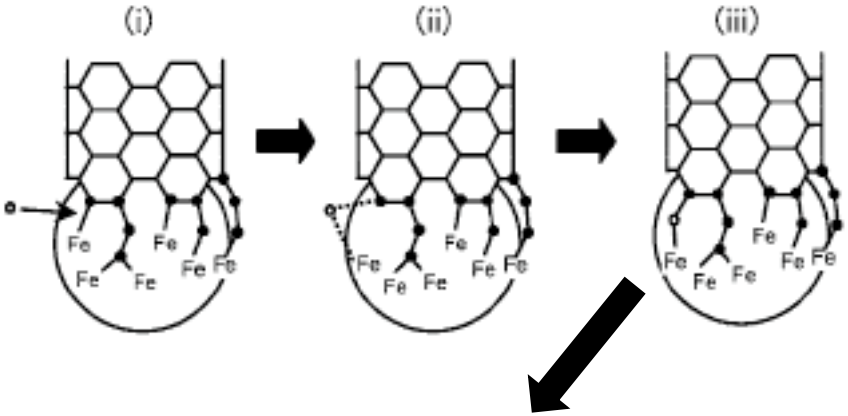
10 Trajectories after 45 ps C supply



Y. Ohta, Y. Okamoto, SI, K. Morokuma, *ACS Nano* **2**, 1437 (2008)

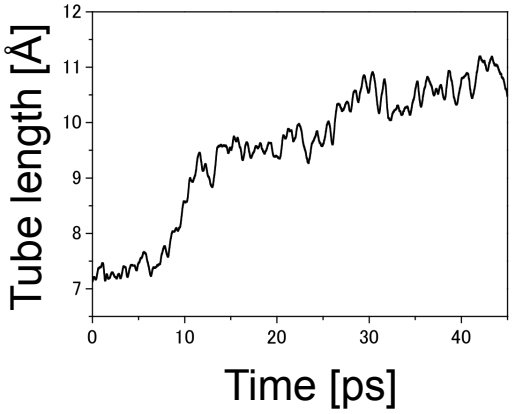


Schematic depiction of C atom insertion events



new 5-, 6-, 7-membered rings

Trajectory F

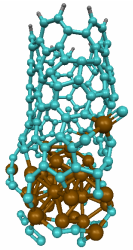


Growth rate: ~10 pm/ps

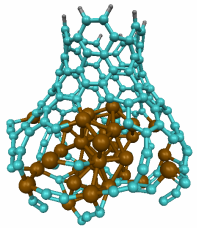
Correlation between ring type and tube length

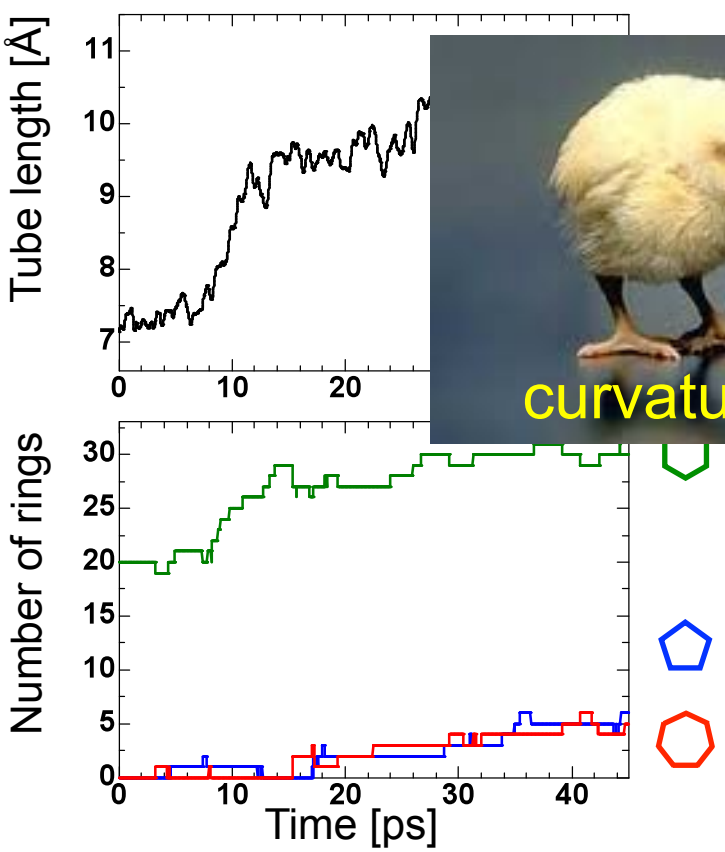
Y. Ohta, Y. Okamoto, SI, K. Morokuma, *J. Phys. Chem. C*, **113**, 159, (2009).

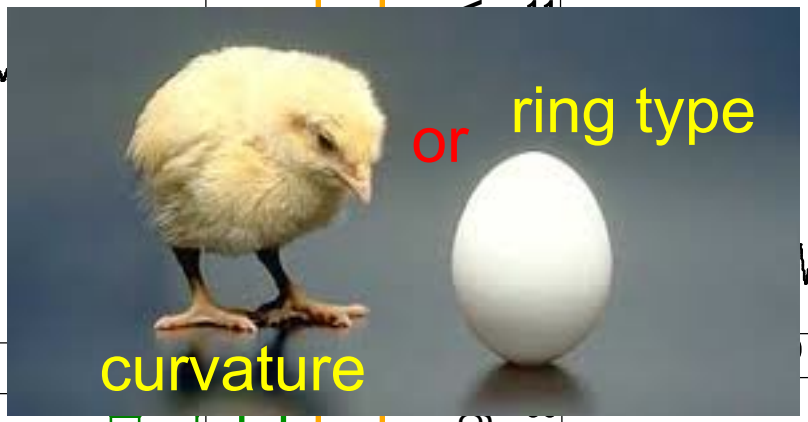
F

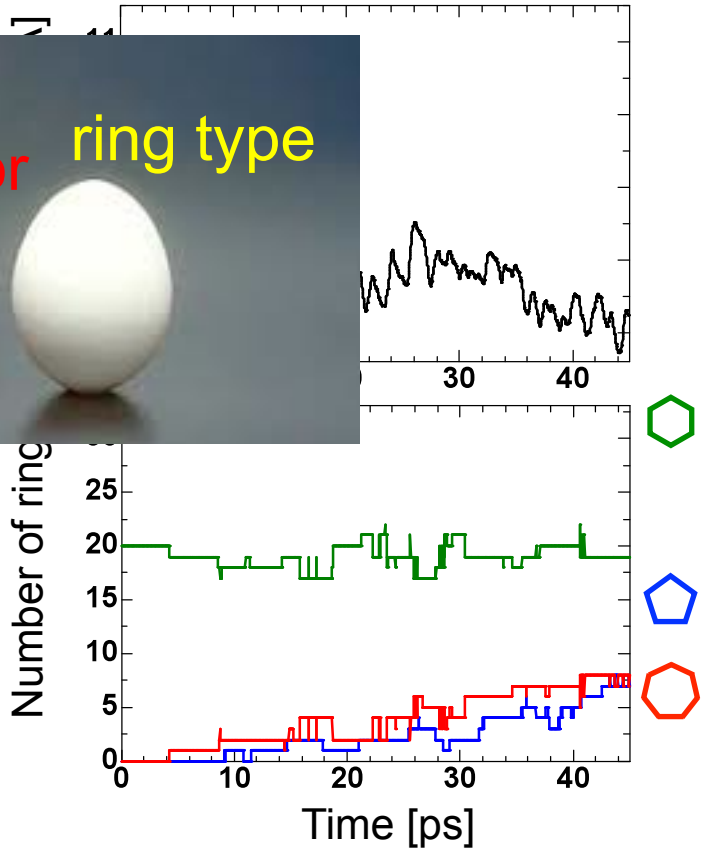


H

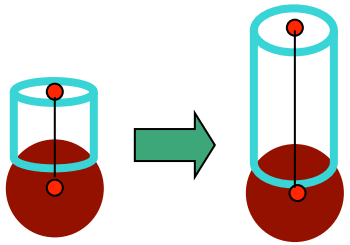




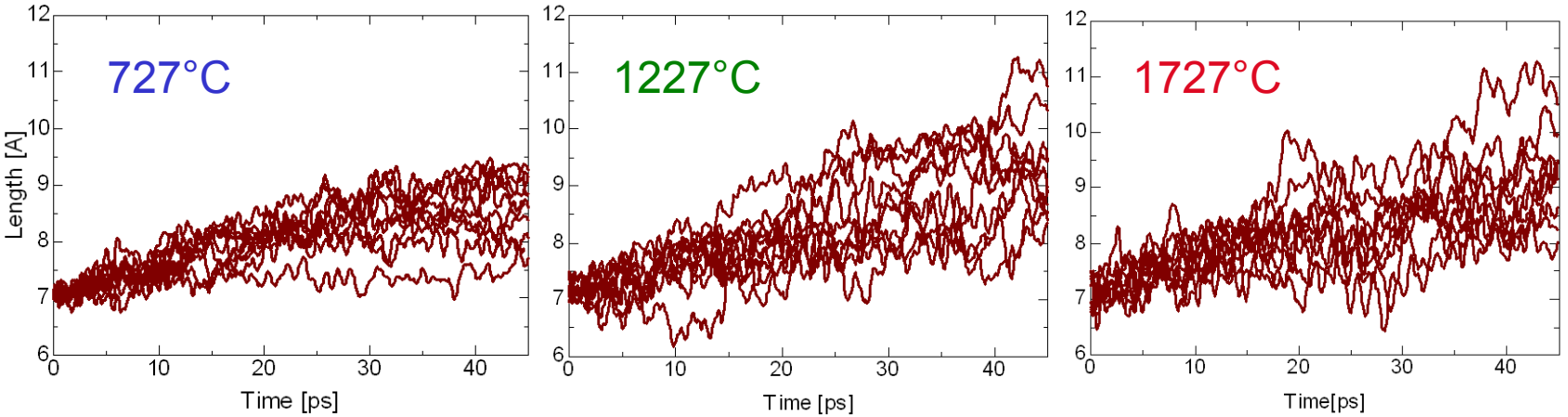




Continued SWNT growth as function of temperature ((5,5) armchair SWNT)



10 Trajectories for 3 temperatures



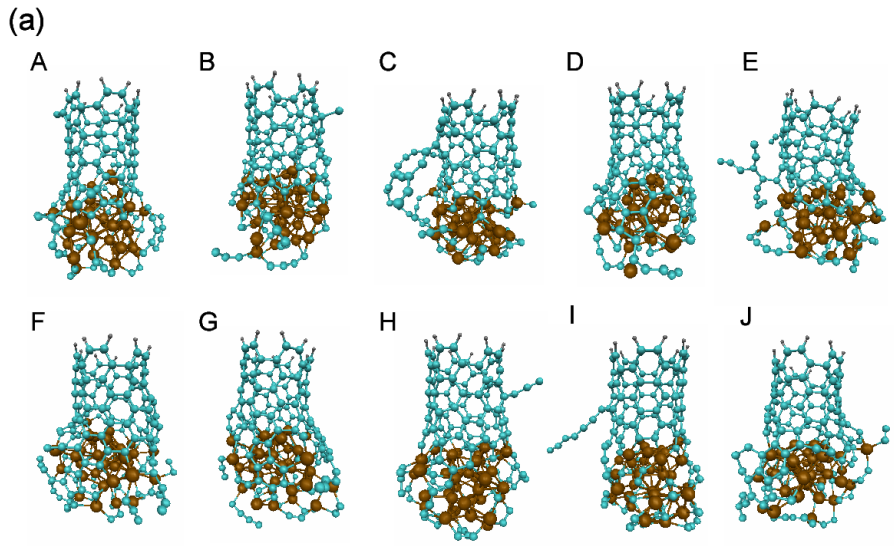
T[°C]	727	1227	1727
Growth rate [pm/ps][a]	3.48	5.07	4.13
Chain carbons[a]	3.9	0.3	0.2
SWNT C atoms[a]	112.9	110.1	102.7

[a]averaged over 10 trajectories/T

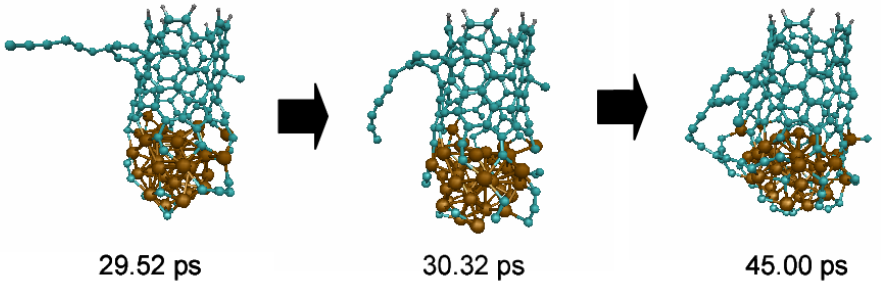
Y. Ohta, Y. Okamoto, SI, K. Morokuma, *J. Phys. Chem. C*, **113**, 159, (2009).

T=727°C

10 Trajectories after 45 ps



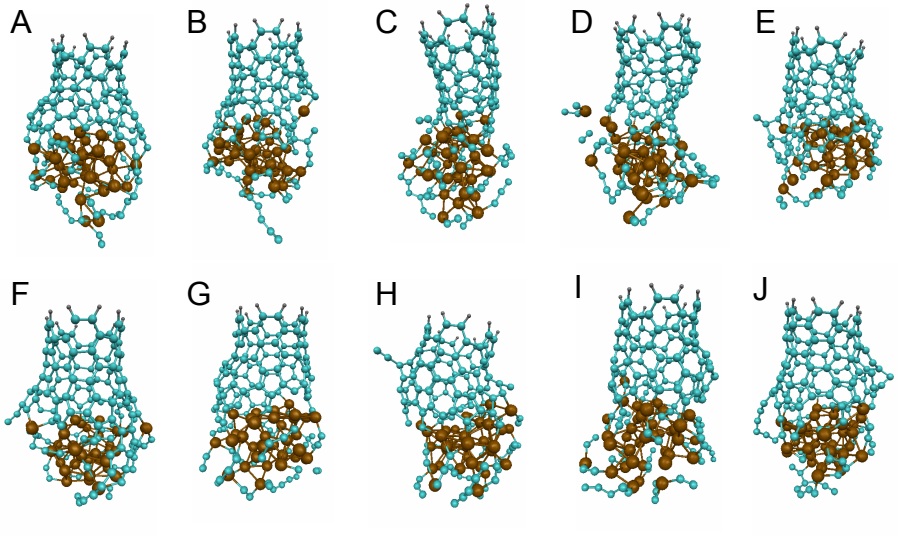
(b) Encapsulation of Fe by polyyne



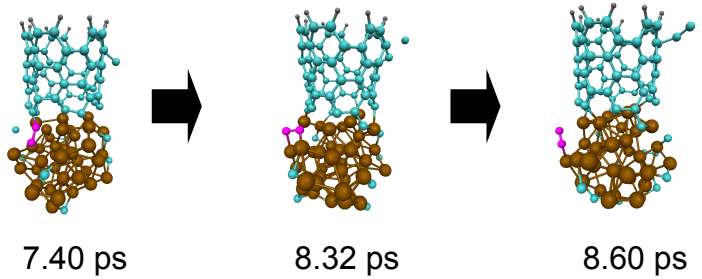
Trajectory C

T=1727°C

(a) 10 Trajectories after 45 ps



(b) Dissociation of C_2 from Fe/C



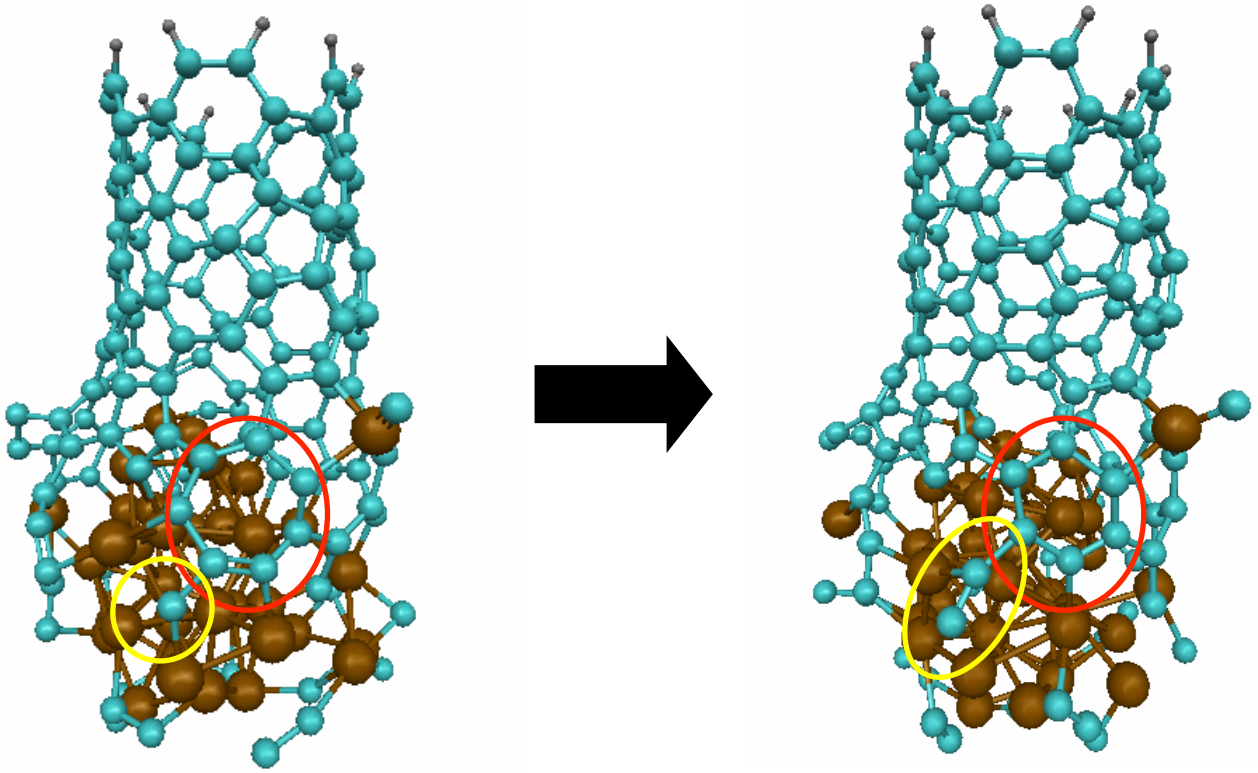
Trajectory G

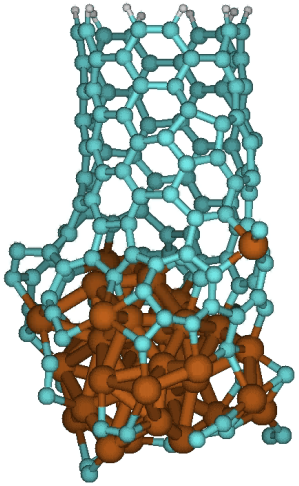
Y. Ohta, Y. Okamoto, SI, K. Morokuma, *J. Phys. Chem. C,* **113**, 159, (2009).

Self-healing process of sidewall (annealing)

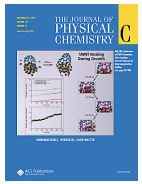
Fe-Carbon mobility at interface important!

Trajectory 6: T_n= 1500 K, T_e = 10k K, C_{int}=1500 K





Movie

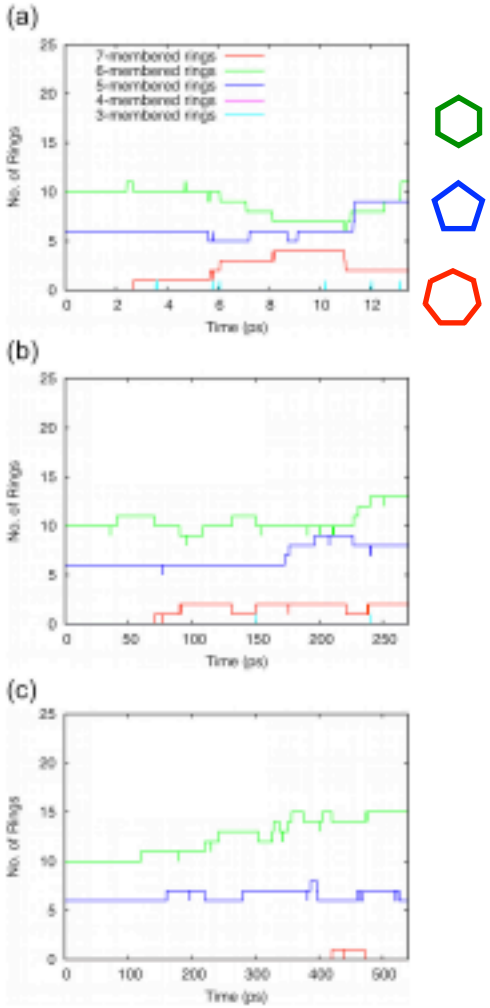


24.5 ps - 27.5 ps

Heptagon + C changes into hexagon + C_2

A. Page, Y. Ohta, Y. Okamoto, SI, K. Morokuma, *J. Phys. Chem. C*, **113**, 20198, (2009)

Carbon Feeding Rate Effect: $M_{38}C_{40}$+nC

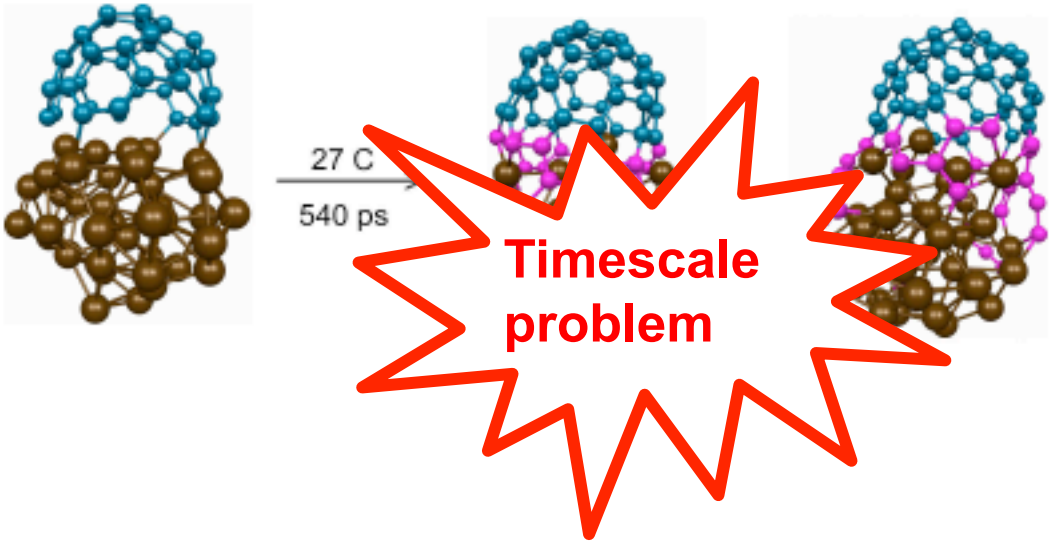


(a) fast (1 C / 0.5 ps)
(b) slow (1 C / 10 ps)
(c) very slow (1 C / 20 ps)

Comparison of "fast", "slow" & "very slow" SWNT growth:

Near-perfect extension of (5,5) sp^2 network obtained with 1 C / 10 ps supply rate.

Even better using 1 C / 20 ps!!



A. Page, S. Minami, Y. Ohta, SI, K. Morokuma, *Carbon* **48**, 3014 (2010)

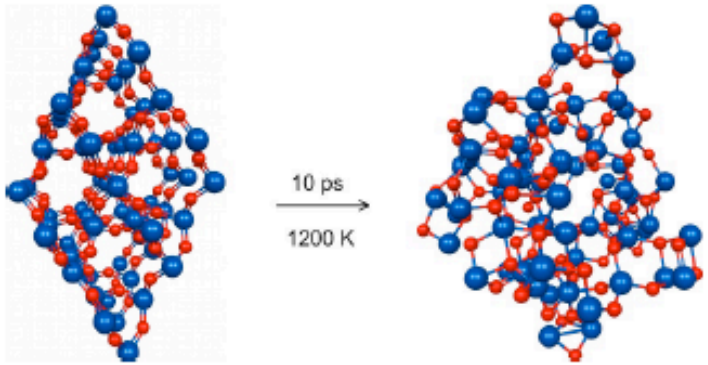
Simulation of CH_4 CVD and SWNT Nucleation on SiO_2-Nanoparticles

A. J. Page, KRS Chandrakumar, SI, K. Morokuma,
J. Am. Chem. Soc. ***133***, 621 (2011).

Computational Details

Catalyst:

- Si-terminated $Si_{63}O_{88}$ nanoparticle.
- Truncated β-SiO_2 structure @ 1078 K. (Kihara *Eur. J. Miner.*, **2** (1990) 63.)
- Dimensions: 1.8 × 1.5 × 1.1 nm^3.

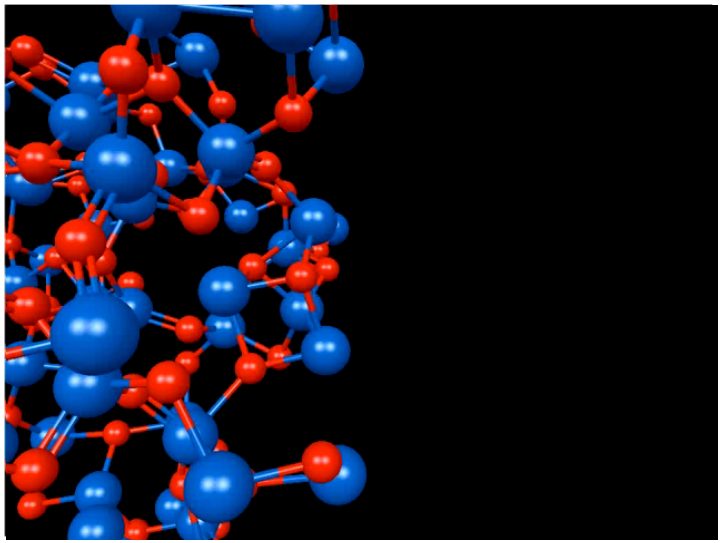


CVD Simulation:

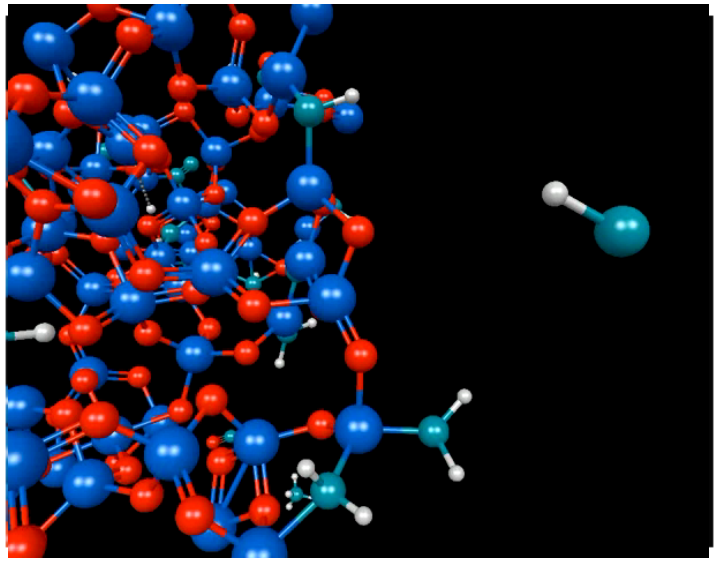
- SCC-DFTB/MD: T_n= 1,200 K; T_e = 1,500 K; Δt=1 fs; Velocity-Verlet integration; Nosé-Hoover Chain thermostat (Ohta-san's Paderborn code); slko.5425 Slater-Koster files.
- 60×60×60 Å³ box.
- × 10 replication.
- Assumption: CH_4 decomposes pyrolytically before adsorption on SiO_2. (Cheng *et al.*, *ACS Nano*, **3**, 3421, (2009)).
- CH_x (x = 0 – 3) shooting (chosen with weighted Poisson distribution) @ rate of 2/1.0ps.
- Random H removal @ rate of 4/1.0 ps, after first 10 ps of simulation.
- 'Target concentration' of carbon on SiO_2 nanoparticle = 60.
- Anneal at constant temperature once target CH_x concentration reached (up to 250 ps).

(1)Run 0.5 ps MD. (2) analyse structure. (3) Remove H. (4) Shoot CH_x if # C on SiO_2-np < 60, else goto (1).

CH_4 CVD on SiO_2 Nanoparticles



H-Abstraction by SiO_2 catalyst

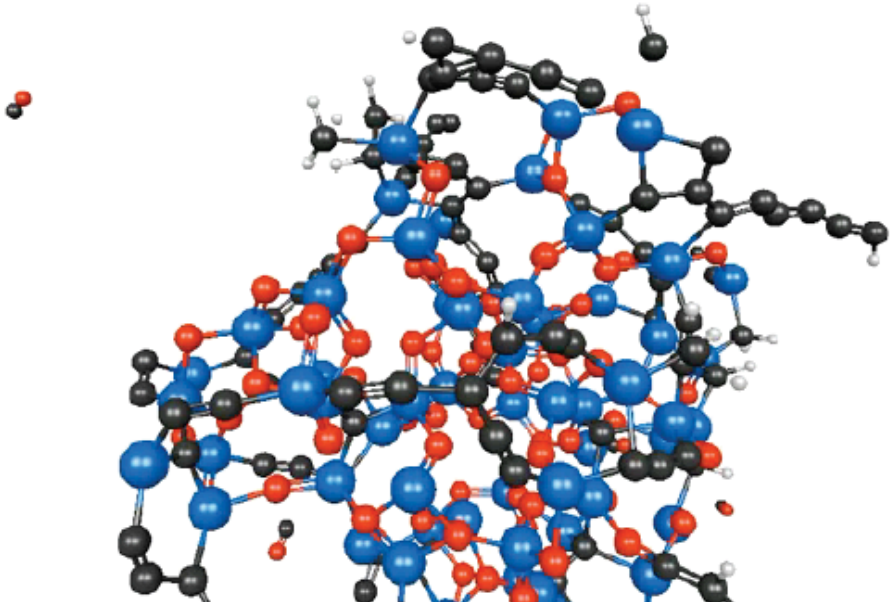


H-Abstraction by surface carbon

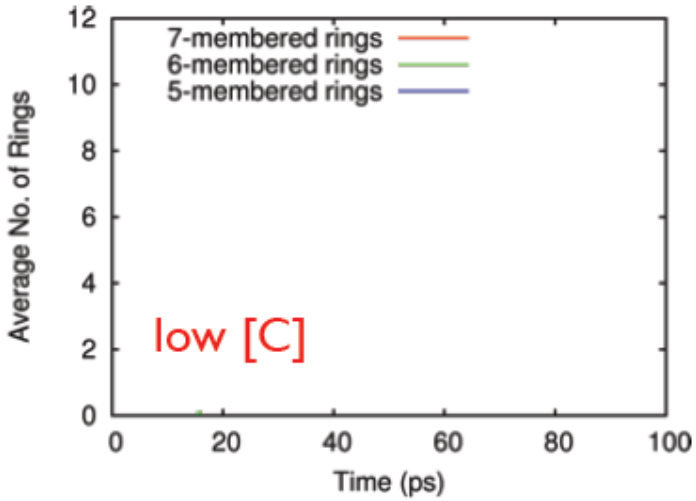
H Abstraction/CO Formation Mechanism

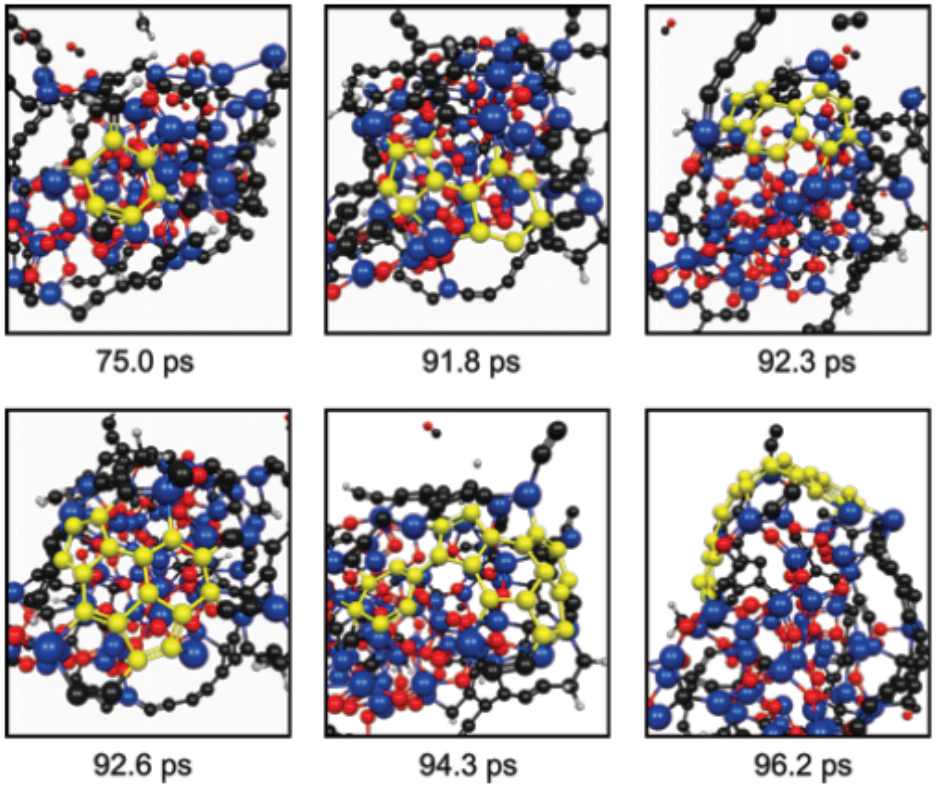
- CO production *always* follows H abstraction from CO carbon.
- H-abstraction mediated by SiO_2 and surface carbon.
- Natural H-removal mechanism observed!
  - H-abstraction from carbon necessary for SWNT nucleation.
  - Mechanism still unknown for transition-metal catalysts...

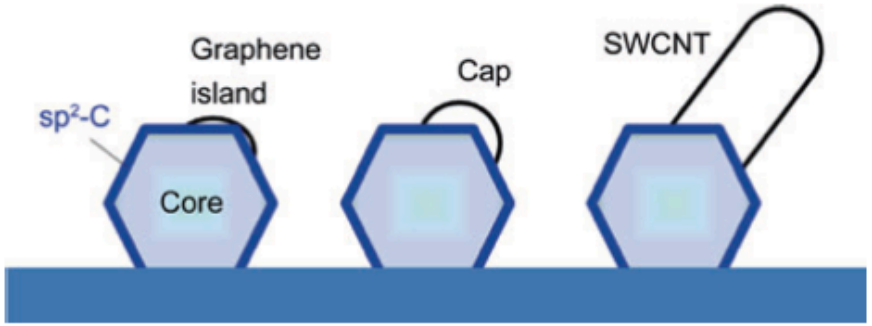
SWNT Nucleation on SiO_2 Nanoparticles



SWNT nucleation:
Requires carbon-saturated SiO_2 surface!



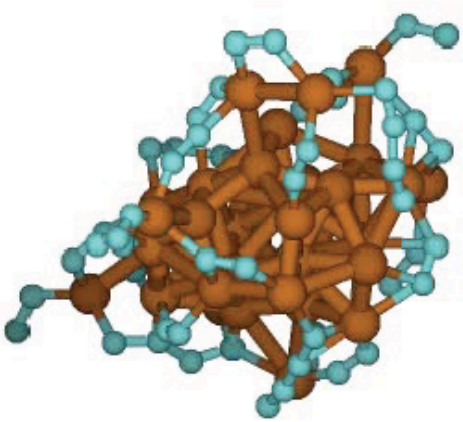




Homma *et al.*, *Nano. Res.* (2009)

Traditional vs. Non-Traditional Catalysts

Fe/Ni-Catalyzed SWNT Nucleation (VLS)

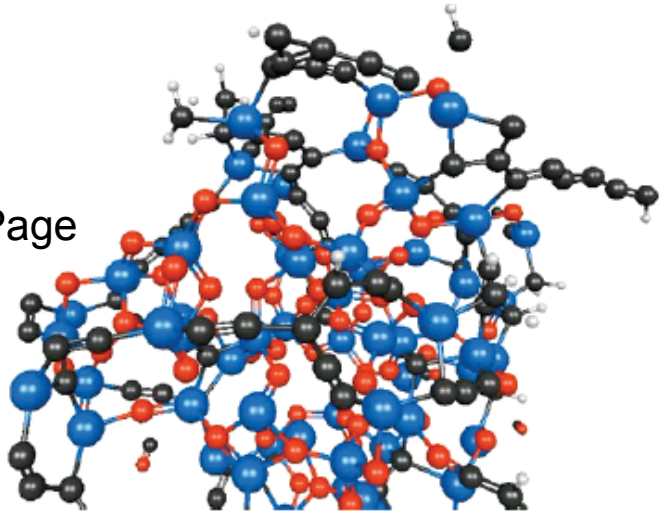


Ohta *et al.*, *ACS Nano*, (2009);
Page *et al.* *J. Phys. Chem. C* (2010)

Poster:
Alister J. Page

1. Bulk carbide, catalyst can be liquid.
2. C_n chains coalesce on catalyst surface.
3. C_n chains exhibit *high* mobility.
4. Pentagon *always* formed first.
5. Further ring condensation *independent of [C]*.
6. Cap-structure formed within 50-400 ps.

SiO_2-Catalyzed SWNT Nucleation (VSS)



A. J. Page, KRS Chandrakumar, SI, K. Morokuma,
J. Am. Chem. Soc. ***133***, 621 (2011).

1. Surface carbide, catalyst is *solid*.
2. C_n chains coalesce on the catalyst surface.
3. C_n chains exhibit *low* mobility.
4. Pentagon or hexagon formed first.
5. Further ring condensation *requires high [C]*.
6. Cap-structure formed over ns timescales.

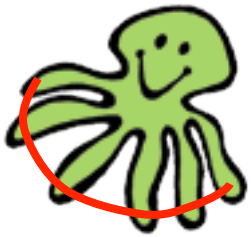
Overview

- Overview: What are MD simulations up against?
- Density-functional tight-binding (DFTB)-based MD
- DFTB/MD Simulations: Acetylene feedstock, carbon-only feedstock, catalytic CVD, catalyst-free CVD
- **Key points: What did we learn?**
- Comparison with thermodynamics and selected experiments
- What is next?

Key points learned — Chicken or egg? Solved.

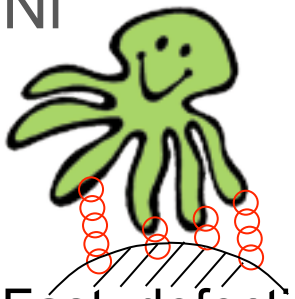
- **Nanocarbons grow as C→C(sp)→C(sp^2), via pentagon-first mechanism**

- **What (fullerene, tube, graphene) we grow depends on the *shape* and *carbon adhesion strength* of the catalyst**



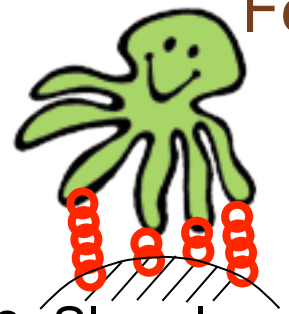
Self-capping, fullerenes

Ni

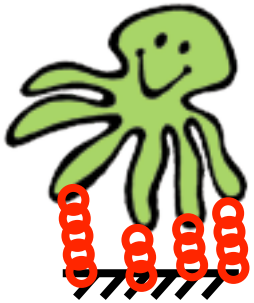


Fast, defective CNT growth

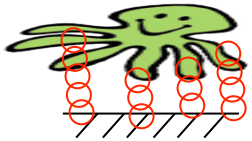
Fe



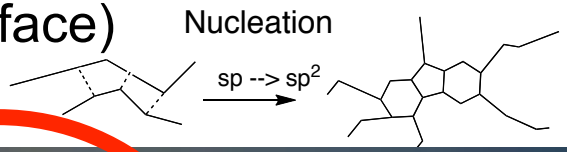
Slow, less defective CNT growth

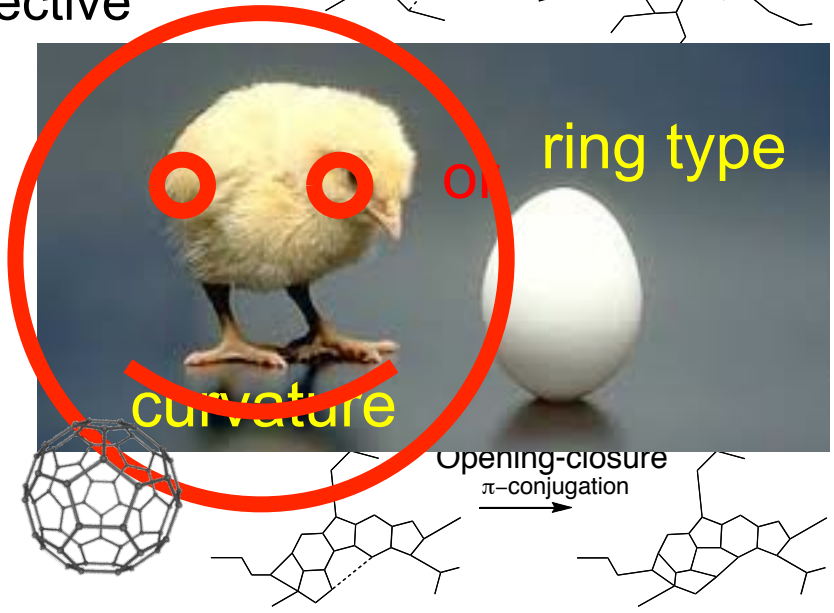


Cap on SiC(C-face)



Graphene



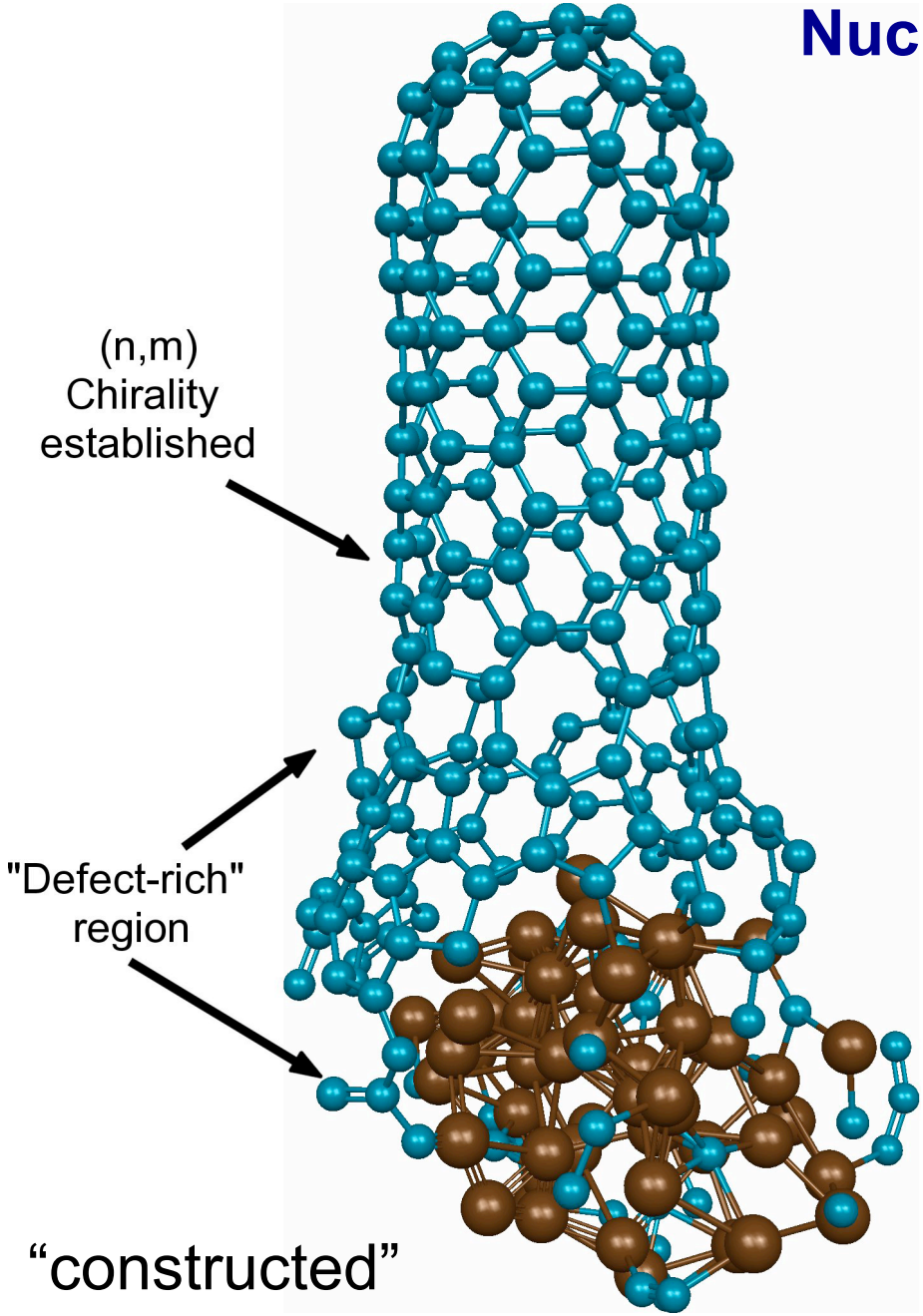


- **Carbon nanostructures grow dynamically in simultaneous processes of chaotic growth and defect healing**

- **Pentagons in nanocarbons are "fossils" from pentagon-first mechanism, "frozen" by shape of carbon superstructure on surface**

Overview

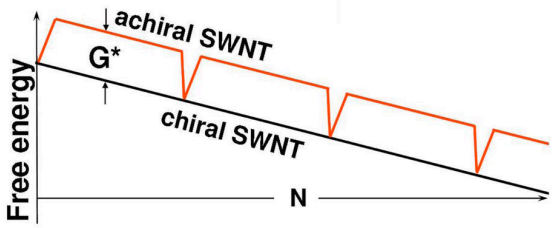
- Overview: What are MD simulations up against?
- Density-functional tight-binding (DFTB)-based MD
- DFTB/MD Simulations: Acetylene feedstock, carbon-only feedstock, catalytic CVD, catalyst-free CVD
- Key points: What did we learn?
- **Comparison with thermodynamics and selected experiments**
- What is next?



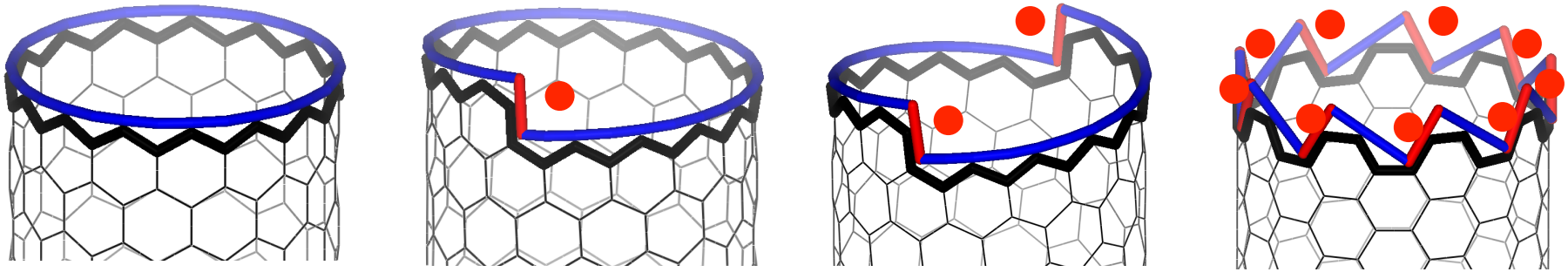
Nucleation and growth hypothesis:

In sharp contrast to:

F. Ding, A. Harutyunyan, B. I. Yakobson, Proc. Natl. Acad. Sci. **106**, 2506 (2009)



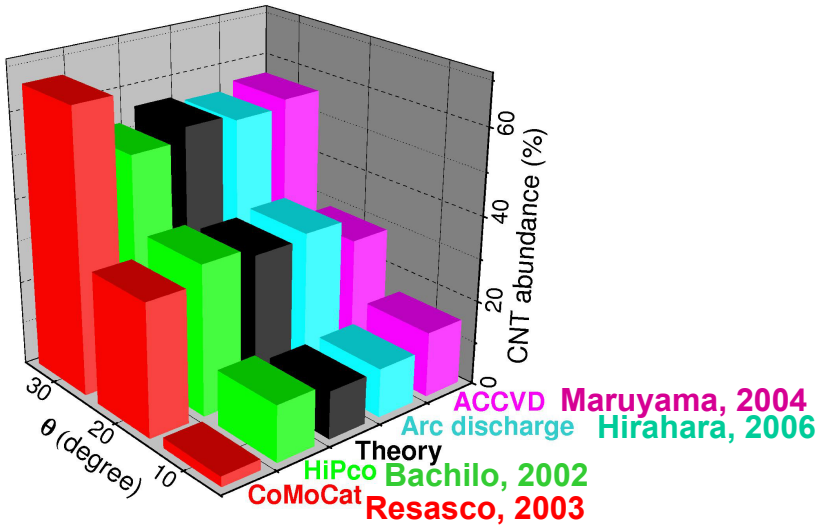
Ding & Yacobsons Nucleation and Growth Hypothesis:

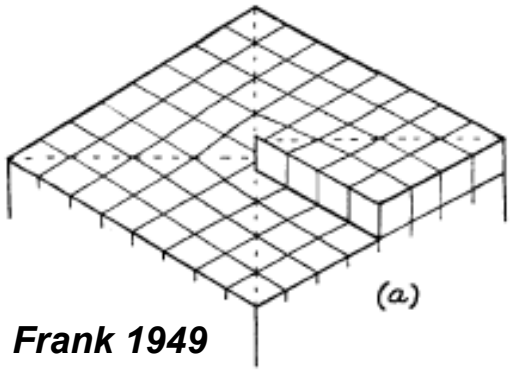


● = C_2

For (n,m) tube, m kinks serve as active sites for C_2 accretion,

Growth rate K ~ m/*d* ~ sin (θ) ~ θ, $0 < \theta < 30^o$



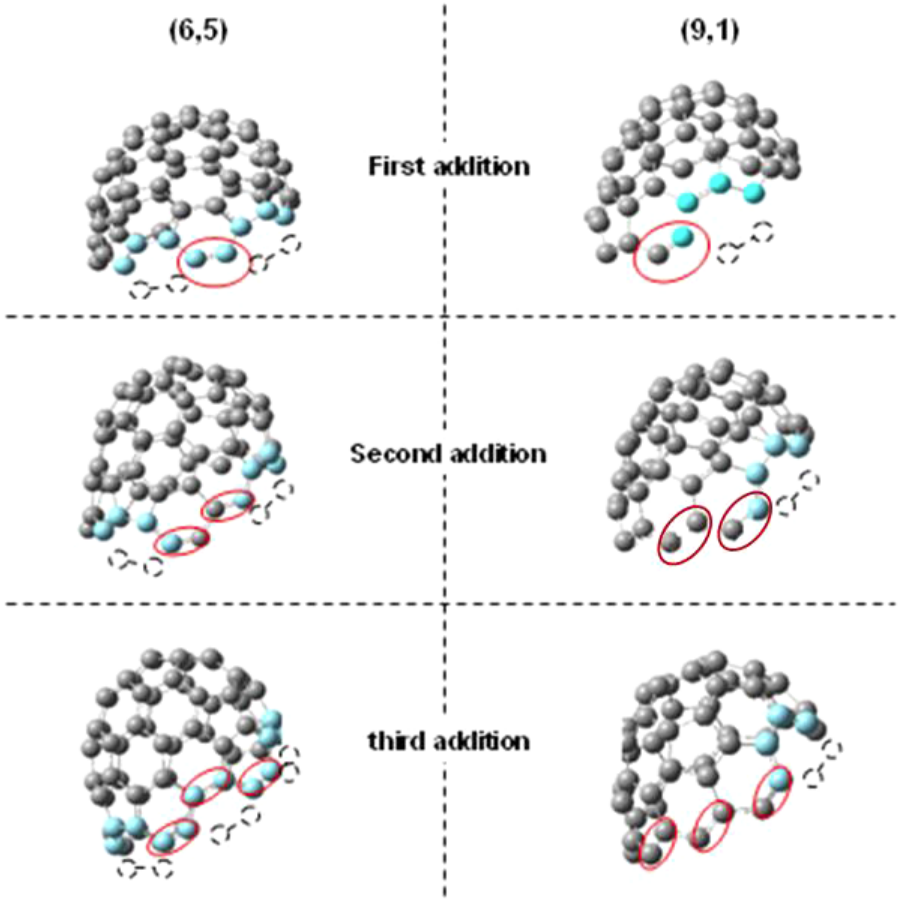


Frank 1949
"cozy corners" J Watson 1950

Source: Boris Yakobson

Earlier Theoretical Studies Predicting (*n*,*n*)>(*n*,0)

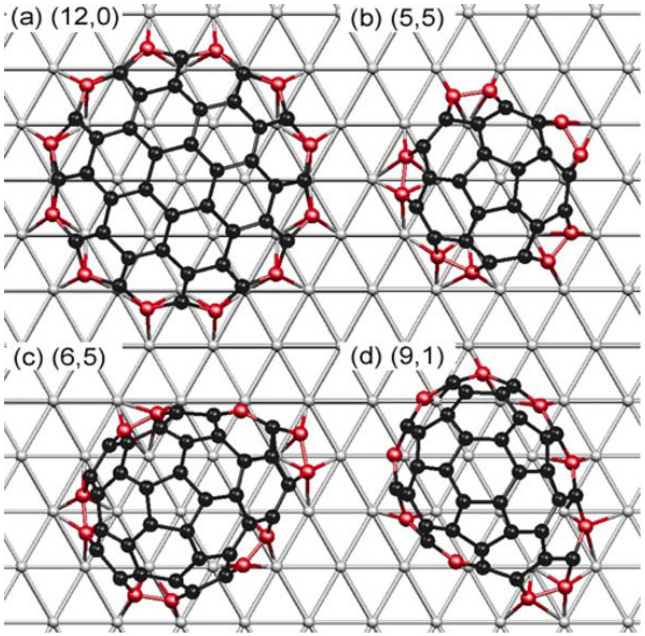
Number of cozy corners (*n*,*n*)>(*n*,0)



Red circled: previously added C_2
Blue spheres: favorable C_2 addition sites
Dashed spheres: possible new C_2s

D. A. Gomez-Gualdron, P. B. Balbuena, Nanotechnology **19**, 485604 (2008)

Edge energies (*n*,0)>(*n*,*n*)



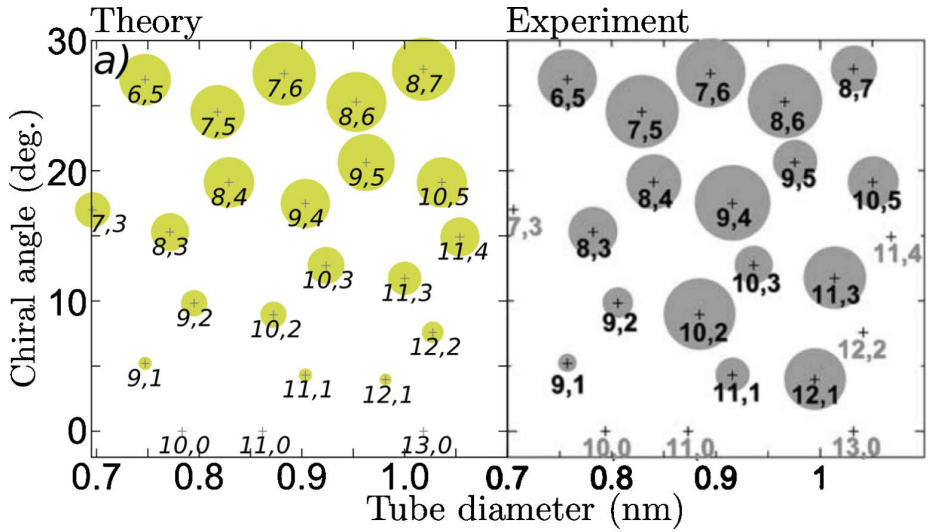
	E_{cap}	E_{CM} (excess energies/C [eV])
(12,0)	0.33	0.01 (*lower* is more stable)
(5,5)	0.42	0.00
(6,5)	0.33	0.10
(9,1)	0.35	0.22

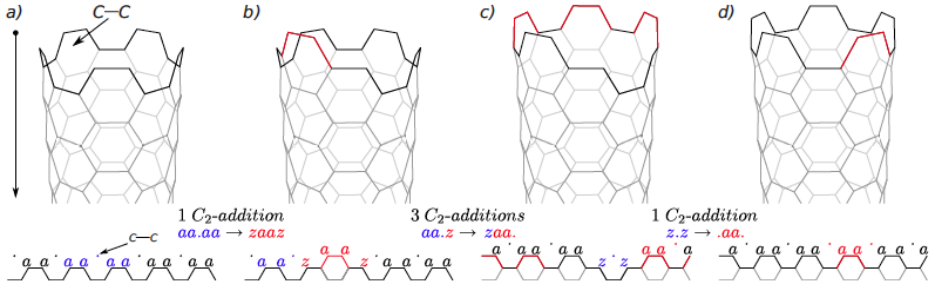
Both (9,1) and (6,5) caps are matching the Ni(111) lattice, but (6,5) has greater thermodynamic stability!

S. Reich, L. Li, J. Robertson, Chem. Phys. Lett. **421**, 469 (2006)

Later Theoretical Studies Predicting (*n*,*n*)>(*n*,0)

Number of cozy corners (*n*,*n*)>(*n*,0)
Barriers of C_2 addition (n,n)<(n,0)

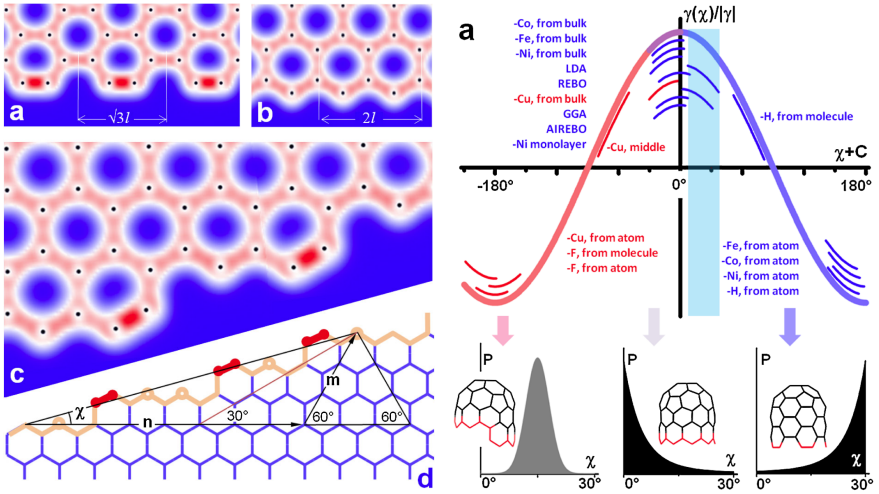




Near-armchair tubes have many addition sites, each addition in cozy corner, zero barrier addition

H. Dumlich, S. Reich, Phys. Rev. B **82**, 085421 (2010)

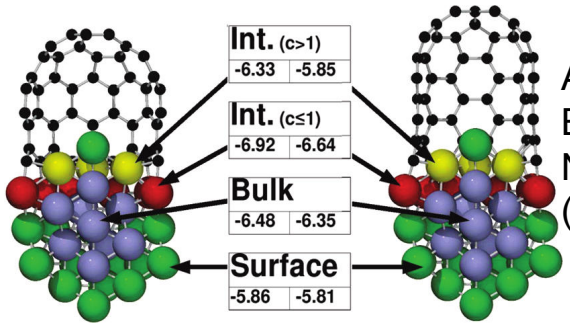
Edge energies (*n*,0)>(*n*,*n*)



Y. Liu, A. Dobrinsky, B. I. Yakobson, Phys. Rev. Lett. **105**, 235502 (2010)

Edge adhesion (*n*,0)>(*n*,*n*)

(10,0)@Ni_{55} (5,5)@Ni_{55}



A. Borjesson, K. Bolton, ACS Nano **5**, 771 (2012)

"Confirmation" of Ding/Yakobson Model by Experiment

nature materials

LETTERS

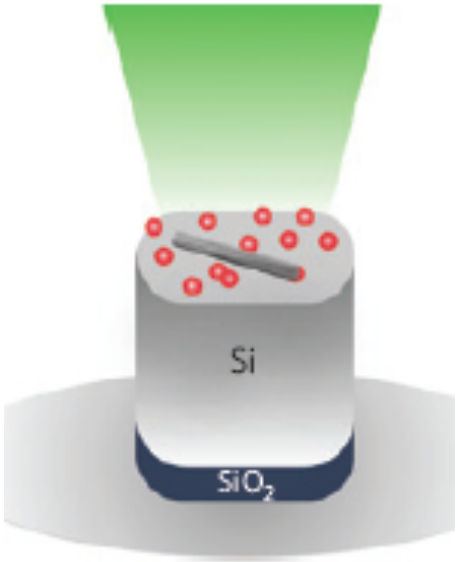
PUBLISHED ONLINE: 29 JANUARY 2012 | DOI: 10.1038/NMAT3231

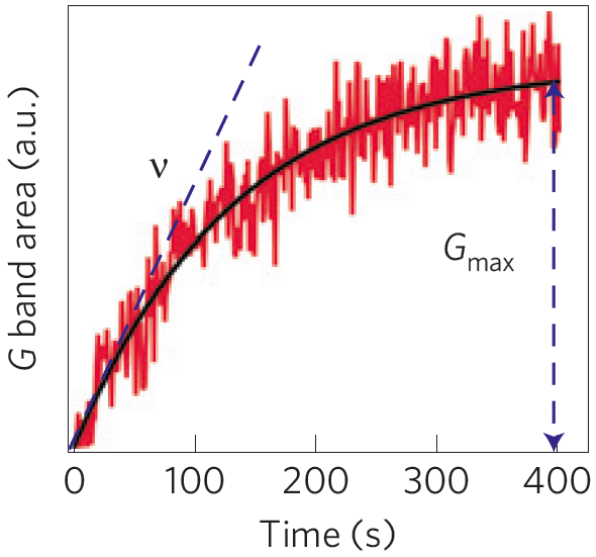
Nat. Mater. **11**, 231 (2012)

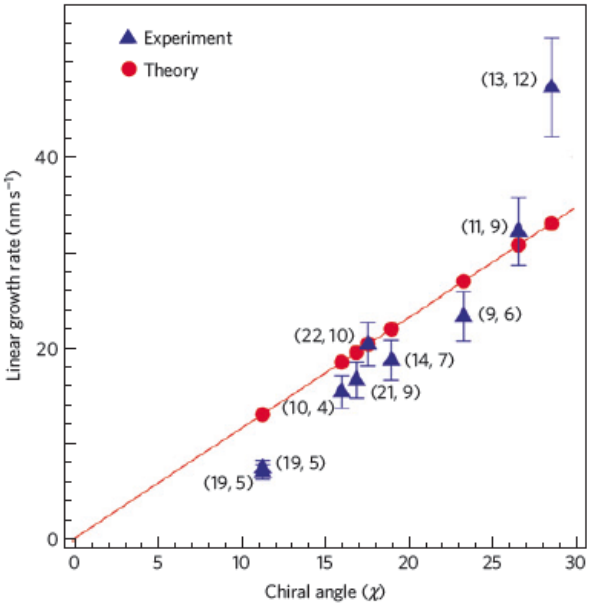
In situ evidence for chirality-dependent growth rates of individual carbon nanotubes

Rahul Rao[1*†], David Liptak[1,2], Tonya Cherukuri[1], Boris I. Yakobson[3] and Benji Maruyama[1*]

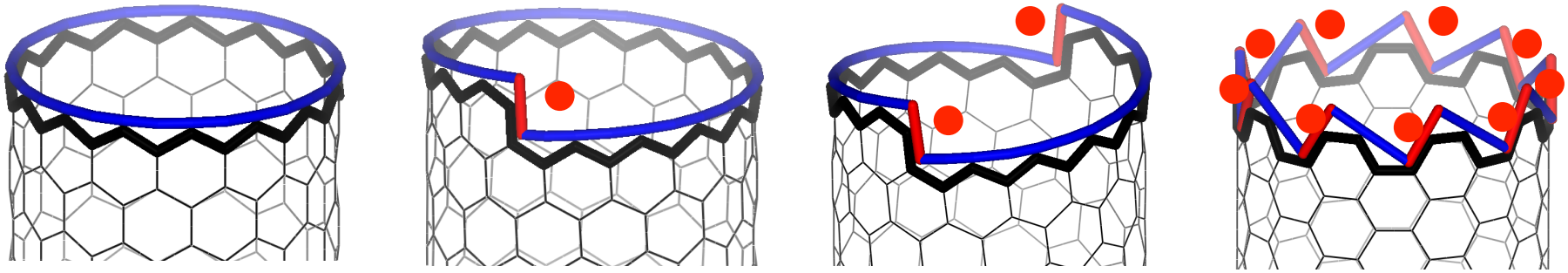
Measuring *growth rates v of individual SWCNTs* by Raman







Ding & Yacobsons Nucleation and Growth Hypothesis:



● = C_2

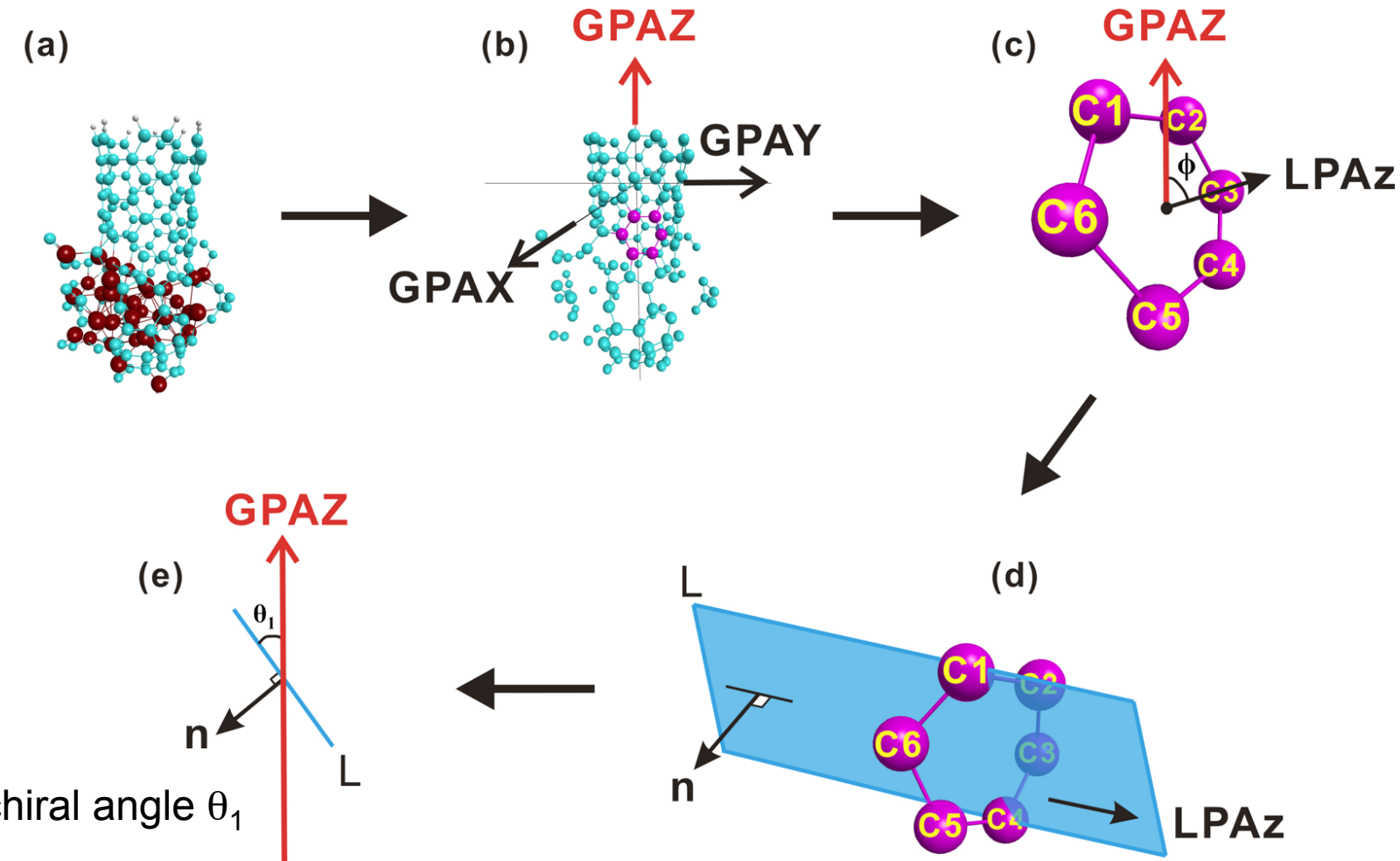
Is there anything in MD simulations, that relates to both Ding/ Yakobson's "Theory" as well as experiments?

Requirement: Need to define tube chiral angle during growth, even in the presence of defects!

Solution: Define chiral angle for each hexagon separately.

Local Chirality Index (LOCI): Definition

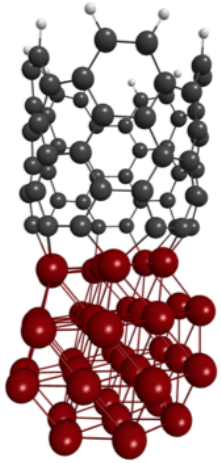
Requires: i) System's global principal axis in tube direction (GPAZ)
ii) Hexagon's local principal axis normal to hexagon plane

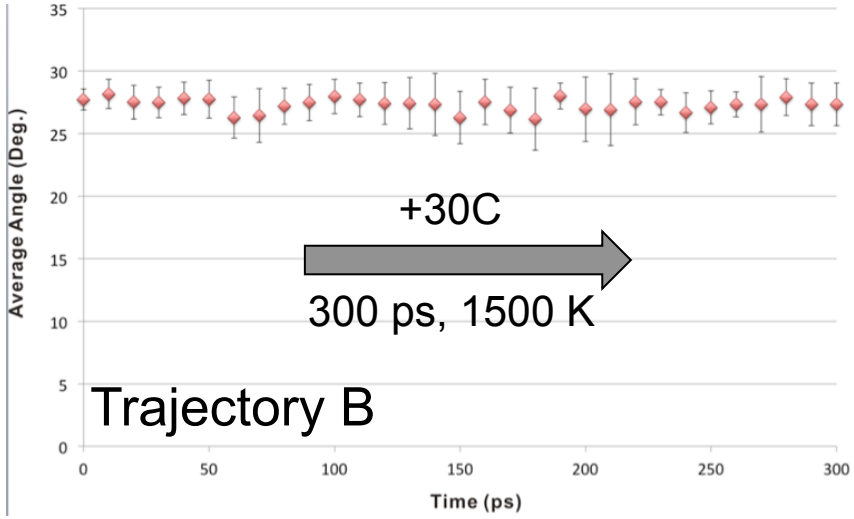


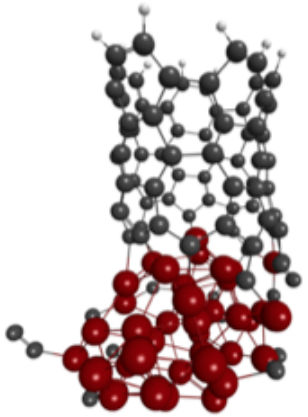
Local chiral angle θ_1

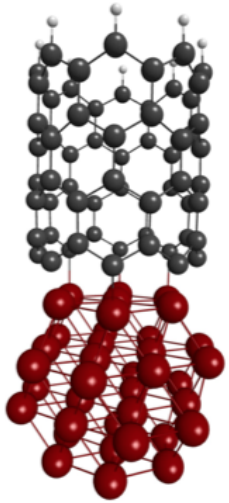
J. Kim, SI, K. Morokuma, *Phys. Rev. Lett.* **107**, 15505 (2011).

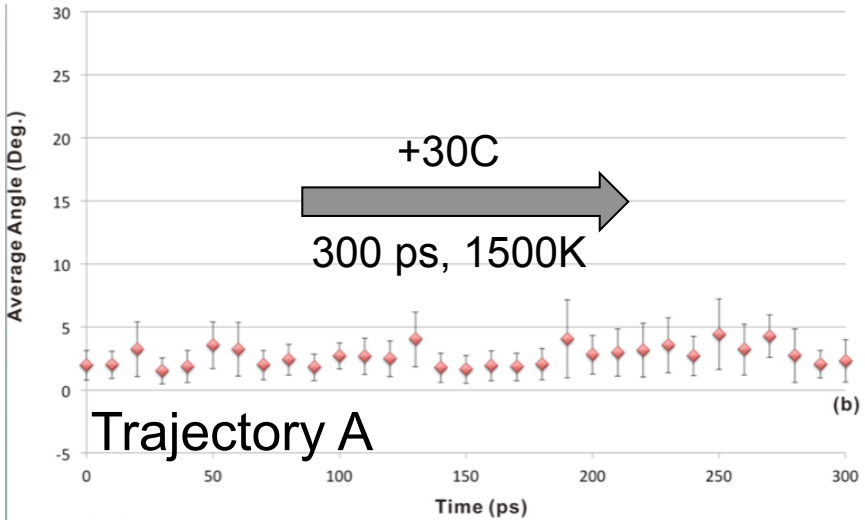
Slow simulations of (5,5) and (8,0) SWCNT growth on Fe_{38}

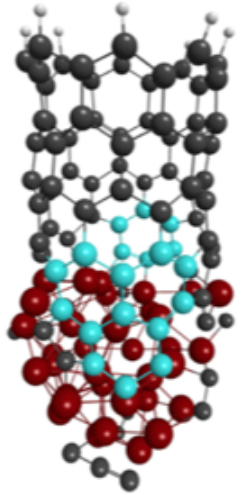








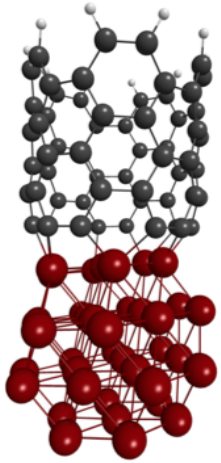


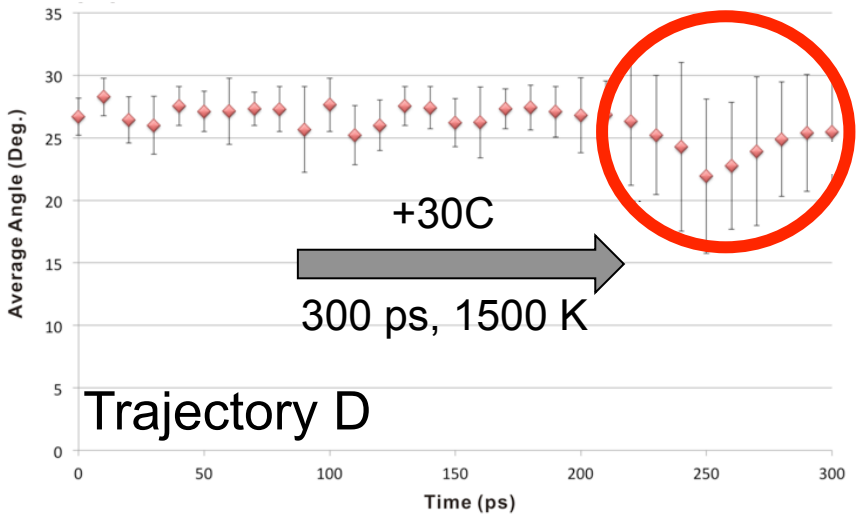


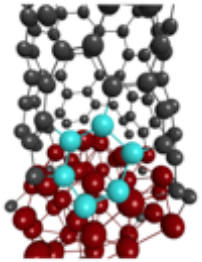
Error bars: Standard deviation σ

J. Kim, A. J. Page, SI, K. Morokuma, *J. Am. Chem. Soc.* **134**, 9311 (2012).

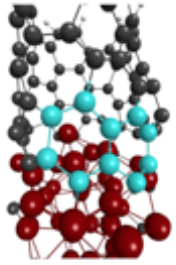
Slow simulations of (5,5) and (8,0) SWCNT growth on Fe_{38}



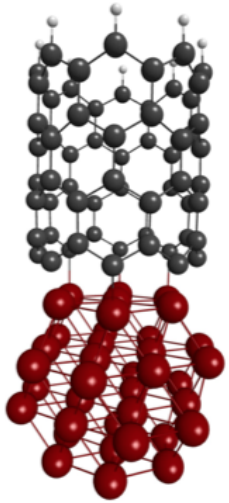


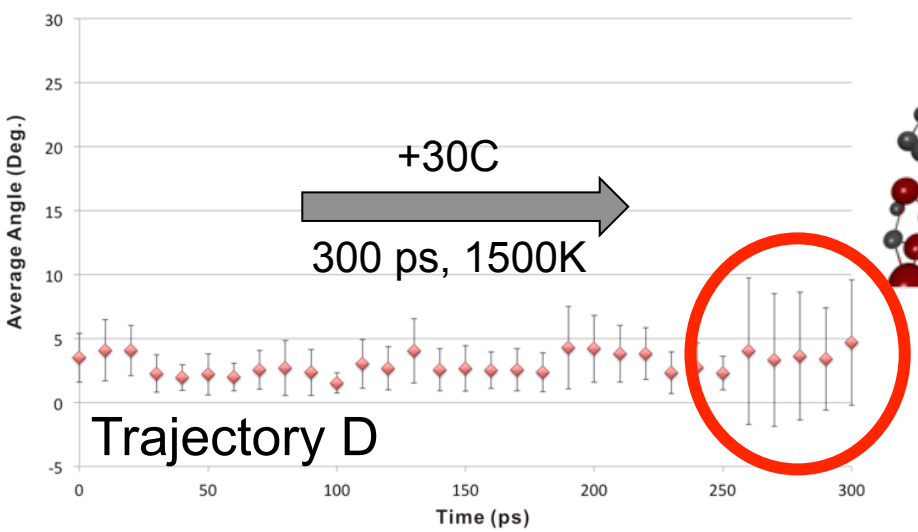


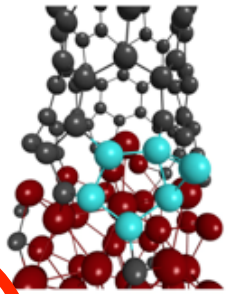
210.28 ps



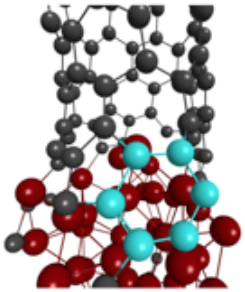
211.36 ps







250.20 ps



250.36 ps

Error bars: Standard deviation σ

J. Kim, A. J. Page, SI, K. Morokuma, *J. Am. Chem. Soc.* **134**, 9311 (2012).

Slow simulations of (5,5) and (8,0) SWCNT growth on Fe_{38}

Statistics based on 10 trajectories[a]		(5,5)	(8,0)
defect formation	pentagon formation	3.2	4.5
	heptagon formation	0.2	0.3
	hexagon → heptagon transformation	2.7	3.7
	hexagon → deformation	1.0	0.6
	hexagon → pentagon transformation	0.1	0.5
	total defects formed ($\sum_1$)	7.2	9.6
defect removal	hexagon formation	3.4	2.1
	heptagon → hexagon transformation	1.1	0.8
	pentagon → hexagon transformation	1.2	0.8
	total defects removed ($\sum_2$)	5.7	3.7
net healing ($\sum_2 - \sum_1$)		−1.5	−5.9

[a] All data are averaged over 10 trajectories following 300 ps of QM/MD simulation.

Conclusions: (5,5) grows less defects than (8,0), heals faster!

J. Kim, A. J. Page, SI, K. Morokuma, *J. Am. Chem. Soc.* **134**, 9311 (2012).

"Confirmation" of Defect/Healing Growth by Experiment

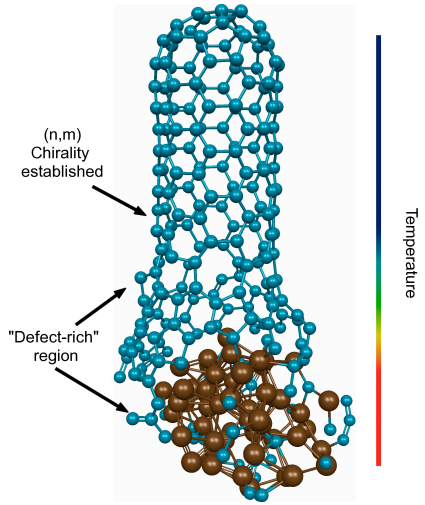
Influence of the growth conditions on the defect density of single-walled carbon nanotubes

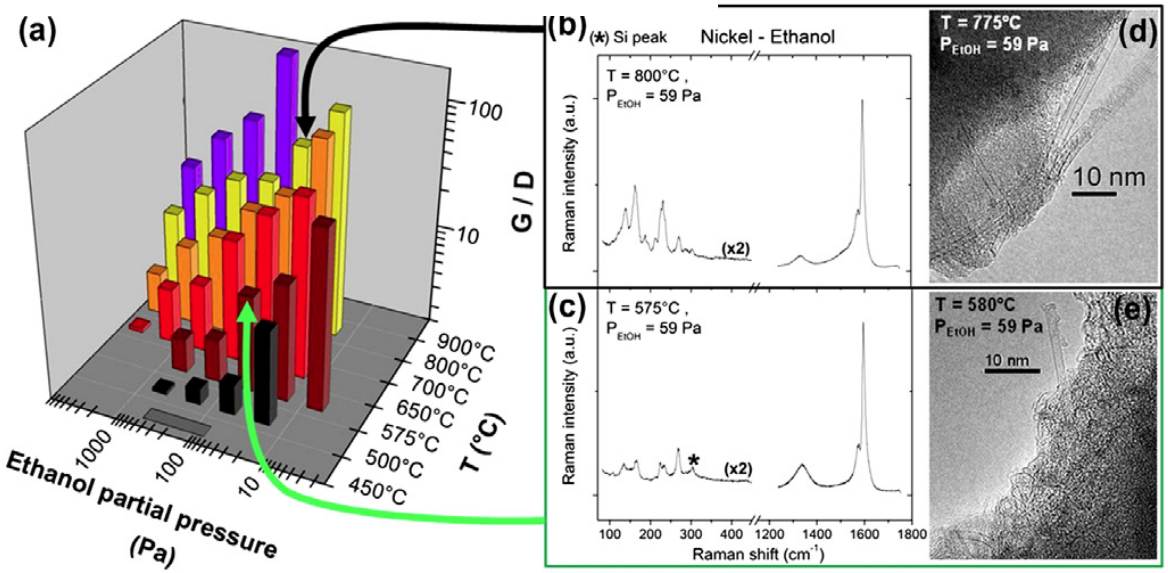
Carbon **50**, 2407 (2012)

Matthieu Picher [a,b], *Hugo Navas* [a,b], *Raul Arenal* [c,d,f], *Etienne Quesnel* [e], *Eric Anglaret* [a,b], *Vincent Jourdain* [a,b,*]

with reactive gas species). Generally speaking, these findings support that disordered structures at the nanotube rim are important intermediates of nanotube growth that should be explicitly considered in atomic-scale growth models.

cf: DFTB/MD growth model





Overview

- Overview: What are MD simulations up against?
- Density-functional tight-binding (DFTB)-based MD
- DFTB/MD Simulations: Acetylene feedstock, carbon-only feedstock, catalytic CVD, catalyst-free CVD
- Key points: What did we learn?
- Comparison with thermodynamics and selected experiments
- **What is next?**

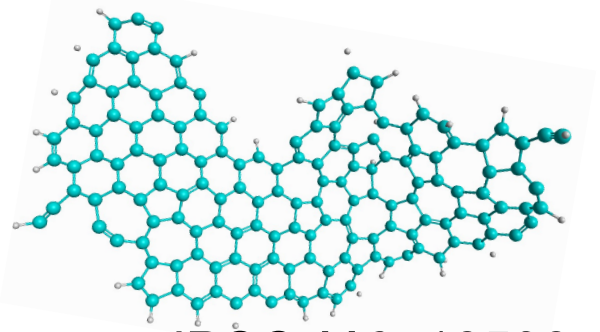
What is next?

We need to address the following urgent issues:

-Timescale problem in MD simulations, will allow to study:
- -Role of carbide formation
- -Role of defect healing
- -More precise mechanism

-Investigate possible mechanism for chirality control at time of nucleation

-Investigate role of hydrogen in greater detail



-Effect of various catalyst substrates

-Effect of etching gas [NH_3, cf S. Taubert, K. Laasonen, *JPCC* **116**, 18538 (2012)]

-Effect of water H_2O