Growth Modes and Chiral Selectivity of Single Wall Carbon Nanotubes

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What I'm going to talk about ….

A number of very promising and exciting paper have been published concerning SWNT growth, chiral selectivity and possible applications …

week ending
16 MAY 2008

Preferential Growth of Single-Walled Carbon Nanotubes with Metallic Conductivity

Avetik R. Harutyunyan,[1]* Gugang Chen,[1] Tereza M. Paronyan,[2] Elena M. Pigos,[1] Oleg A. Kuznetsov,[1] Kapila Hewaparakrama,[2] Seung Min Kim,[3,4] Dmitri Zakharov,[4] Eric A. Stach,[3,4] Gamini U. Sumanasekera[2]

Science 2009

PHYSICAL

PRL 100, 195502 (2008)

Reduced Carbon Solubility in Fe Nanoclus… of Single-Walled Carbon

Chirality-specific growth of single-walled carbon nanotubes on solid alloy catalysts

Nature 2014

…Xiao Wang[1], Daqi Zhang[1], Juan Yang[1], Da Luo[1], Ziwei Xu[2], Jiake Wei[3], Jian-Qiang Wang[4], Zhi Xu[3], Fei Peng[1], …Yilun Li[1], Meihui Li[1], Xuedong Bai[3], Feng Ding[2] & Yan Li[1]

Arrays of horizontal carbon nanotubes of controlled chirality grown using designed catalysts

Nature 2017

Shuchen Zhang[1]*, Lixing Kang[1,2]*, Xiao Wang[3,4], Lianming Tong[1], Liangwei Yang[1], Zequn Wang[1], Kuo Qi[5], Shibin Deng[1], Qingwen Li[2], Xuedong Bai[5], Feng Ding[3,4,6] & Jin Zhang[1]

What I'm **NOT** going to talk about ….

A number of very promising and exciting paper have been published concerning SWNT growth, chiral selectivity and possible applications …

Too difficult for the moment …

Focus on simpler, easier to reproduce results

Close interaction between experiments
and theory / computer simulations

Arrays of horizontal carbon nanotubes of controlled chirality grown using designed catalysts Nature 2017

Shuchen Zhang[1]*, Lixing Kang[1,2]*, Xiao Wang[3,4], Lianming Tong[1], Liangwei Yang[1], Zequn Wang[1], Kuo Qi[5], Shibin Deng[1], Qingwen Li[2], Xuedong Bai[5], Feng Ding[3,4,6] & Jin Zhang[1]

Understanding CVD synthesis of SWNT

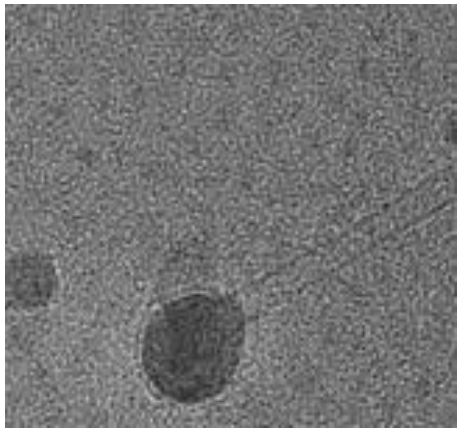
… using « simple » catalysts (Ni, Co, Fe)

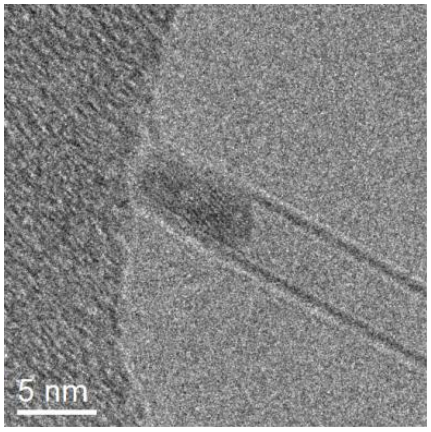
State of catalyst nanoparticle under CVD conditions

- Thermodynamics of isolated NPs + C / Phase diagrams / Nucleation

Tangential and perpendicular growth modes

- Understand why ? Can we control them ?
- Selectivity In perpendicular mode
- Role of tube/NP lateral interaction in tangential mode



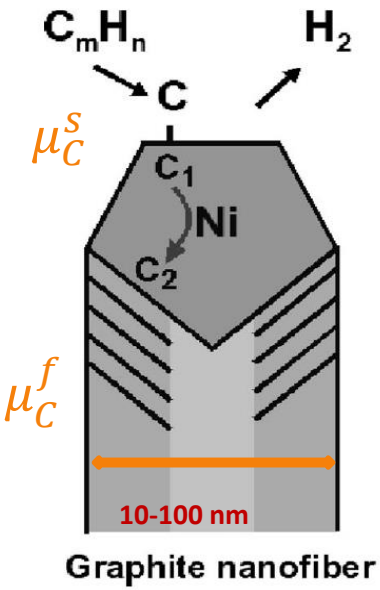


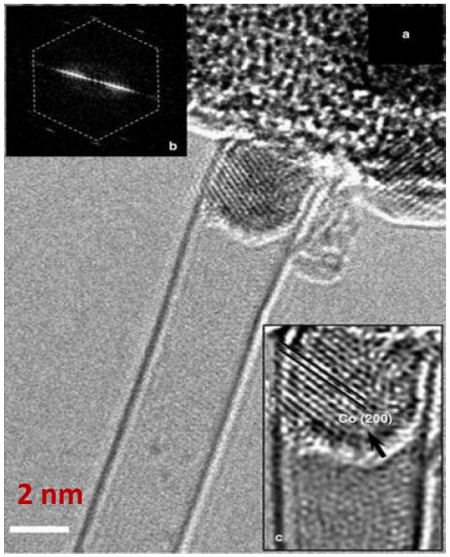
Perpendicular mode : $R_d = {}^{D_{Tube}}/_{D_{NP}} < 1$ Tangential mode : $R_d = {}^{D_{Tube}}/_{D_{NP}} \sim 1$

Carbon fiber versus SWNT growth : nanoscale matters !

Growth results from gradient of μ_C

- μ_C^S is imposed on NP surface by thermochemistry of feedstock decomposition
- Once a tube is formed, it acts as a carbon sink, hence μ_C^f is fixed and lower than μ_C^S





Zhu *et al.*, Small 2005

- Smaller NPs and tubes (1-4 nm)
- Experimental investigation are difficult
- **Surface and interface become important**
- **Computer simulations are essential to understand mechanisms**

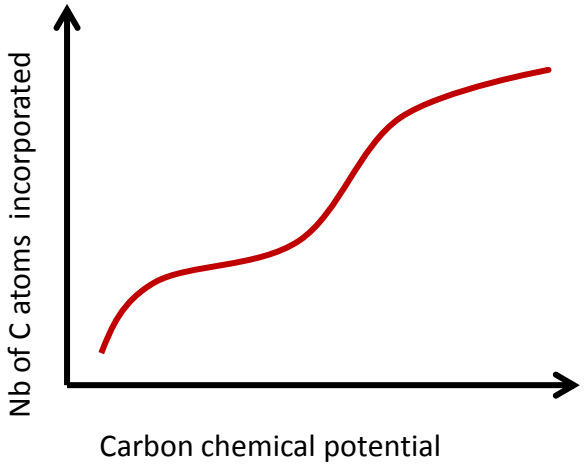
Snoeck *et al. J. Catal.* 1997, *169*, 240–249.
Abild-Pedersen *et al. Phys. A. B* 2006, *73*, 1–13.

Computer simulation tools

Parameterized **tight binding model** 4th moment approximation for **Nickel + Carbon,** now also for Platinum + Carbon

Amara *et al.* Phys. Rev. B 73, 113404 (2006)
Phys. Rev. B 79, 014109 (2009)
J. H. Los *et al.* Phys. Rev. B 84, 085455 (2011)

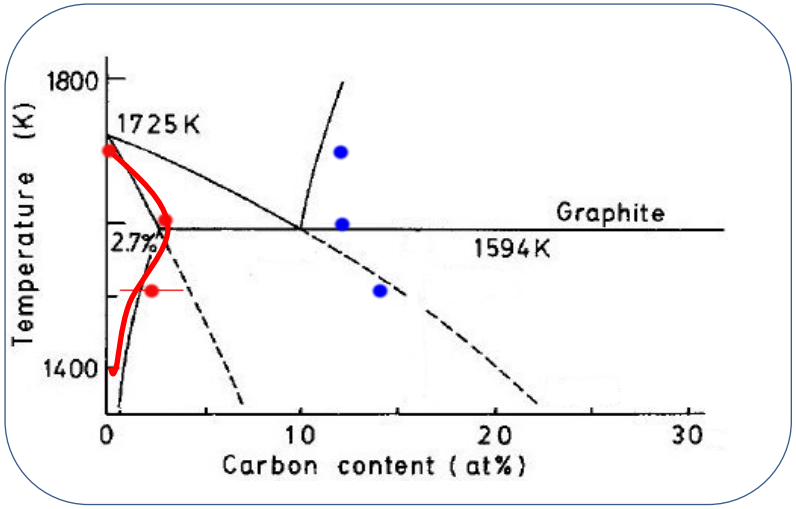
Grand Canonical Monte Carlo simulations
to focus on thermodynamics



Surface energy
Ni (111) : 1.35 J/m^2
Ni (100) : 1.64 J/m^2

Ni clusters
FCC 201 atoms : 2.10 J/m^2
FCC 405 atoms : 2.05 J/m^2
Liquid 405 atoms : 2.0 – 1.0 J/m^2
(depending on C fraction)

Bulk solubility in agreement with experiments



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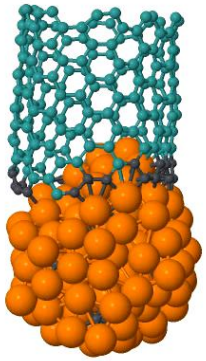

Amara *et al.* Phys. Rev. B 73, 113404 (2006)
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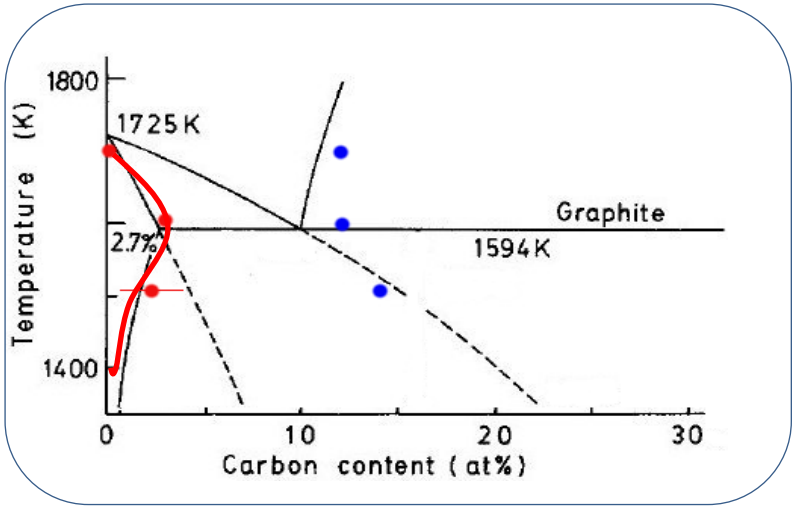
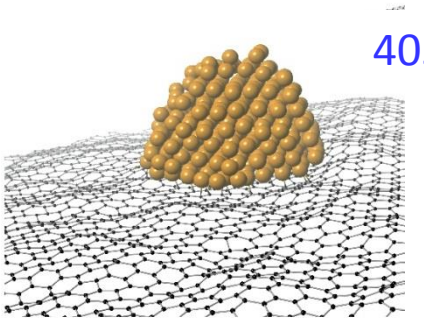


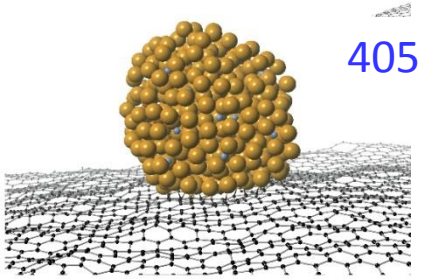
Wetting of Ni+C nanoparticles on graphene

(a)



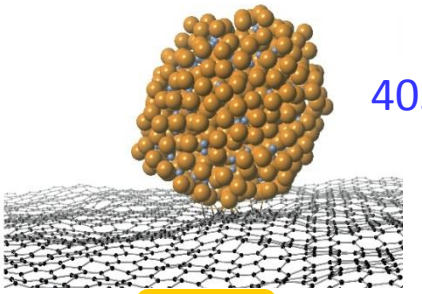
405 Ni

(b)



405 Ni +11 % C

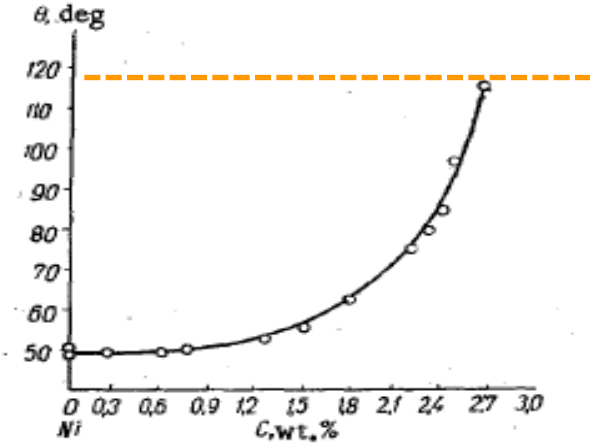
(c)

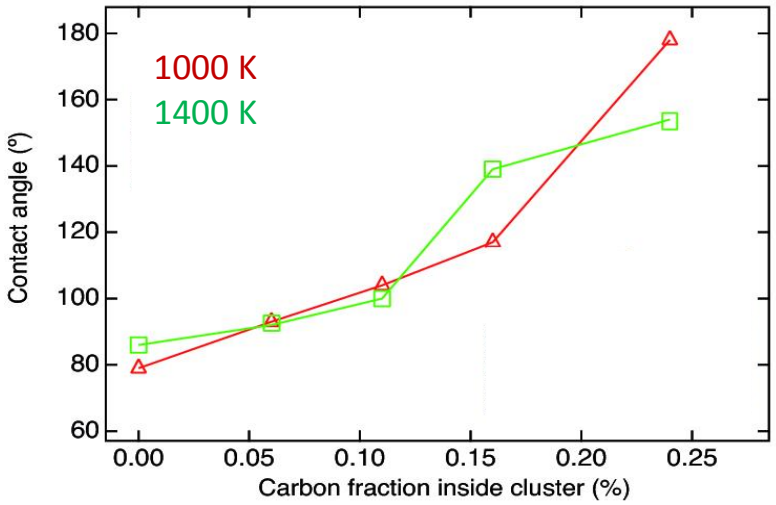


405 Ni + 24 % C

1400 K

Bulk **Ni , Fe, Co** : Naidich et al. 1971



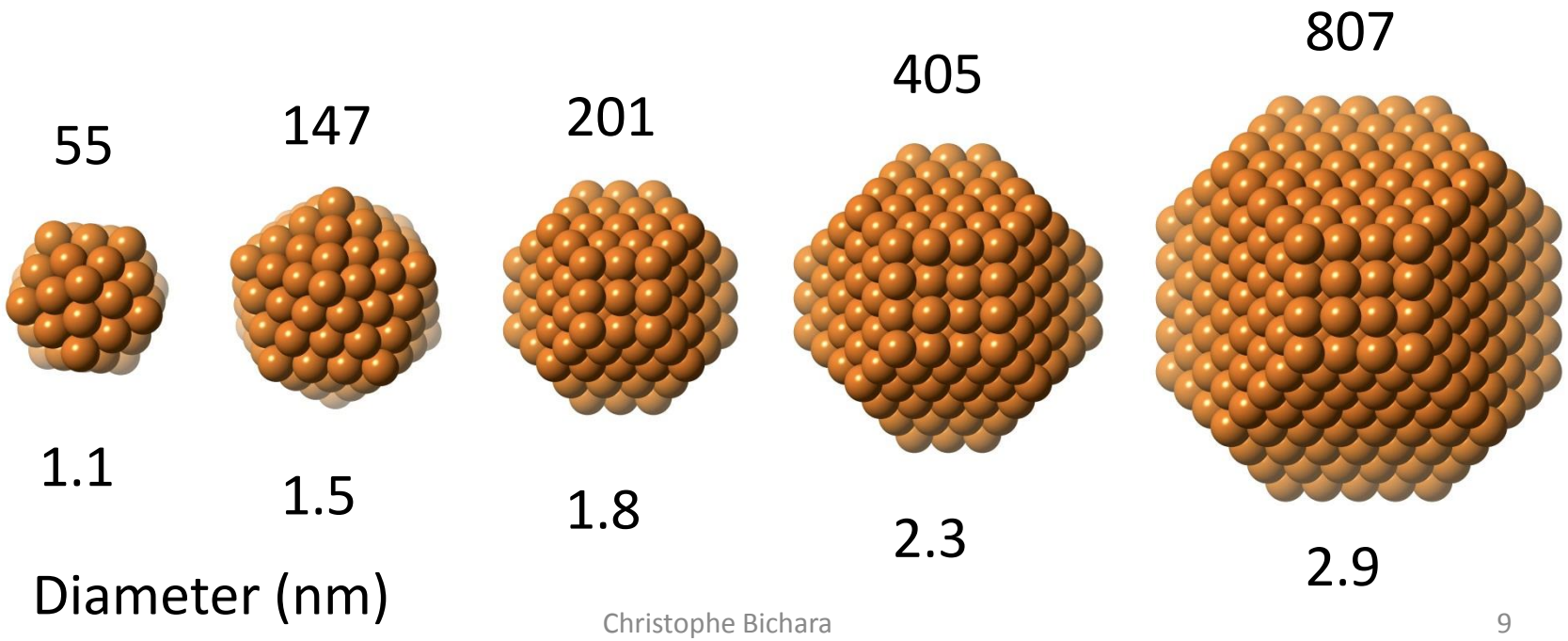


Contact angle increases (tendency to dewet graphene layer) for carbon rich Ni nanoparticles

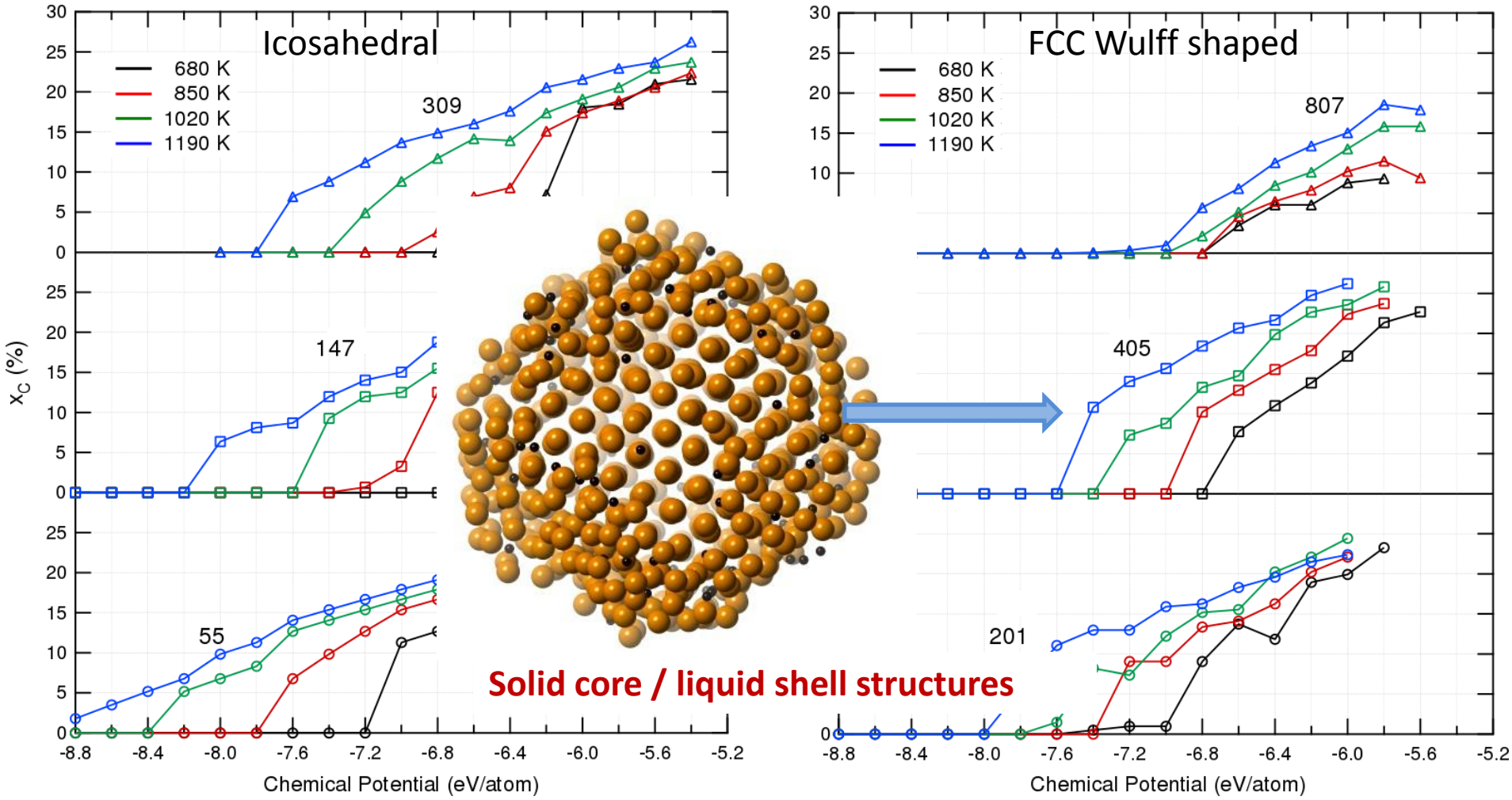
Interaction of C with Nickel nanoparticles

Calculate « sorption » isotherms:

- Mole fraction of carbon inside Ni NP, as a function of C chemical pot.
- At different temperatures
- For different nanoparticle sizes



Carbon solubility in Nickel Nanoparticles

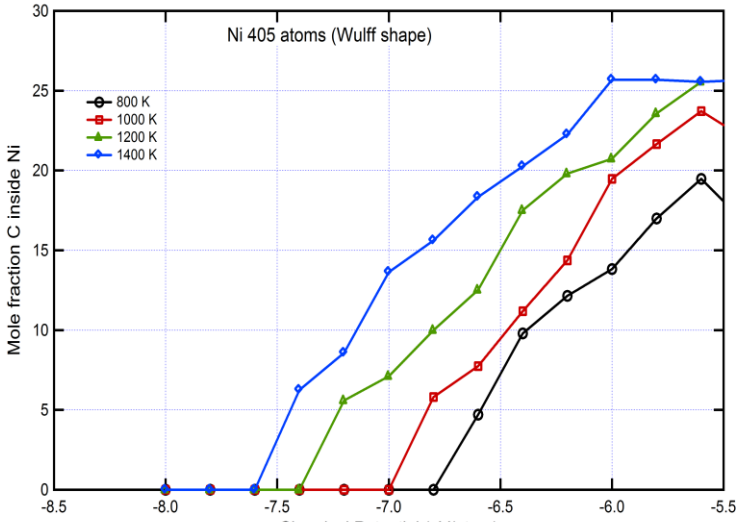


Grand Canonical Monte Carlo calculations

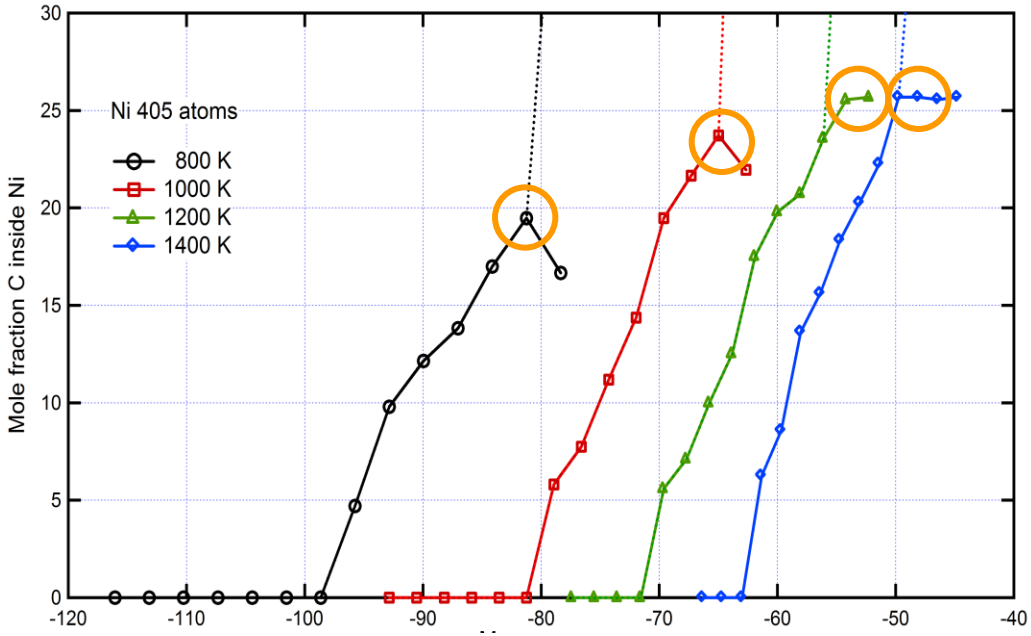
Diarra Phys. Stat. Sol. 2012; PRL 2012

Carbon solubility in nanoparticles: effect of temperature

Same data, plotted as function of :



… Carbon chemical potential μ_C



μ_C/ kT ~ Ln (Pressure), if ideal gas

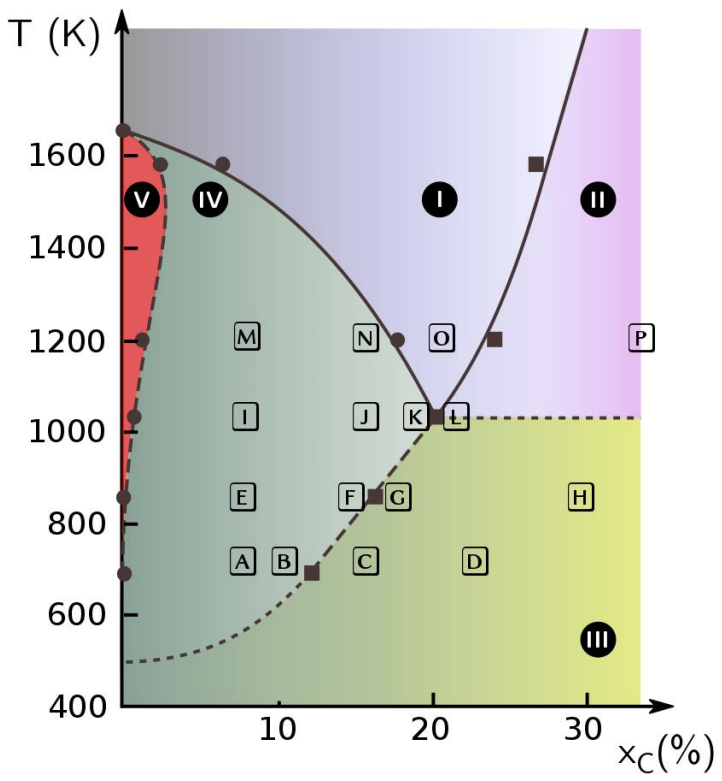
Solubility limits ◯ increase with T

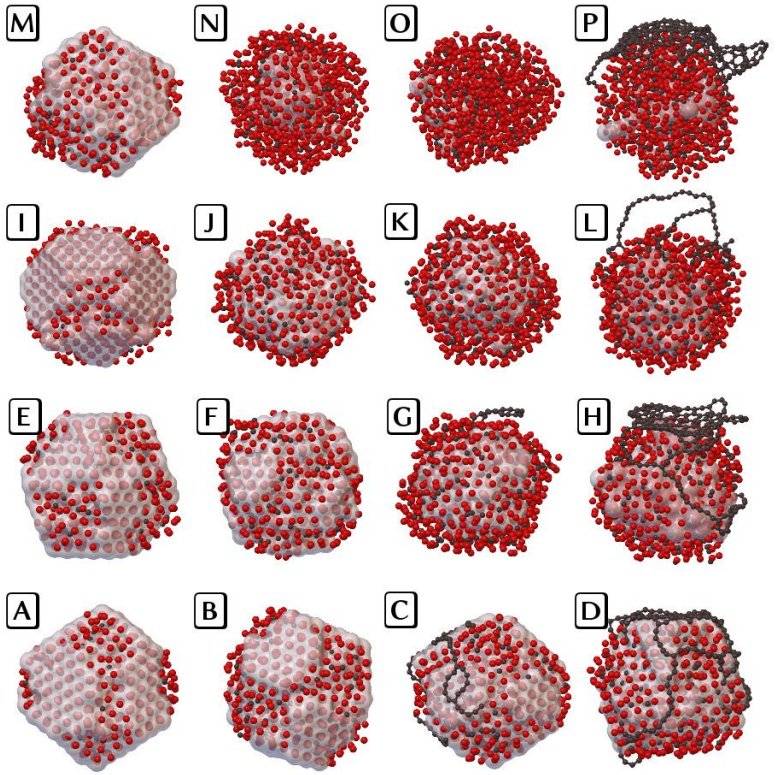
Pressure to reach this solubility limit also increases with T

Explains **pressure threshold** for nucleation of SWNT

- Cf : in situ Raman during SWNT growth
  M. Picher *et al.* Nano Letters (2009), 9 (2), 542–547

Phase diagram for Ni_{807} + C nanoparticle





I : homogenous liquid

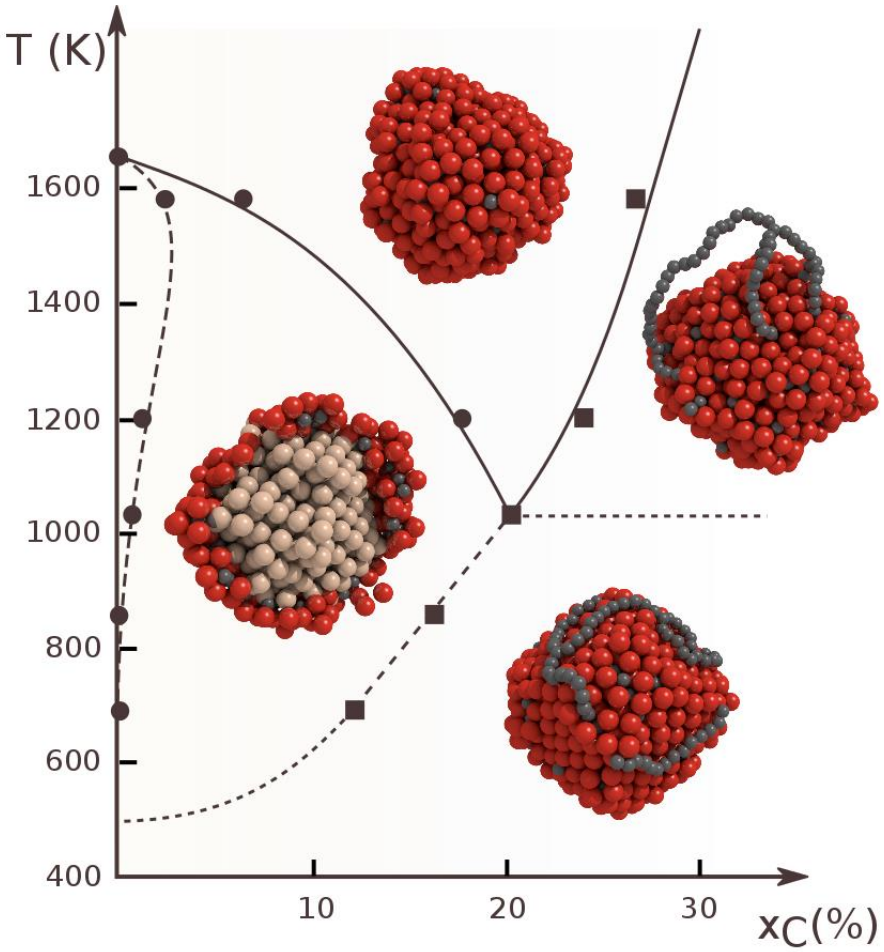
II : carbon segregation from homogenous liquid

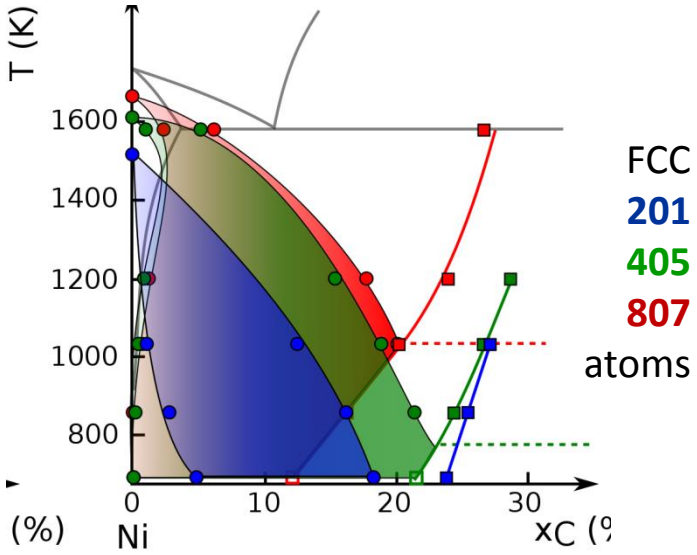
III : carbon segregation from core / shell NP

IV : solid core / liquid shell … different from bulk !

V : solid solution

Phase diagram for Ni_{807} + C nanoparticle

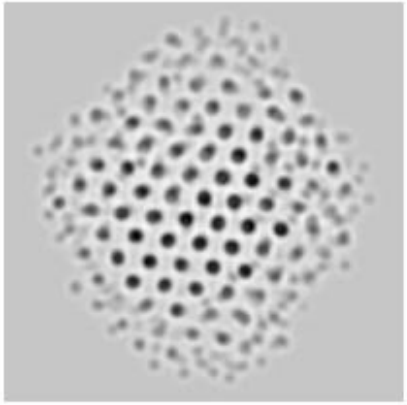




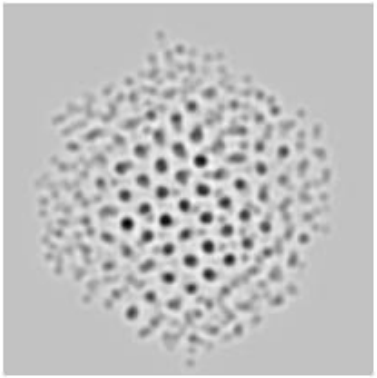
- Core / shell stucture instead of liquid-solid coexistence
- Much deeper eutectic point
- (1000 K ~ 60% Tm of pure Ni)
- Carbon segregation from crystalline NPs only at very low T
  (850 K ~ 50% Tm of pure Ni)

Magnin PRL 2015

How would these NPs look like in a TEM ?



Config F: ~ 1 disordered layer



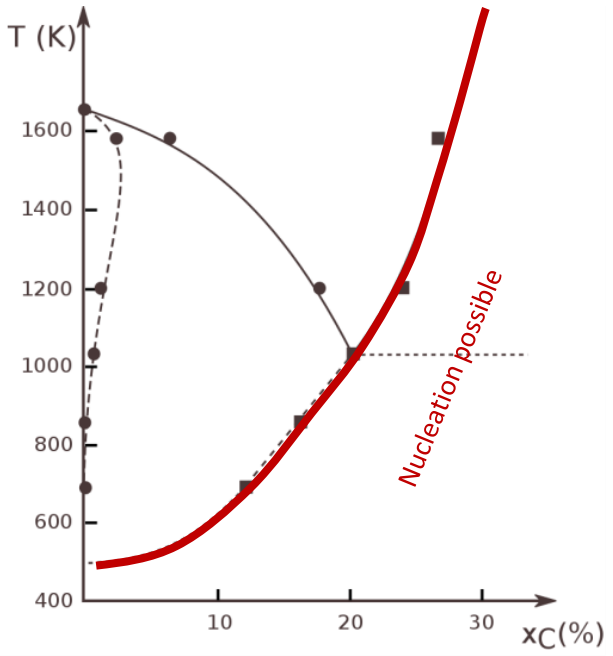
Config K: ~ 2/3 disordered layers

Images calculated on one single configuration, with parameters for a state of art TEM.

In solid core / disordered shell structures, the outer shell is hardly seen,

NPs appear smaller and crystalline

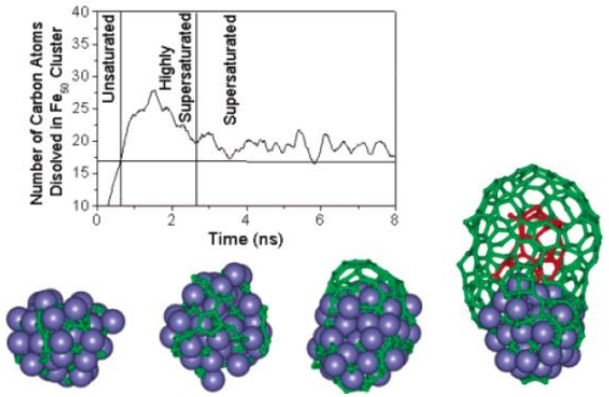
Relevance to SWNT synthesis … **nucleation**



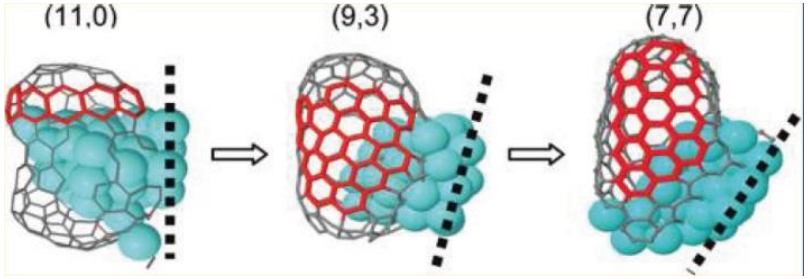
Nucleation possible beyond saturation line

Either on a liquid NP, saturated with C, or on essentially solid NP, with a disordered surface

Nucleation has been studied by other groups:



Feng Ding J. Phys. Chem B 2004

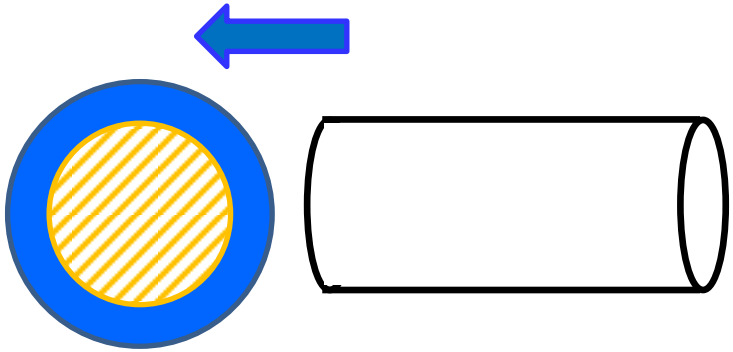


Neyts JACS 2011

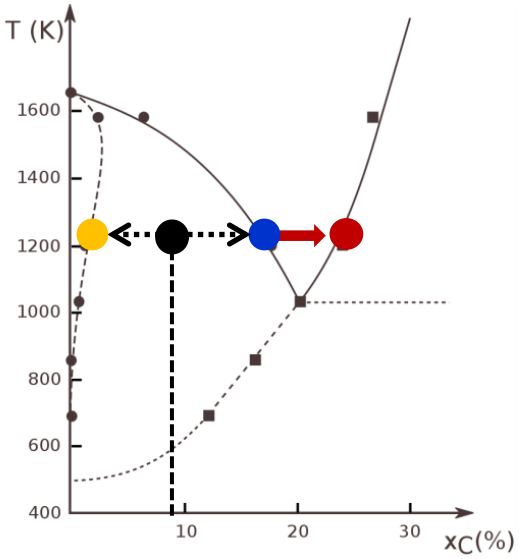
Chirality control at nucleation step ?
Highly debated …

During **growth** Nanoparticle is in contact with SWNT

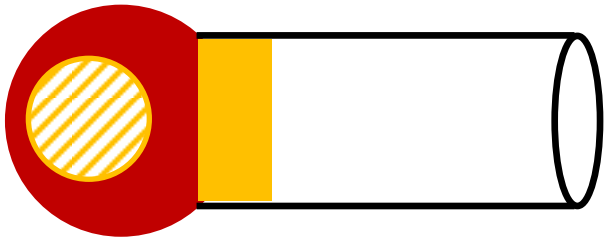
Isolated NP is Core / Shell



Contact of Nanoparticle with Nanotube



% C in nanoparticle should shift to **saturation line**
If possible (size, state of NP) Ni wets inner Nanotube

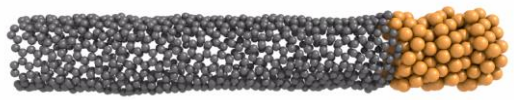


Complex thermodynamic system
requires computer simulation …

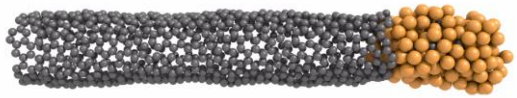
Catalyst / tube Interfacial properties

Wetting of **Nickel** on C sp^2 wall strongly depends on %C dissolved

0 % C : Nickel wets the tube



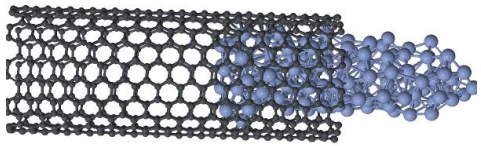
10 % C : partial wetting



23 % C : complete dewetting

Different behavior for **Platinum**

0 % C : Pt does not wet the tube



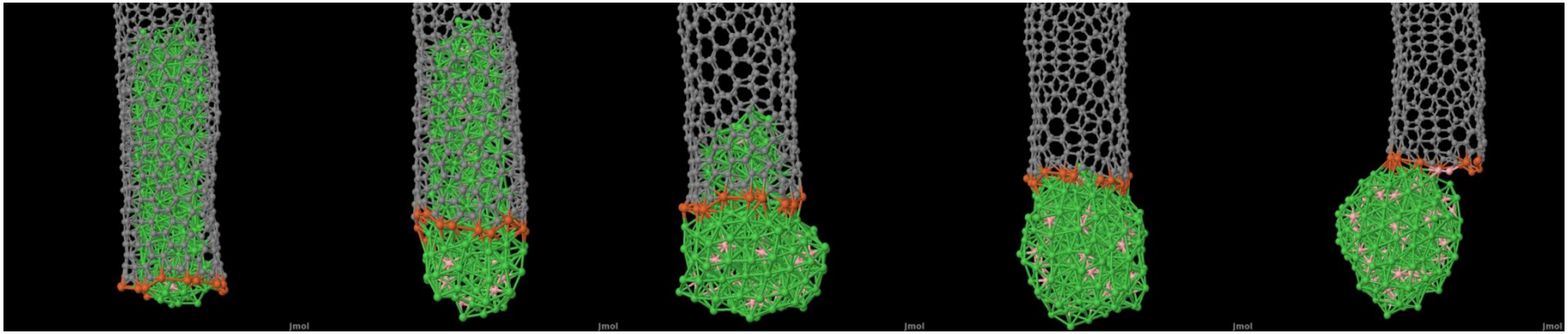
Different wetting properties will lead to different **growth modes** $R_d = {}^{D_{Tube}}/_{D_{NP}}$

that depend on

- Nature of **catalyst** :Ni, Fe, Co … Pt, CoW, Mo_2C, WC ?
- Nature of C **precursor** (CO vs CH_4)

Fixed chirality, different carbon fractions

Tube chirality (10, 7)



0 % C | 6 % C | 12 % C | 18 % C | 24 % C

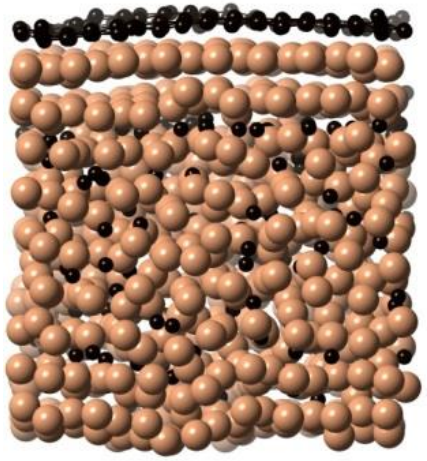
Tendency for dissolved C atoms (pink) to avoid tube lip and inner space

Similar to what we saw for graphene on Ni : ***Depletion of C in Ni subsurface, once graphene layer is formed***

Unexpected behavior of carbon metal interfaces with Ni (Co, Fe)

Subsurface interstitials most favorable to incorporate individual Carbon atoms on free Ni surface

BUT

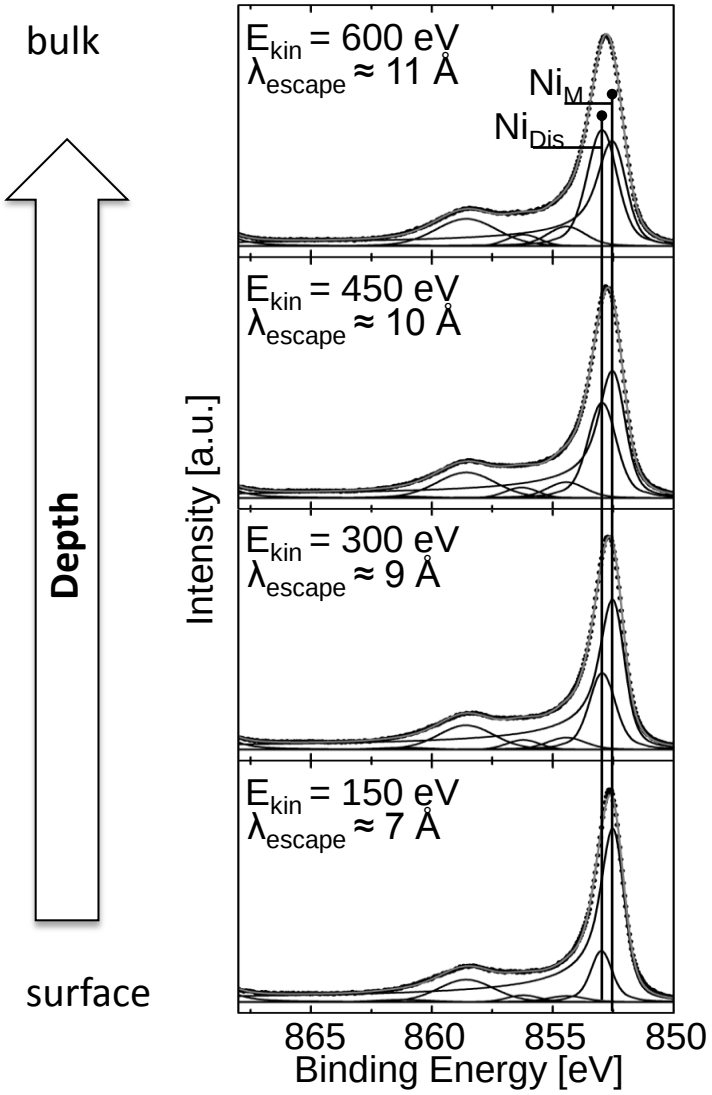


Depletion of dissolved C close to graphene wall …

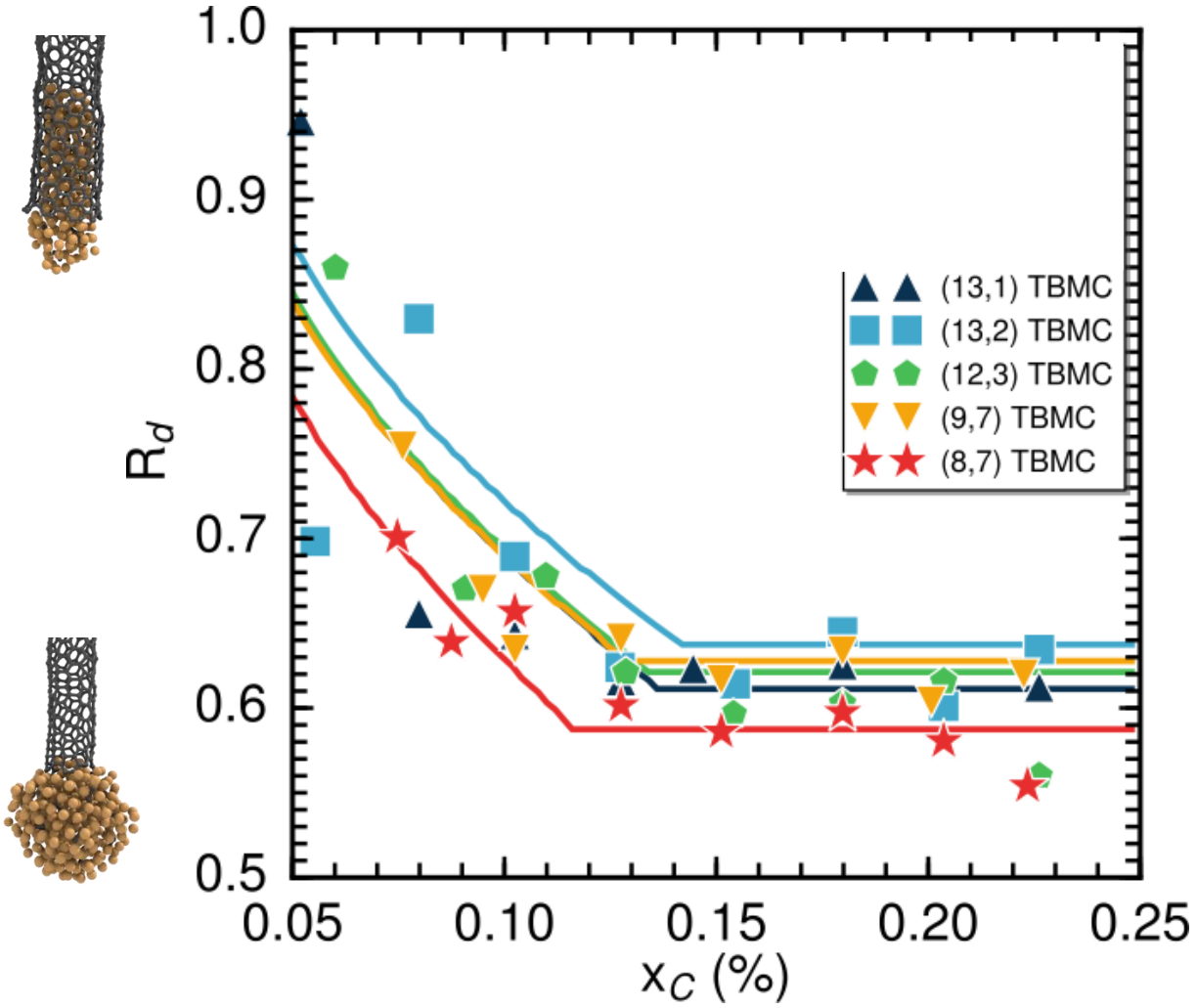
confirmed by *in situ* XPS

Weatherup *et al.* JACS **136**, 13698 (2014)

Benayad *et al. J. Phys. Chem. C* ***117***, 4727 (2013)



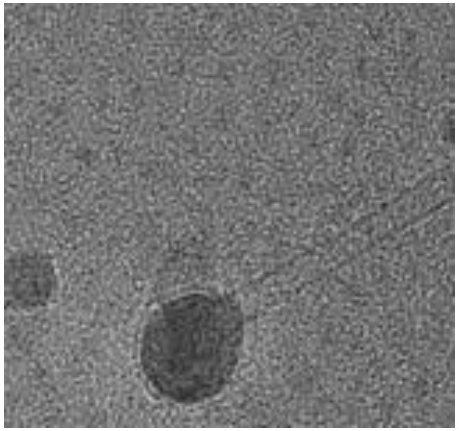
Quantitative analysis of Monte Carlo data: SWNT/NP diameter ratio

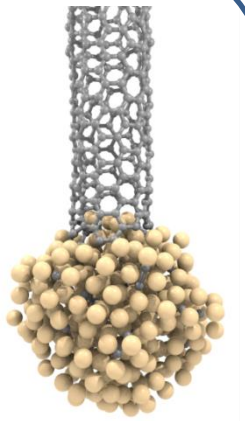


Aspect ratio $R_d = {}^{D_{Tube}}/_{D_{NP}}$ depends : strongly on %C dissolved

weakly on tube chirality

TEM observation of different growth modes

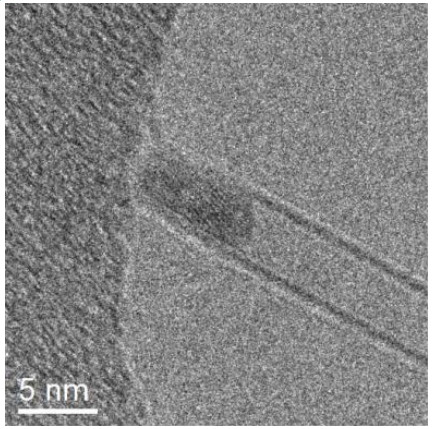


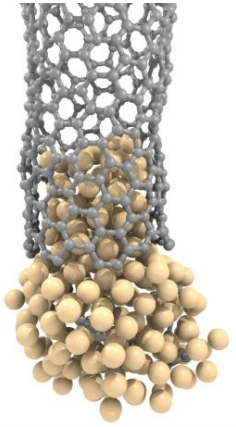


Perpendicular mode

$$R_d = {}^{D_{Tube}}/_{D_{NP}} < 1$$

Line contact between Tube and NP





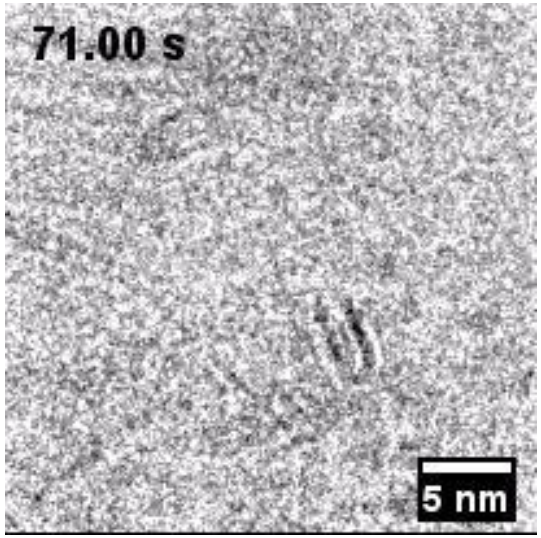
Tangential mode

$$R_d = {}^{D_{Tube}}/_{D_{NP}} \sim 1$$

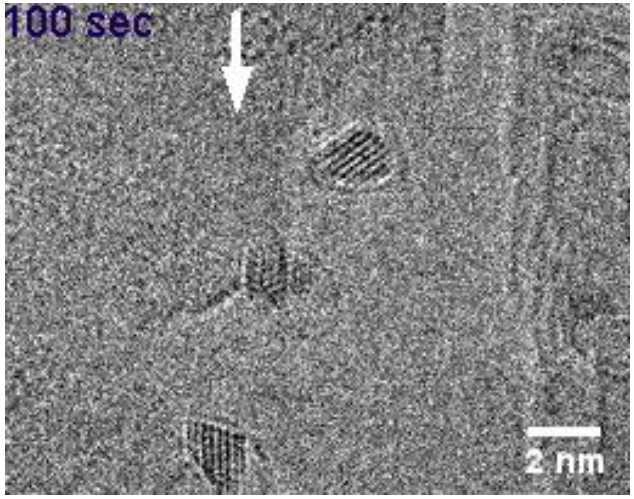
Surface contact between tube and NP

TEM performed **after synthesis** (Maoshuai He, Aalto Univ. + LEM/ONERA)

In situ TEM observation of different growth modes



Co on MgO + EtOH – 700°C



Pt on MgO + EtOH – 550°C

In situ TEM during growth : Jens Kling, Lili Zhang, J. B. Wagner (DTU Denmark)

Can we control SWNT growth modes ?

Idea is to control metal – carbon interfacial properties. How can this be achieved ?

1. Use surfactant
   - Has been done : Windle + others : adding Sulfur or …

2. Temperature changes during growth
   - Yao et al. : Nat. Mat. 2007; J. Phys. Chem. C 2009

3. **Control carbon fraction in catalyst**
   - Experimentally : icosahedral versus f.c.c. Au nanoparticles
     He *et al.*, *Nanoscale* **2015**, *7*, 20284–20289.
   - Numerically, thanks to our Tight Binding model
     Aguiar et al. , submitted to Carbon (arXiv:1702.06742)

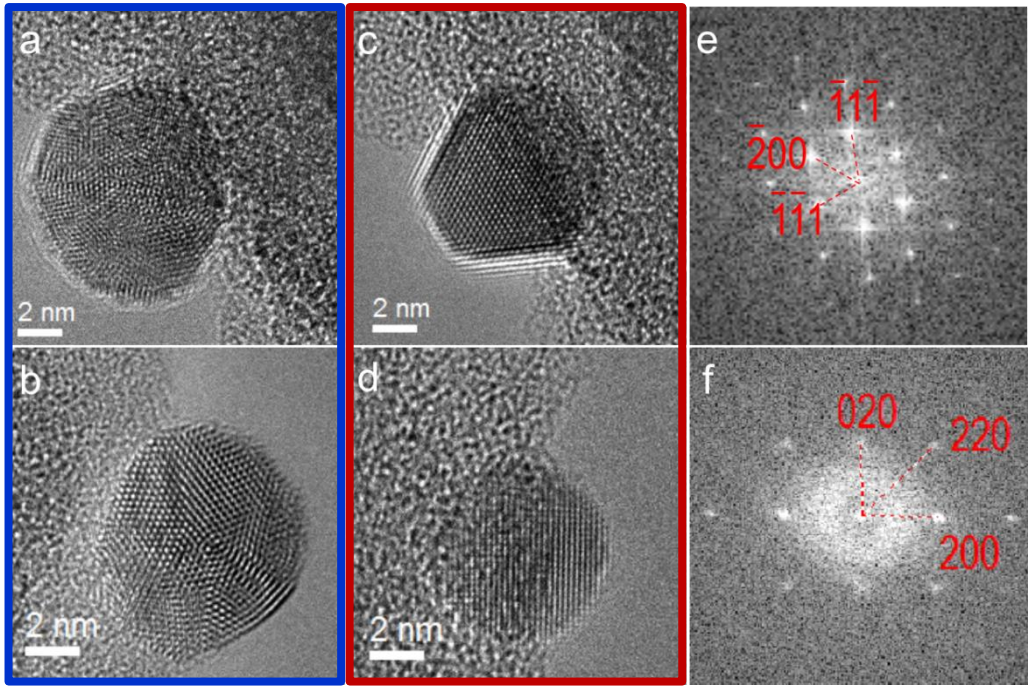
4. Control via gas phase : ambient, feedstock
   - Chenguang Lu and Jie Liu; J. Phys. Chem B 2006; Thurakitseree ACS Nano (2011)
   - Alternating CH_4 and CO feedstocks

5. Use bimetallic catalyst ?
   - Not very clear yet

CVD on Au : growth when FCC, no growth when icosahedral

Expt^{al} work : Maoshuai He, E. Kauppinen + Aalto group, Annick Loiseau

As prepared Au NPs are Icosahedral

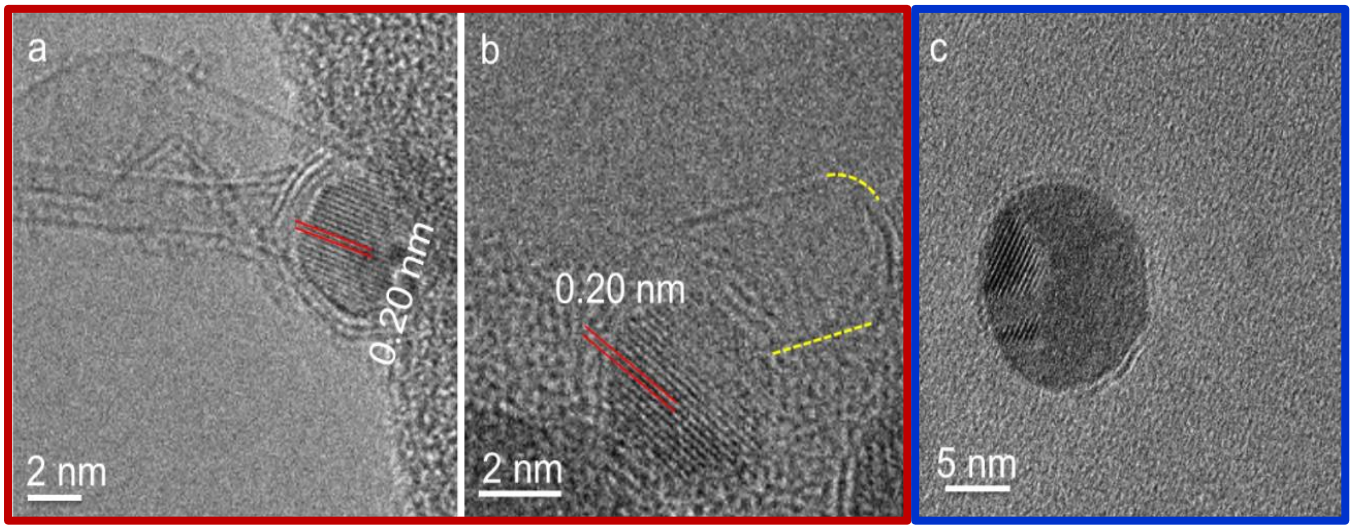


After 2h @ 800°C in air

- some NPs transform into FCC (top)
- some remain Icosahedral (bottom)

CVD on Au : growth when FCC, no growth when icosahedral

CVD growth with CO at 1 atm and T ranging from 600°C to 800°C



800 C 600 C

FCC Au nanoparticles promote SWNT growth

Icosahedral NPs are encapsulated by C and don't grow tubes

Can we explain why ?

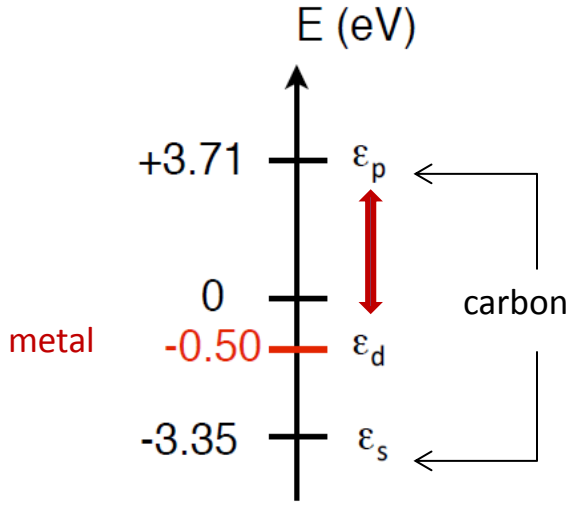
Change C solubility in Nanoparticle

Thanks to Tight Binding model, it's easy to change heat of C solution in metal …

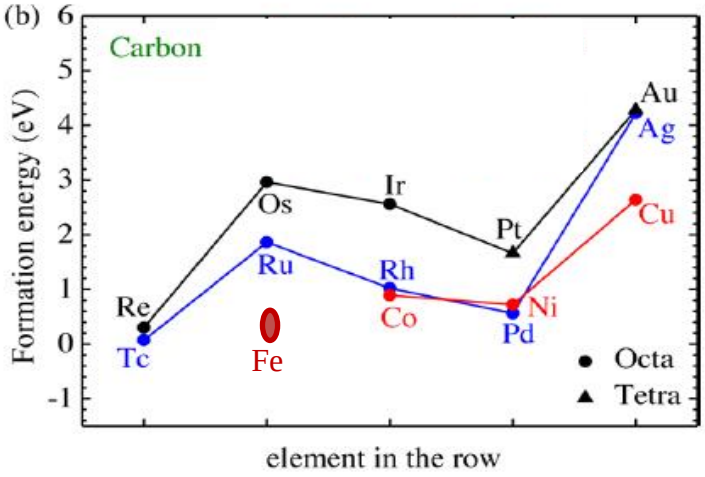
Key parameter

Heat of solution of C atom in bulk metal,

Driven by (carbon p-metal d) energy level difference

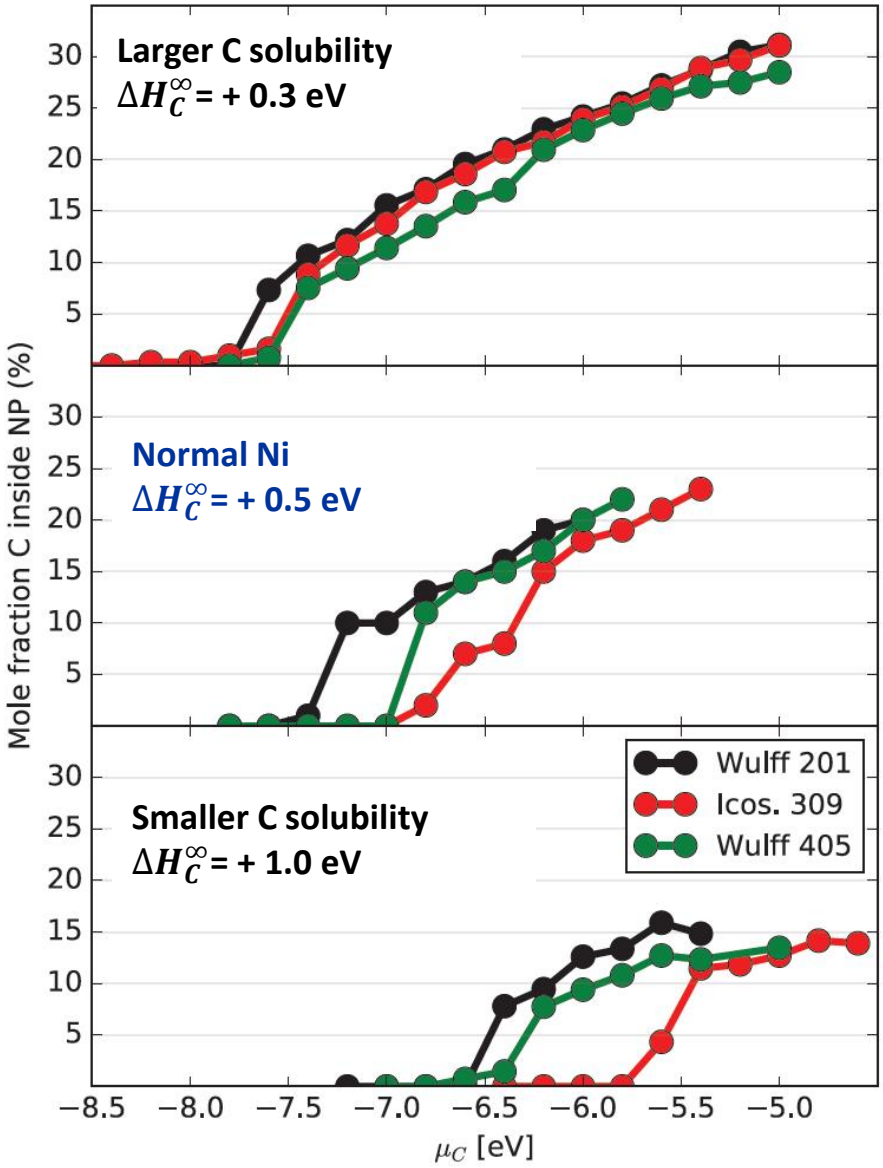


$(\varepsilon_p - \varepsilon_d) = -2.7$ eV	$\Delta H_C^\infty =$ **+ 0.3** eV	**Ni^+ ~ Fe**
$(\varepsilon_p - \varepsilon_d) =$ -4.2 eV	**$\Delta H_C^\infty =$ + 0.5 eV**	**real Ni**
$(\varepsilon_p - \varepsilon_d) = -5.2$ eV	$\Delta H_C^\infty =$ **+ 1.0** eV	**Ni^-**
	+ 2.0	Cu
	+ 4.0	Au

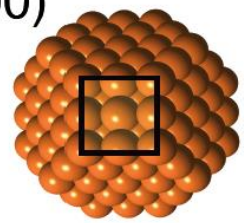


Hu *et al. J. Phys. Chem. Lett.* **2015**, 3263

Why FCC Au NPs work and Icosahedral don't …

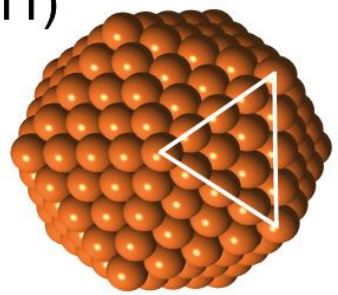


(100)



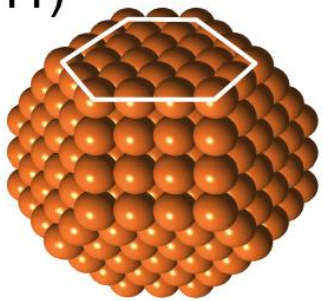
Wulff 201

(111)



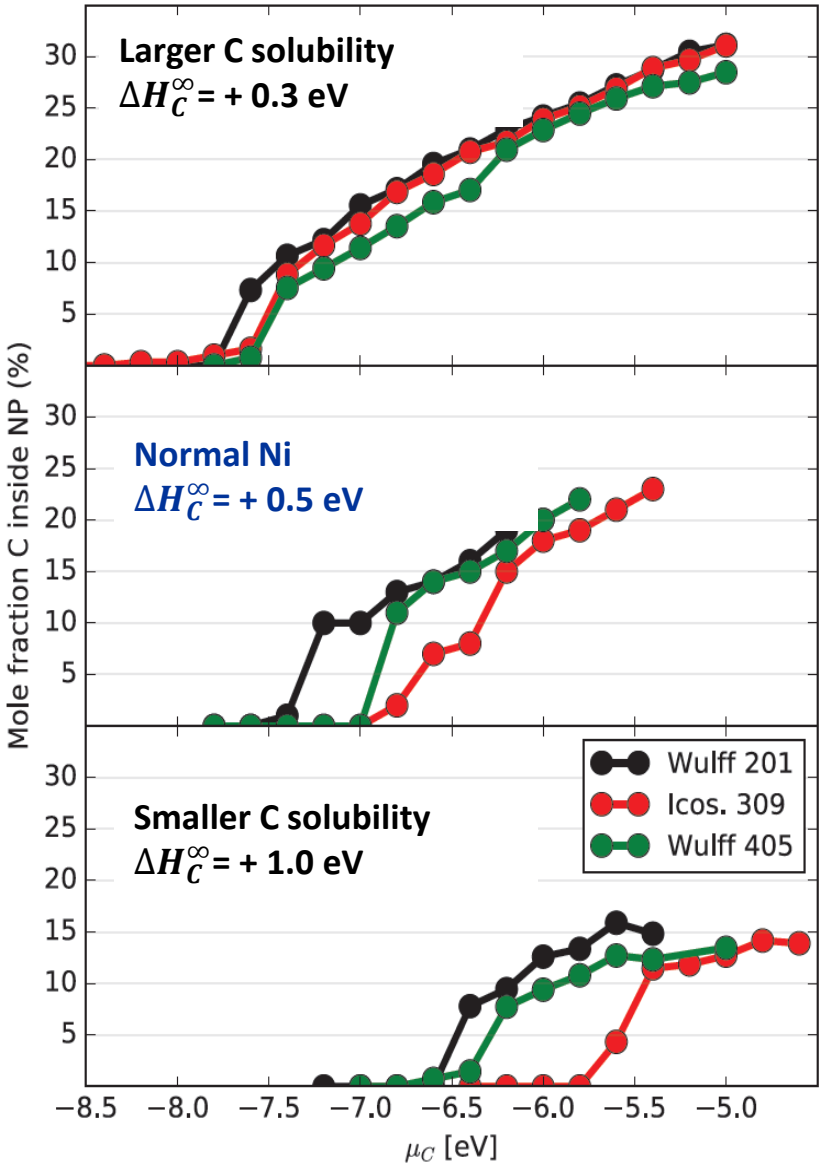
Icosahedral 309

(111)



Wulff 405

Why FCC Au NPs work and Icosahedral don't …



- icosahedral NP :

  Adsorption isotherm for is shifted for system with lower C solubility

  C incorporation more difficult

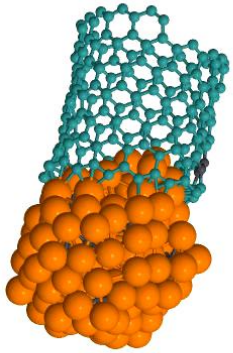
- **Pressure range where only fcc NP are activated for growth**

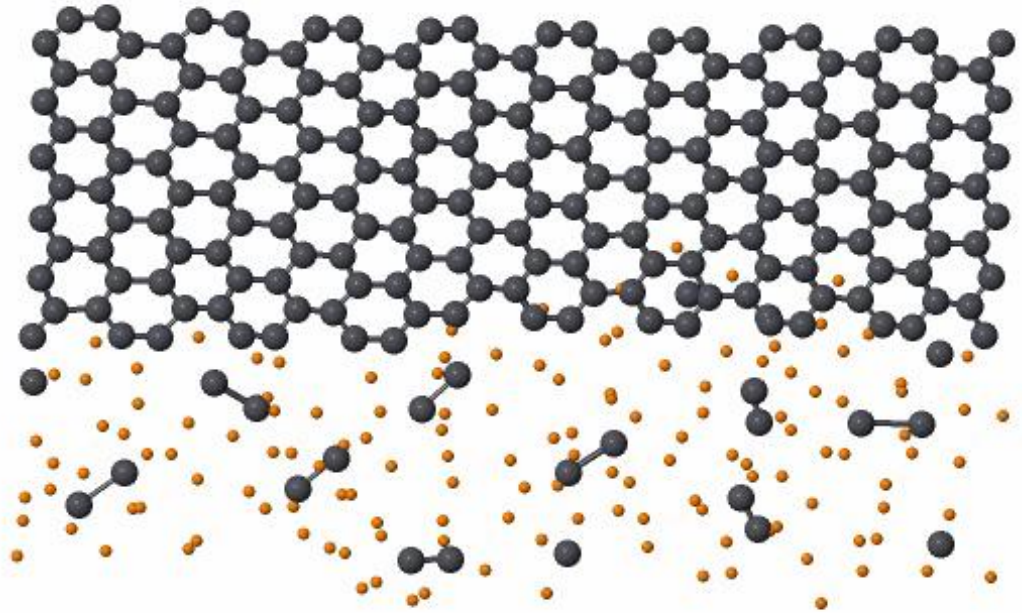
- **C goes in subsurface for fcc structure, enabling sp^2 cap lift-off**

- **C remains on surface for ico Au, leading to encapsulation**

He et al. *Nanoscale* **2015**, *7*, 20284

Growth sequence with **Nickel**



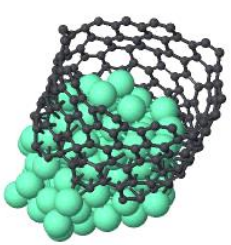


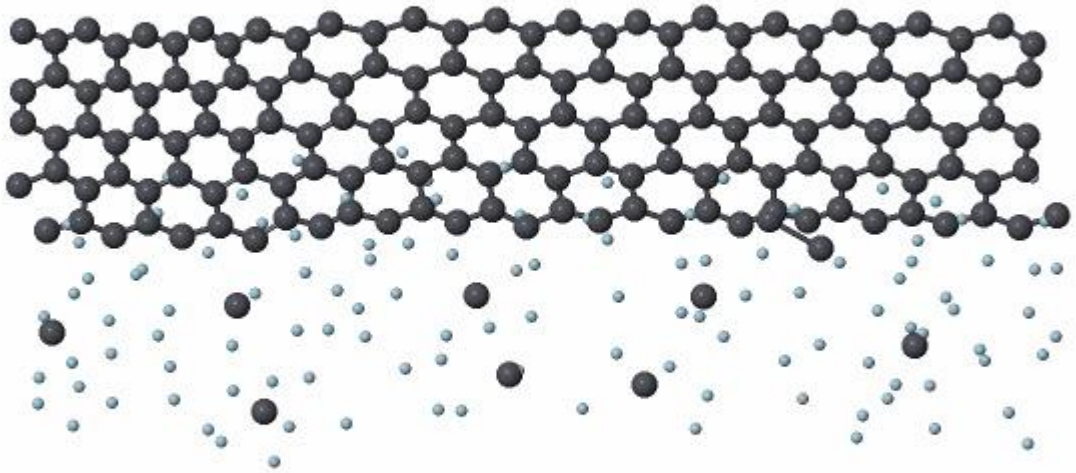
Grand Canonical MC simulations
1200 K, μC = -6.20 eV/C

Carbon dimers are taken out of the NP, because larger %C dissolved
Long chains are formed, detached from surface
Tendency to dewet and detachement of NP
Alltogether, rather messy growth … with defects

Jmol

Growth sequence with Nickel with **reduced carbon solubility**





Grand Canonical MC simulations
1200 K, μC = -6.20 eV/C

Jmol

Shorter chains, in contact with metal when pure, avoiding contact with Ni+C dissolved
Tendency to encapsulate NP, because of more wetting tendency
Less defects, slower, more controlled growth

Can we control SWNT growth modes ?

Idea is to control metal – carbon interfacial properties. How can this be achieved ?

1. Use surfactant
   - Has been done : Windle + others : adding Sulfur or …
2. Temperature changes during growth
   - Yao et al. : Nat. Mat. 2007; J. Phys. Chem. C 2009
3. Control carbon fraction in catalyst
   - Experimentally : icosahedral versus f.c.c. Au nanoparticles
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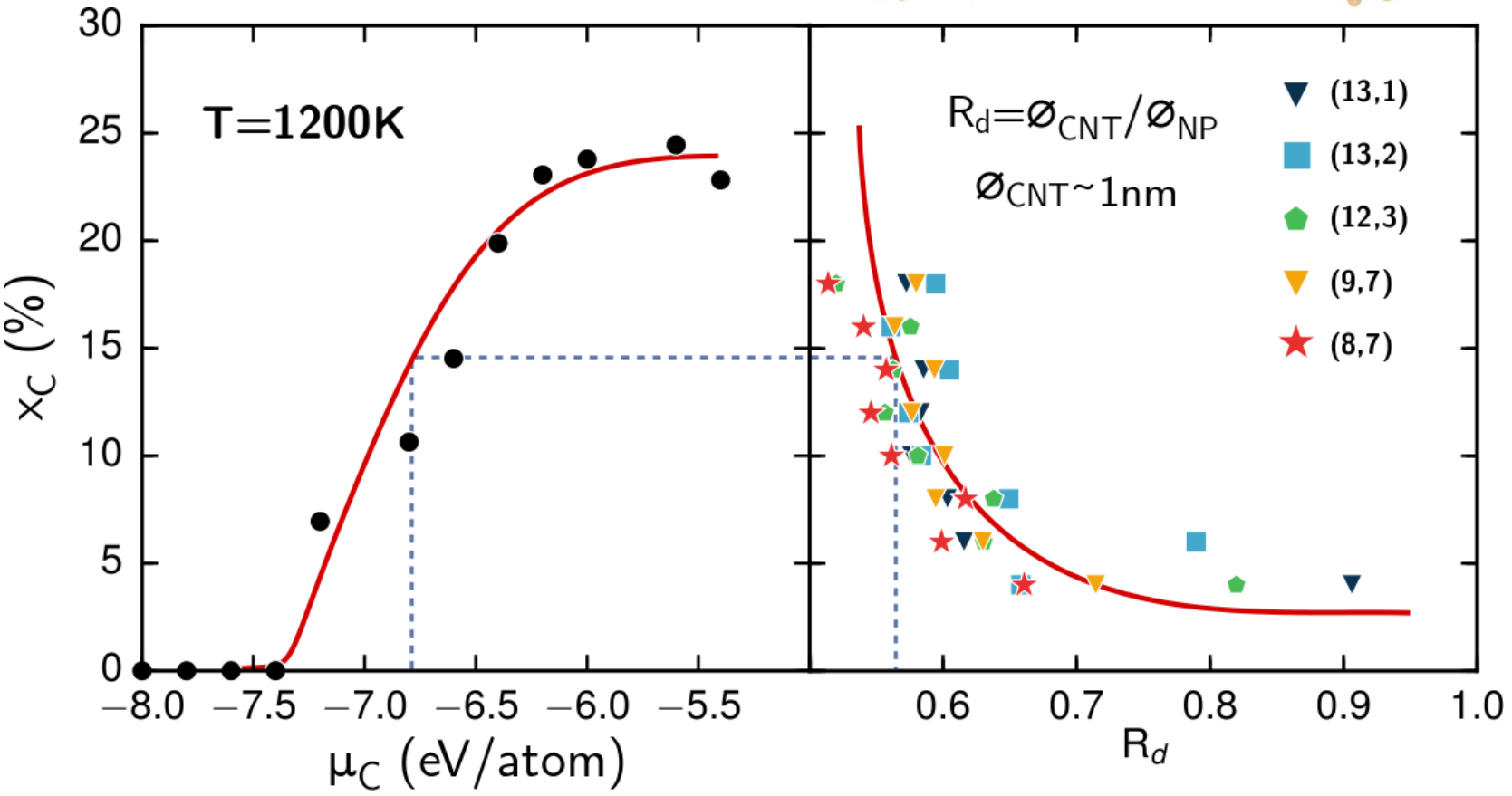
4. **Control via gas phase : ambient, feedstock**
   - Chenguang Lu and Jie Liu; J. Phys. Chem B 2006; Thurakitseree ACS Nano (2011)
   - Alternating CH_4 and CO feedstocks
5. Use bimetallic catalyst ?
   - Not very clear yet

Growth modes controlled by carbon fraction dissolved in catalyst

Large x_C : perpendicular

Small x_C : tangential

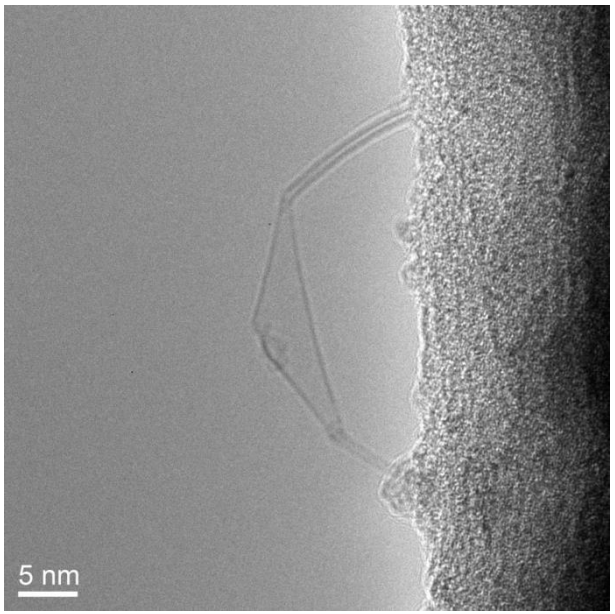


Reversibly tuning growth modes

Alternating 1min CO, 1 min CH_4 $\Rightarrow$ nanotube junctions with large diameter difference

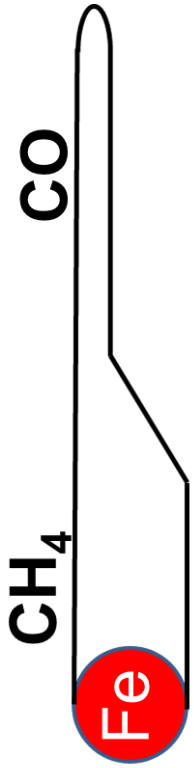
CO CH_4 CO CH_4

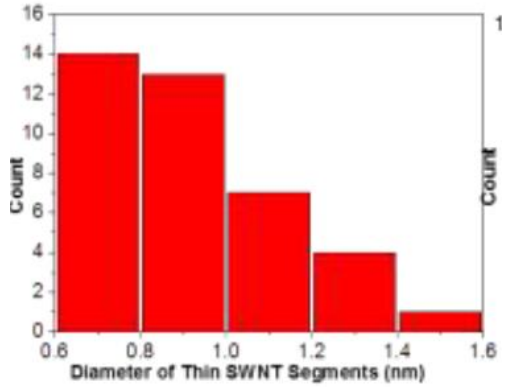
1min 1min 1min 1min



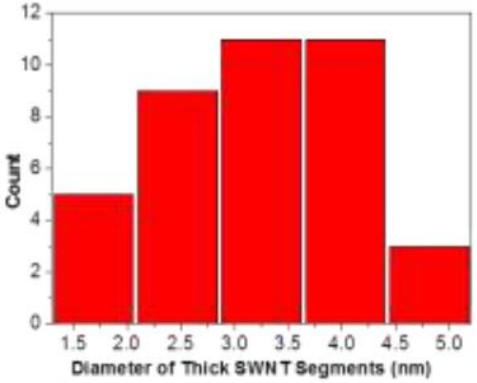
reversible … !

Experiments by Maoshuai He





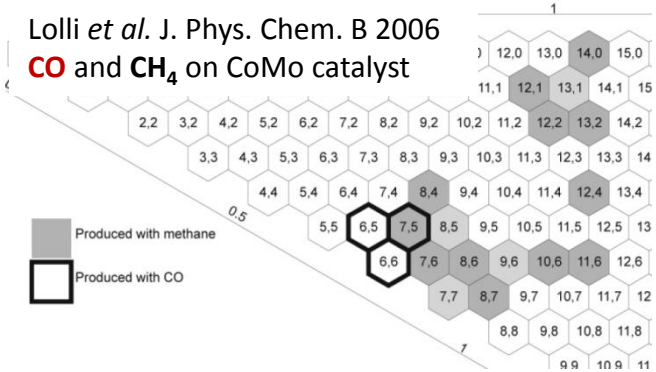
Narrow width distribution for thin segments
: perpendicular mode



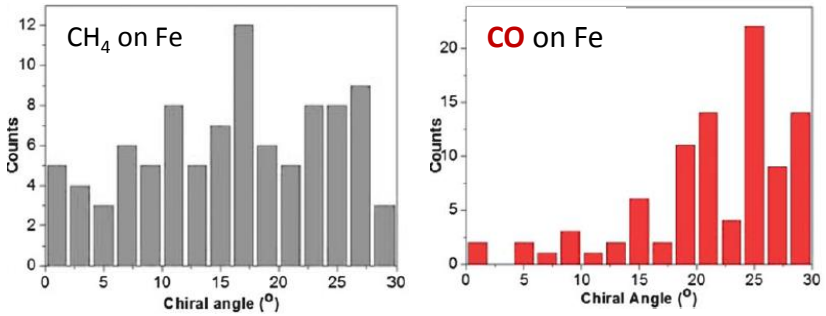
Broad width distribution for thick segments

Near armchair chiral preference in **perpendicular** growth mode …

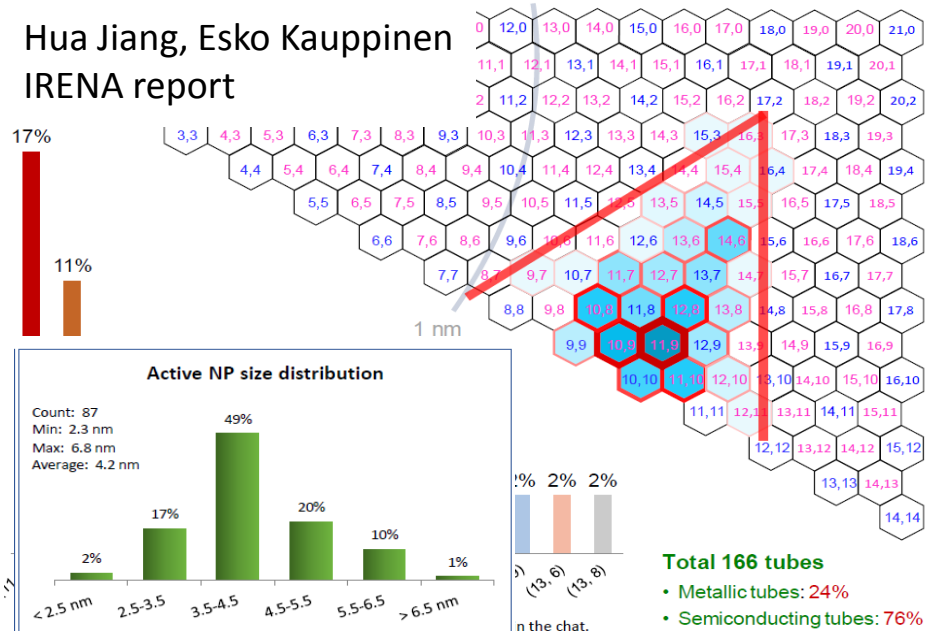
Lolli *et al.* J. Phys. Chem. B 2006
CO and **CH_4** on CoMo catalyst



Maoshuai He *et al. Nanoscale* **2012**, 7394–7398.

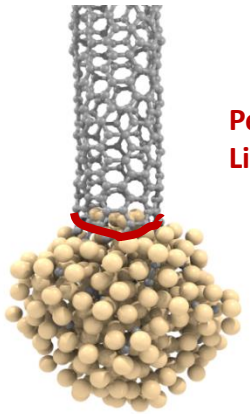


Hua Jiang, Esko Kauppinen
IRENA report



CO is more active than CH_4 to carburize NP
- Perpendicular mode with Fe
- also with CoMo ?

Can we explain near armchair selectivity ?

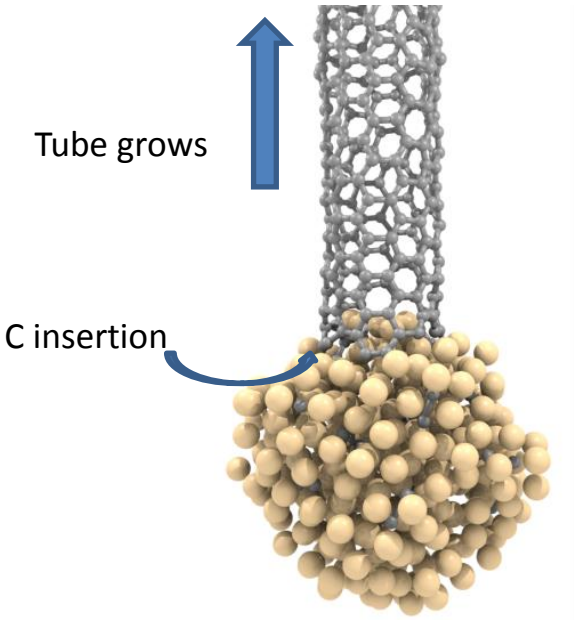


Perpendicular mode
Line contact only !

Tangential growth mode ?

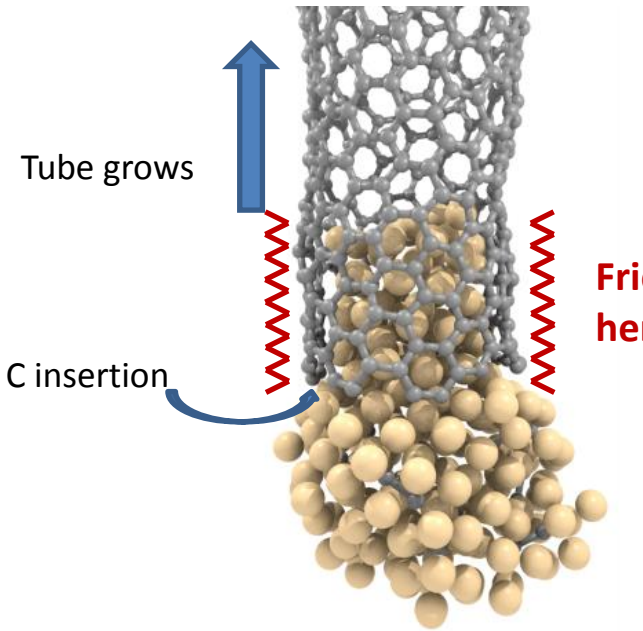
Different growth modes can be observed, and tuned by experimental conditions

Perpendicular



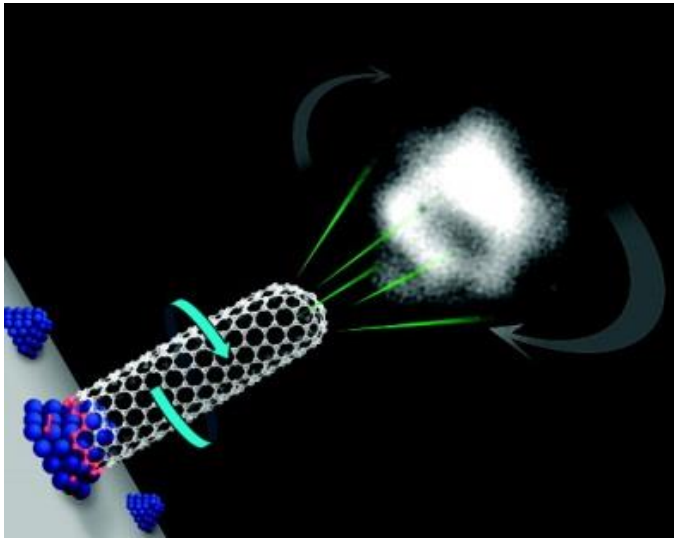
Line contact

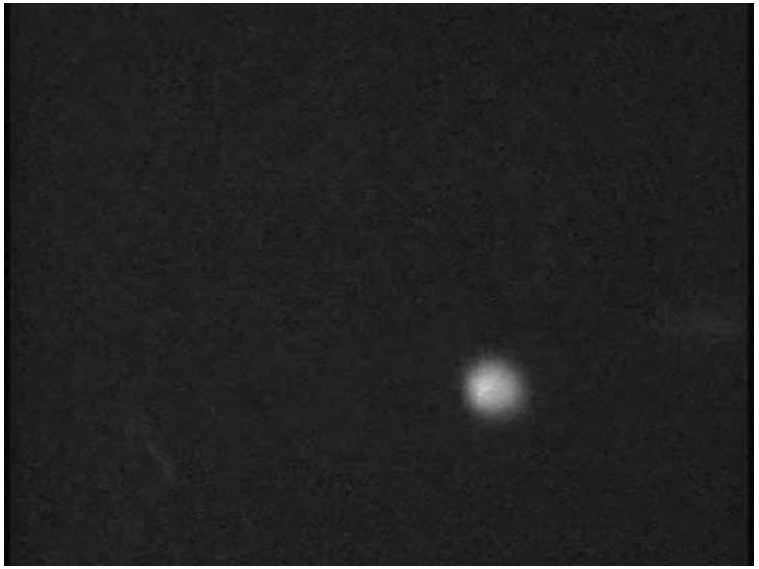
Tangential



Tube slides along
Nanoparticle : friction ?

SWNT growth experiments in C. Journet, S. Purcell & coworkers





Driving force for rotation ?

Yakobson proposed dimer incorporation at « cosy corner », thus supporting his spiral growth model …

Growing a Carbon Nanotube Atom by Atom: "And Yet It Does Turn"

Mickaël Marchand,[†] Catherine Journet,[†] Dominique Guillot,[†] Jean-Michel Benoit,[†] Boris I. Yakobson,[‡] and Stephen T. Purcell*[,†]

NANO LETTERS

2009
Vol. 9, No. 8
2961-2966

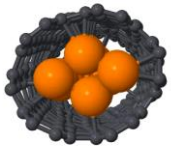
Idea : slide a piece of Nickel inside a SWNT … and see what happens

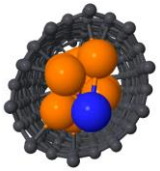
ReaxFF Molecular Dynamics à 300 K. **Constant bias force along z axis for Ni atoms**. One C atom fixed
For appropriate parameters, **rotation of the metal inside the tube**. Blue atom follows a zig-zag line

(6, 6)

(6, 5)

(10,0)





Main findings

Carbon interaction with metal

- Surfaces / nanoparticles
- Size dependent phase diagram of Ni+C nanoparticles
  - Downshift of eutectic point
  - Solid core / disordered shell

Growth modes identified (Fiawoo PRL 2012), but now, *understood*

- Large carbon fraction in NP $\Rightarrow$ perpendicular growth
- Low carbon fraction in NP $\Rightarrow$ tangential growth

Growth modes can be tuned by

- Carbon solubility in metal catalysts
- Carbon feedstock nature and decomposition (μ_C^S)

Growth modes may play role in selectivity

- Perpendicular mode : line contact with NP, near armchair selectivity possible
- Tangential mode : line + surface contact with NP … still to be explored

Thank you for your attention !

Thanks to :

Yann Magnin
Rafael Martinez Gordillo
Mamadou Diarra
Alexandre Zappelli
CINaM - CNRS and Aix Marseille Univ

Jan H. Los
Radboud Univ. Nijmegen

Hakim Amara
Juan Aguiar
LEM - CNRS and ONERA

Maoshuai He
Annick Loiseau
François Ducastelle

Very good question ….

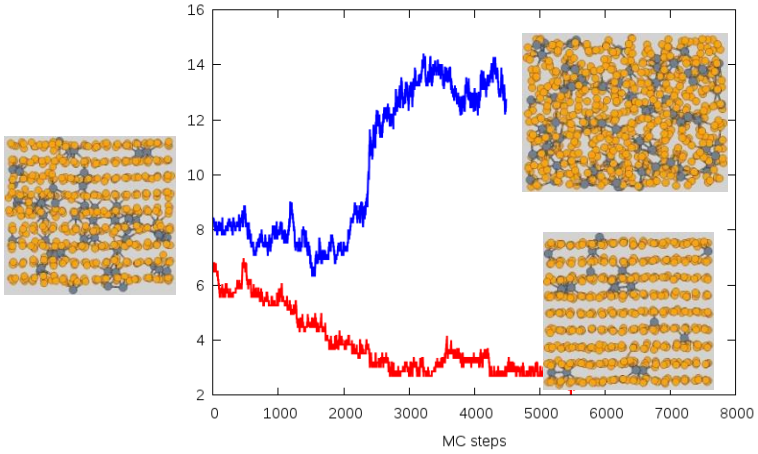
« In theory, there is no difference between practice and theory …

… in practice, there is »

Yogi Berra

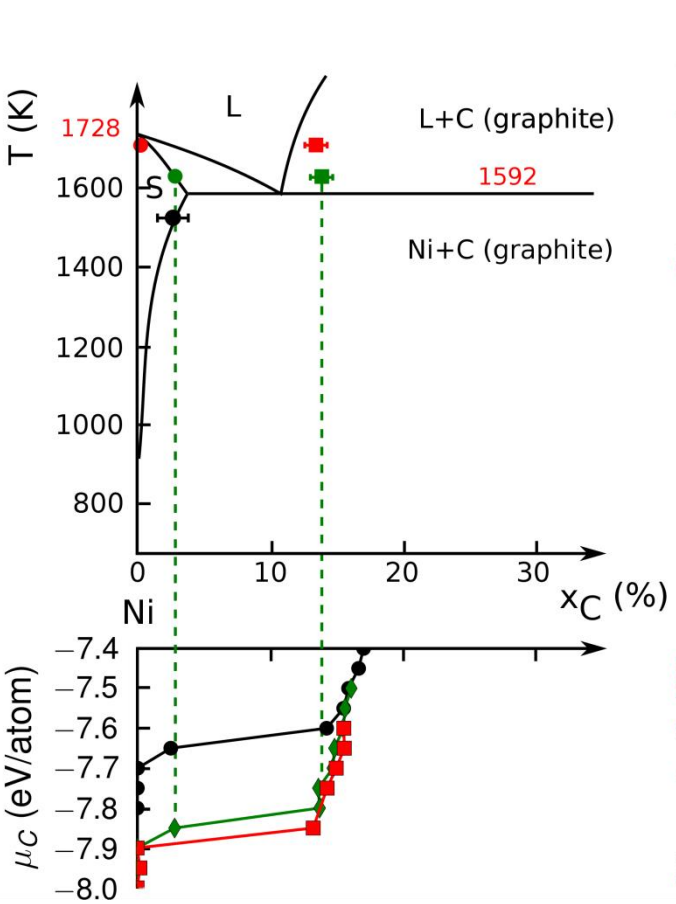
(base ball player and famous coach)

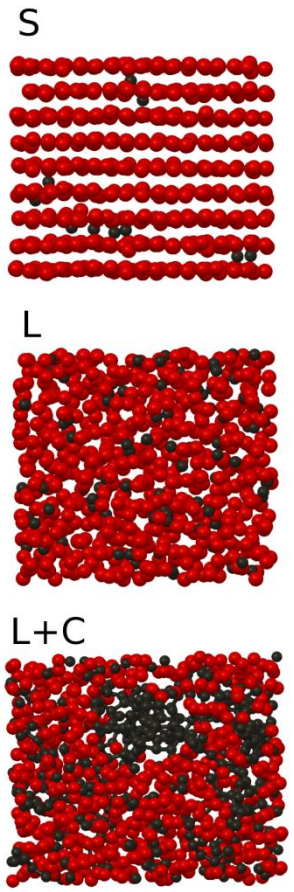
Model validation: carbon solubility in **bulk** Ni



Monte Carlo calculations in ***osmotic*** [(*)] ensemble N_{Ni}, μ_C, Pext (=0), T fixed to account for lattice expansion upon C incorporation

[(*)] *J. Am. Chem. Soc.* **2008**, *130*, 14294–14302





Calculated solubility limit below 5% in crystal agrees with experiment

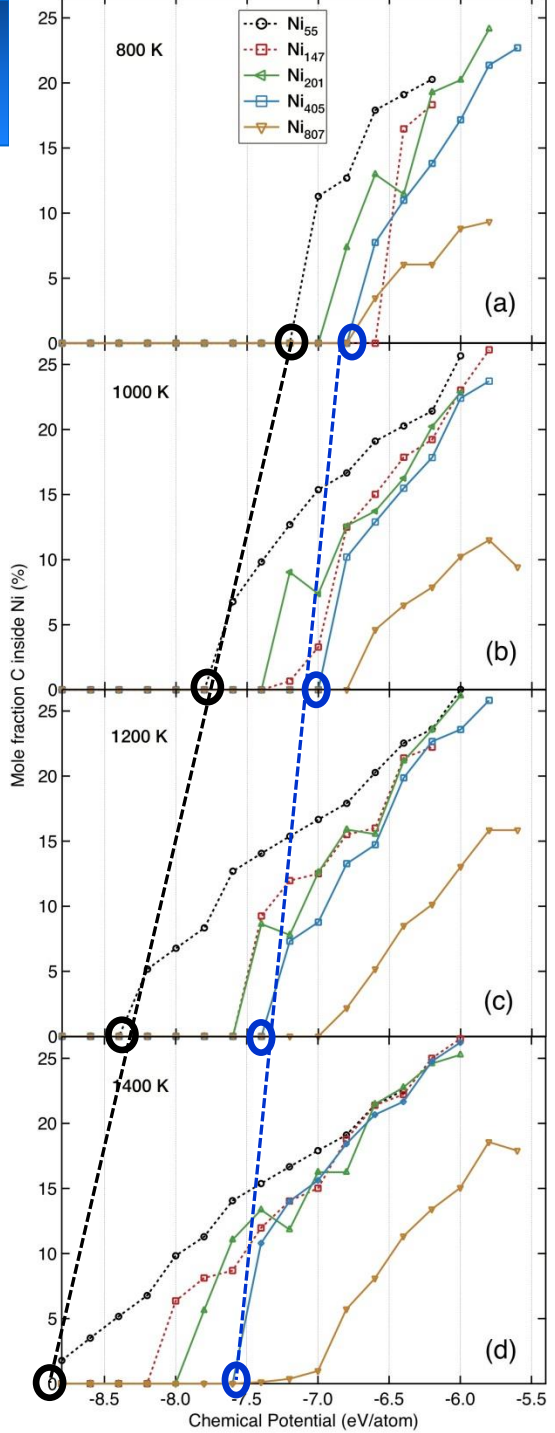
Carbon solubility in nanoparticles

Adsorption thresholds O O depend more strongly on temperature for smaller nanoparticles

Tuning growth conditions could be more difficult for smaller NPs and SWNTs ?

Diarra *et al.*,

Phys. Stat. Sol. 249, No. 12, 2629–2634,2012



From adsorption isotherms to phase diagram …

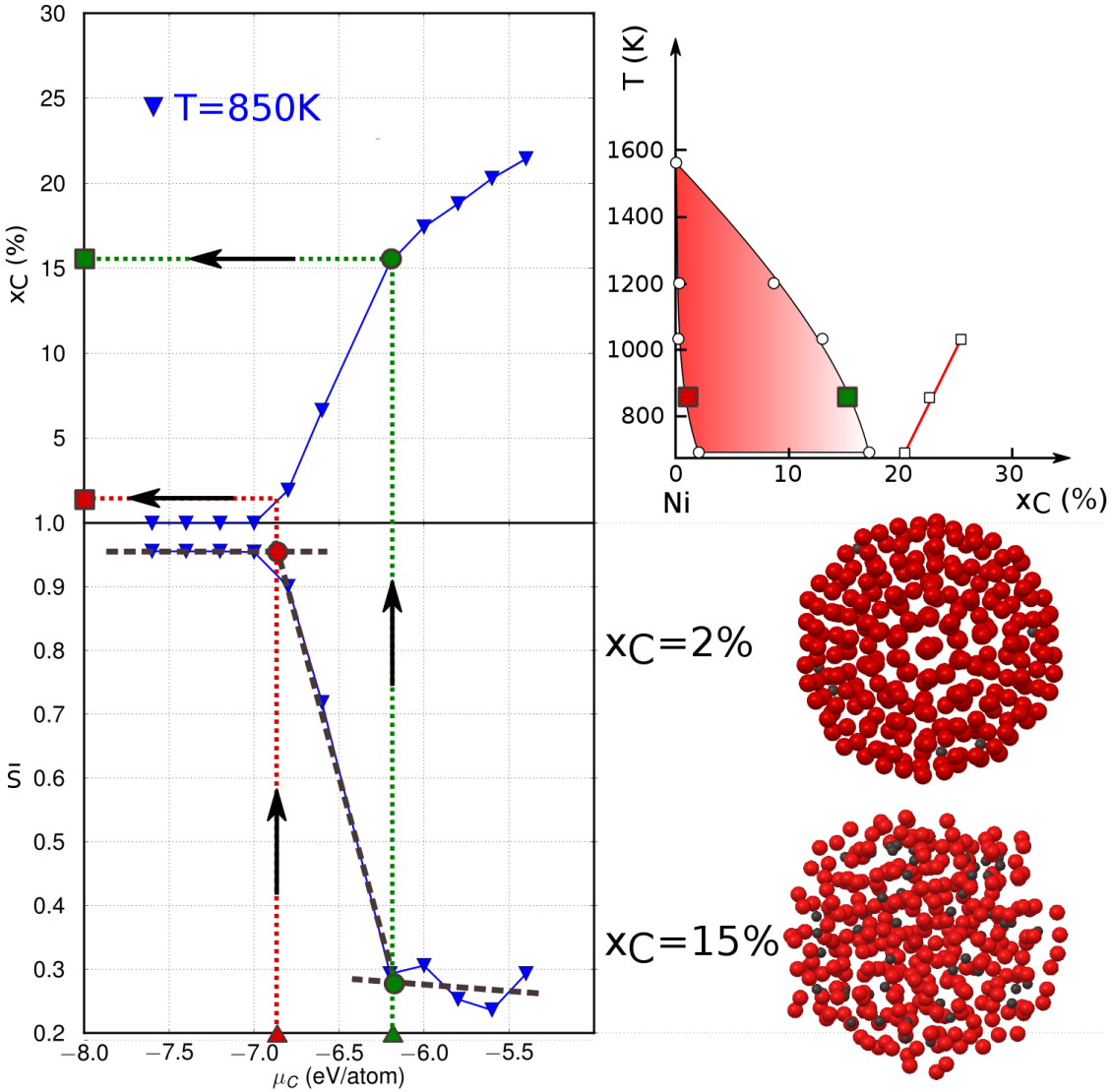
How to ***quantitatively*** define phase boundaries ?

Orientational order parameter ***S*** :

P. Steinhardt *et al.*
Phys. Rev. B, 28, 2, 784–805, 1983

crystalline (***S*** > 0.85)

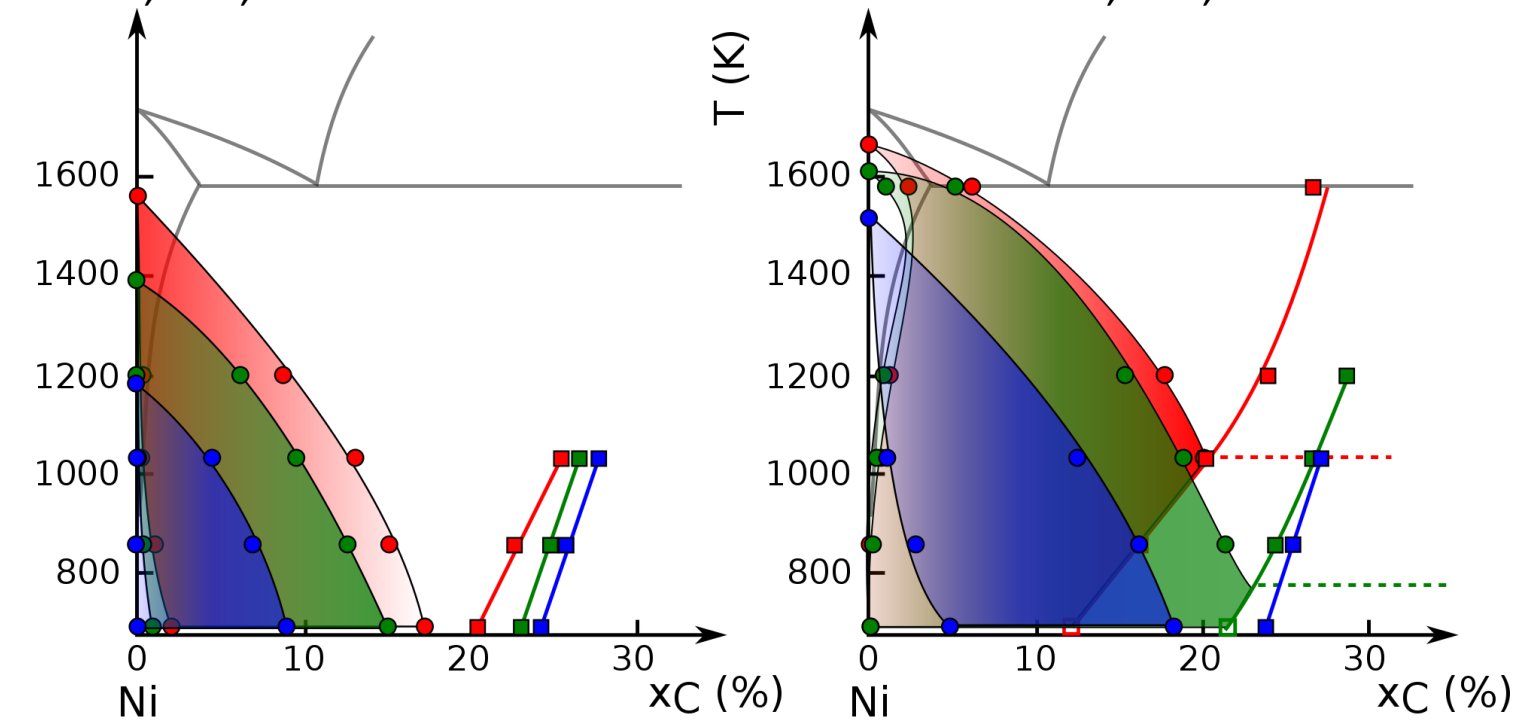
liquid or amorphous (***S*** <0.35)



Size dependent phase diagram for Ni-C nanoparticles

Ico : 55, 147, 309 Ni atoms

FCC : 201, 405, 807 Ni atoms



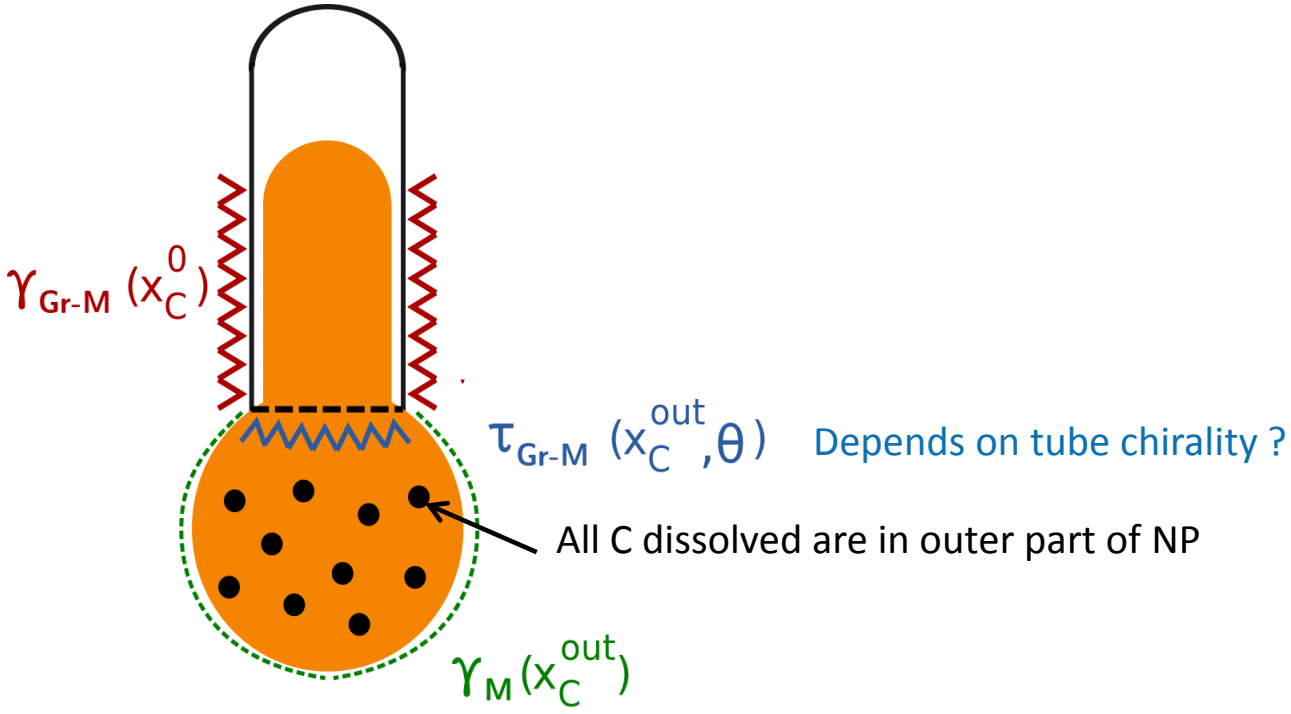
Red, green, blue areas are solid core / liquid shell

As compared to bulk, eutectic shifted to lower Temperature and larger %C

Liquidus lines shifted to large %C for larger NPs

Magnin *PRL 2015*

Thermodynamic modeling of tube / NP interface

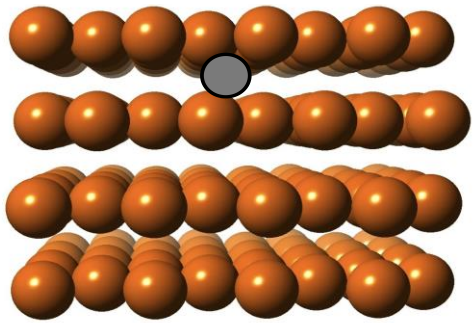


Gibbs energy of system, as a function of NP size, temperature, *fraction of C dissolved* in NP

$$\begin{aligned}\mathcal{G}(x_c) &= \mathcal{G}_M^{out}(x_c^{out}) + 4\pi R^2(x_c^{out})\,\gamma_M(x_c^{out}) \\ &+ \mathcal{G}_M^{in}(x_c^0=0) + 2\pi r\, h(x_c^{out})\,[\gamma_{C-M}(x_c^0=0)-\gamma_C] \\ &+ \mathcal{G}_{cnt} + 2\pi r\,[\tau_C(\theta)-\tau_{C-M}(x_c^{out},\theta)].\end{aligned}$$

Dissolution energy calculations : tight binding

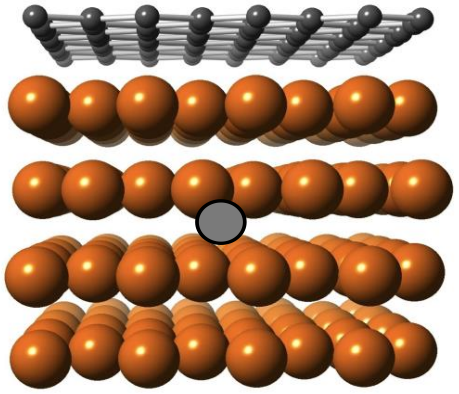
Without graphene



Subsurface :
Binding energy -8.21 eV

Subsubsurface :
Binding energy -7.31 eV

With graphene overlayer



Subsurface :
Binding energy -6.79 eV

Subsubsurface :
Binding energy -7.77 eV

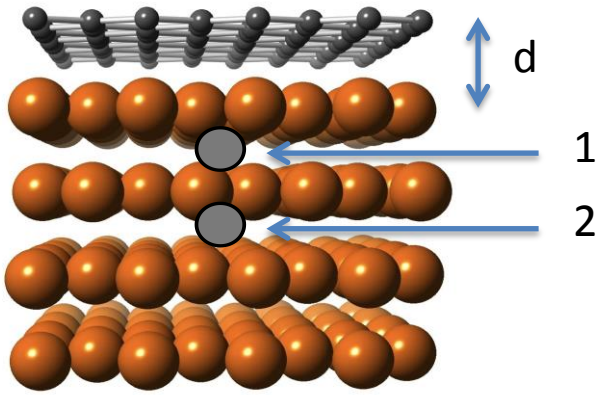
Moors *et al.* ACS Nano, 2009, 3 (3), 511-516

Weatherup *et al.* JACS. **136**, 13698 (2014)

Dissolution energy calculations : DFT

DFT calculations

- VASP code – (PAW; GGA; spin-polarized,…)
- 6 atomic planes (9 Ni atoms)
- Graphene (18 C atoms)



Graphene - Ni distance varied :

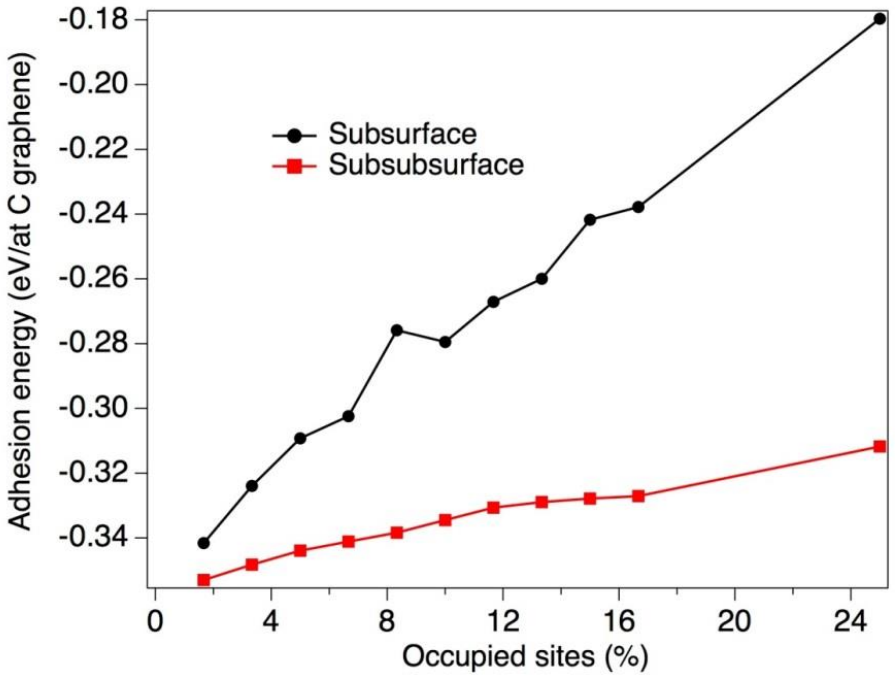
d(A)	ΔE (1-2) (eV)
3.50	-0.90
2.00	-0.10
1.80	**+0.31**

When graphene is closer to surface, subsurface carbon atoms are less stable than sub-subsurface

Tight Binding model
is qualitatively correct

Graphene – Ni interaction

Adhesion of graphene layer weaker when C is dissolved close to Ni surface



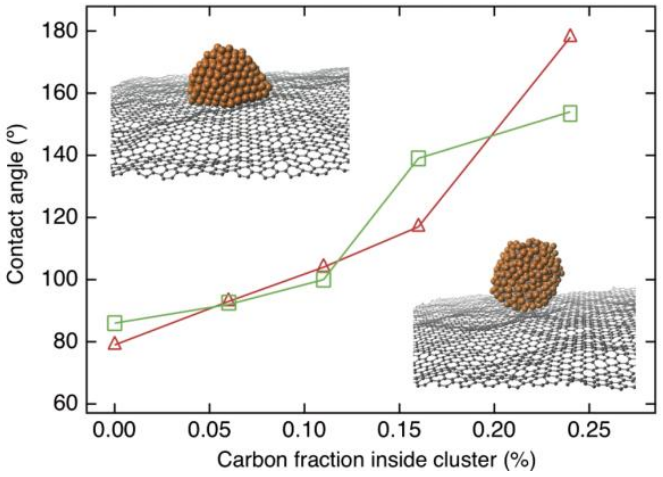
Young Dupré :

$$1 + cos\theta = \frac{W_{adh}}{\gamma_{(Ni+C)}}$$

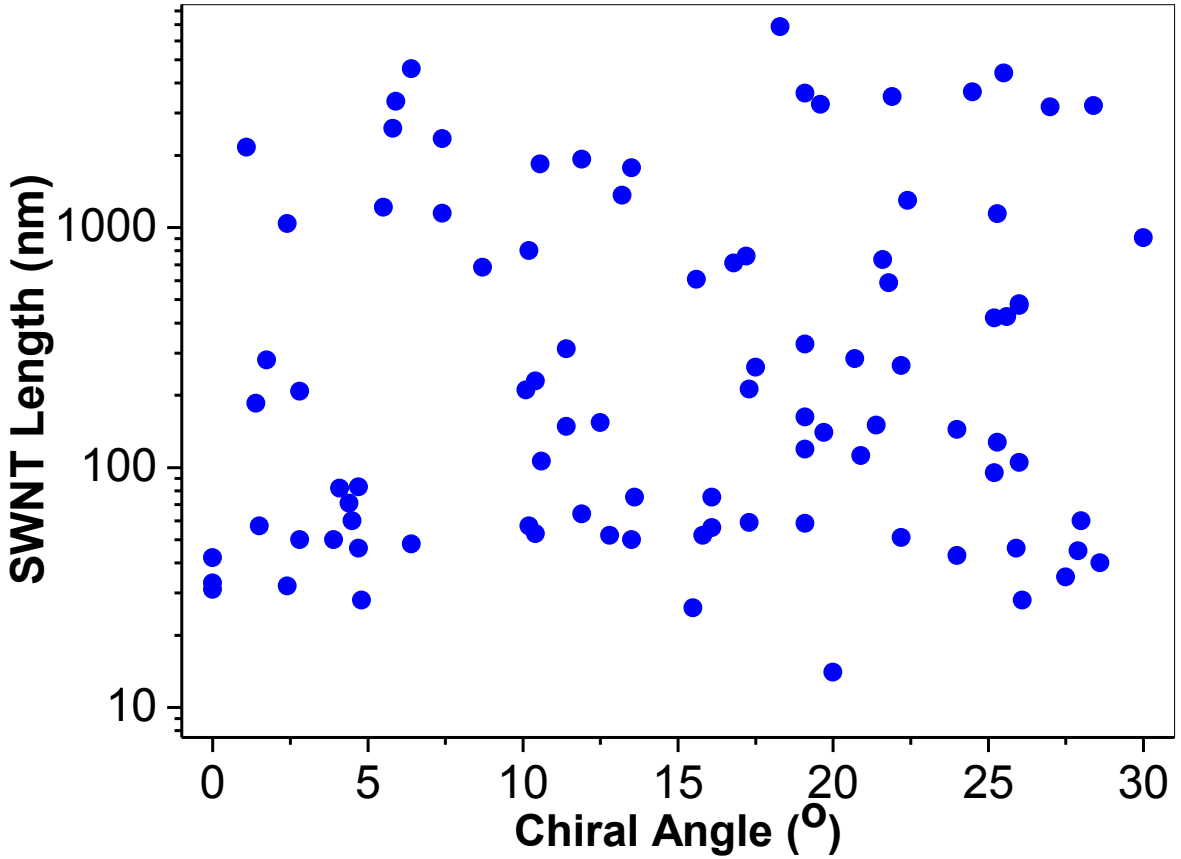
Θ = 90° → W_{adh} = γ

Θ = 180° → W_{adh} = 0 !

Explains dewetting of Ni NPs on graphene, when stuffed with carbon

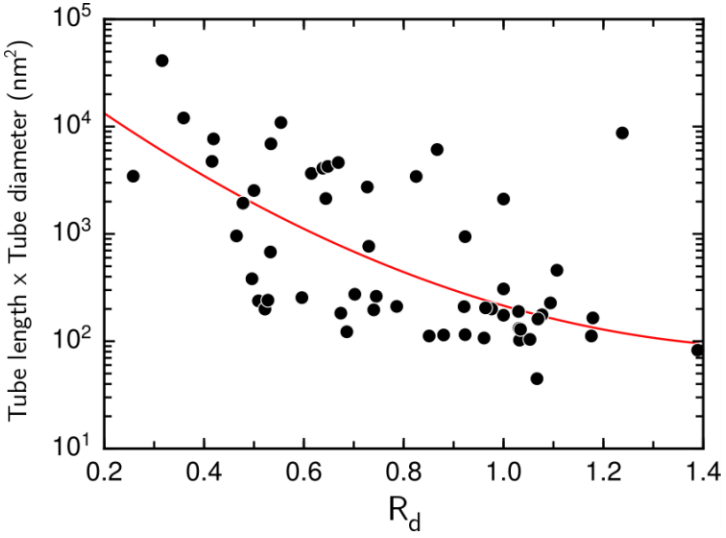


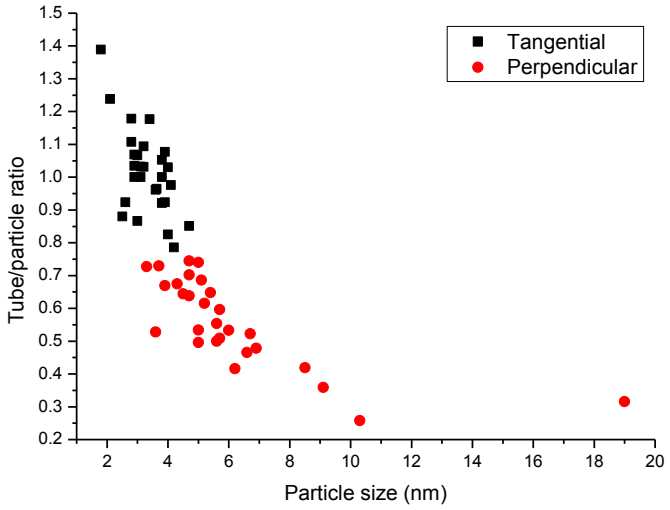
Statistics on 92 isolated SWNTs



There is ***no*** correlation between SWNT lengths and chiral angles.

CH_4 with Fe NPs on MgO : tangential growth leads to shorter tubes





Tangential mode : short tubes

Perpendicular long tubes

He, M. *et al.* Carbon *N.* **2017**, *113*, 231–236.

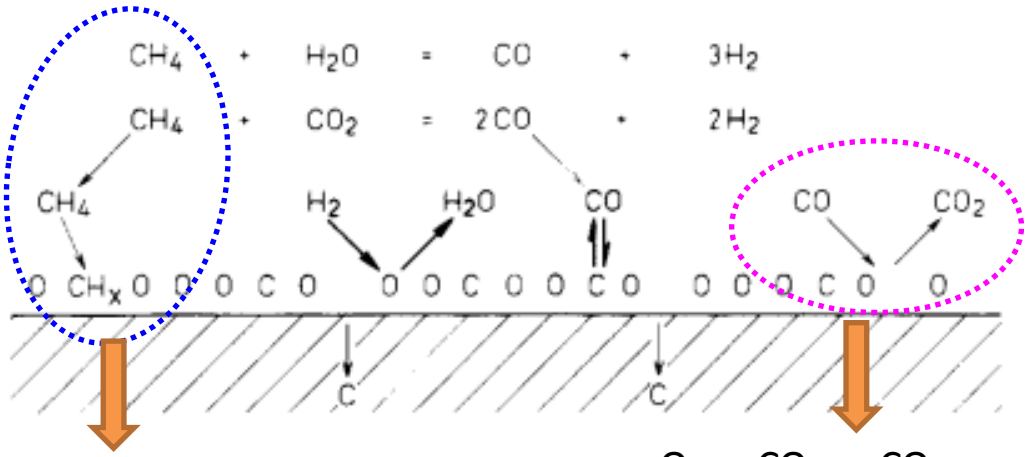
CH_4 Fe/MgO experiment

Smaller NP : tangential

Larger NP : perpendicular

Smaller NP, that sustain tangential growth, get more easily encapsulated (deactivated) than larger ones ?

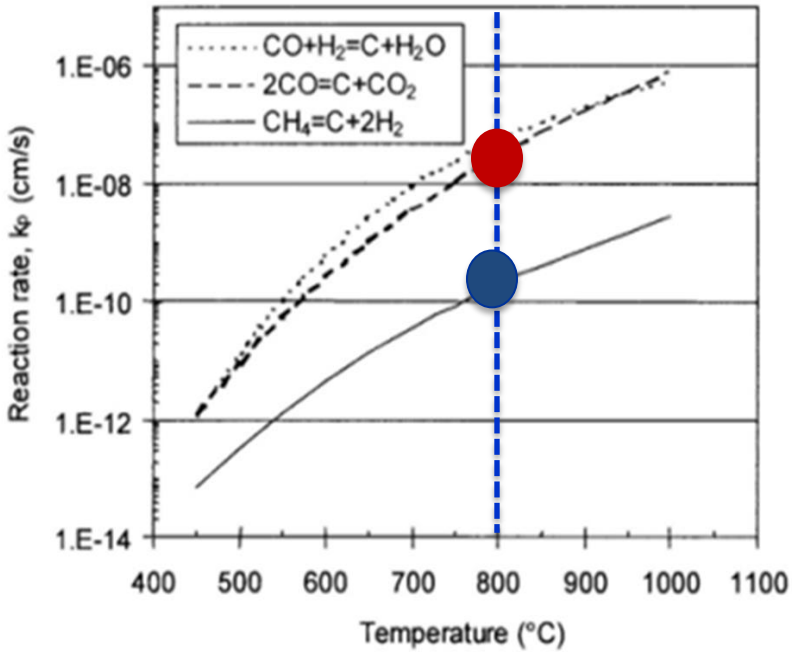
Carburization efficiency of CO and CH_4 on Fe



$CH_{3(s)} = H_{(s)} + CH_{2(s)}$

$O_{(s)} + CO_{(g)} = CO_{2(g)}$

Grabke, H. *J. Mater. Corr*. **2003**, 54, 736.*MTAEC*, **2002**, 36, 297.



Hosmani, S. S. et al. An Introduction to Surface Alloying of Metals. *Springer* **2014**.

Rate constant for carburization on Fe (920°C):

CH_4: 1.9 x 10^{-6} mol/cm^2 ^{s} bar

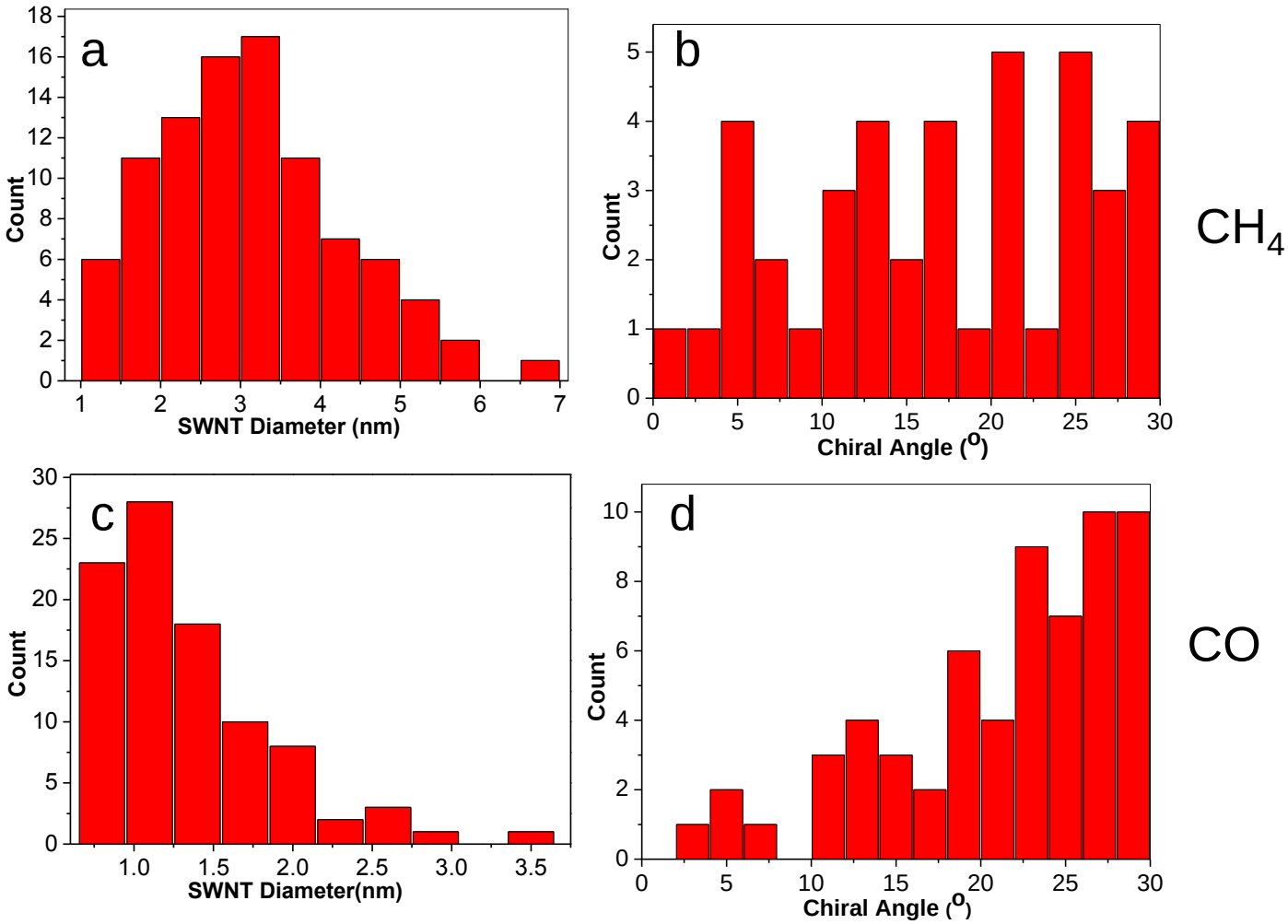
CO: 1.5 x 10^{-4} mol/cm^2 ^{s} bar

- Decomposition of CO on Fe is much easier than CH_4
- The carburization rate of CO is **2** orders of magnitude higher than CH_4

With CO, Fe nanoparticles are saturated with C → perpendicular mode

with CH_4, variable fraction of C, depending on NP size → all growth modes observed

CO favors growth of near-armchair SWNTs with small diameters

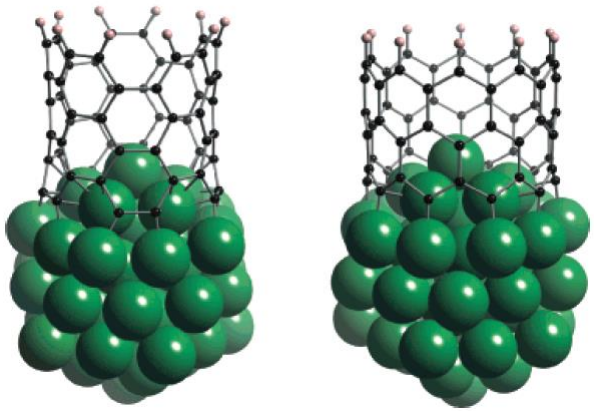


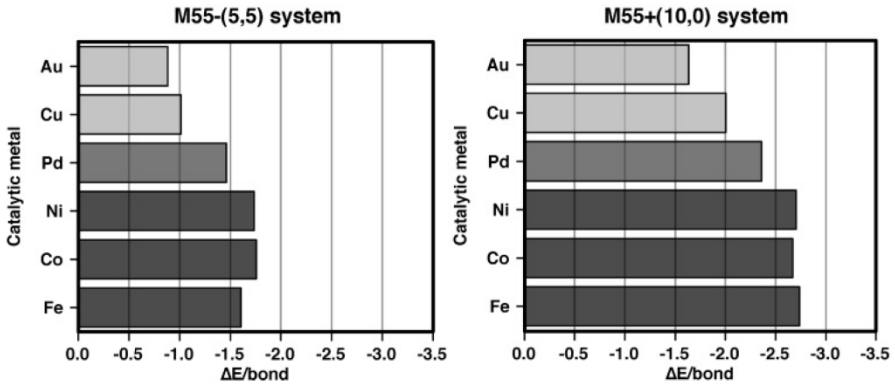
CH4 mixed growth modes

CO perpendicular mode

data Maoshuai He

Ding … Bolton NanoLett 2008





Metal	Armchair	ZigZag	ZZ-Arm
Au	0,9	1,63	0,73
Pd	1,49	2,35	0,86
Co	1,79	2,66	0,87
Ni	1,76	2,71	0,95
Cu	1	2	1
Fe	1,61	2,73	1,12

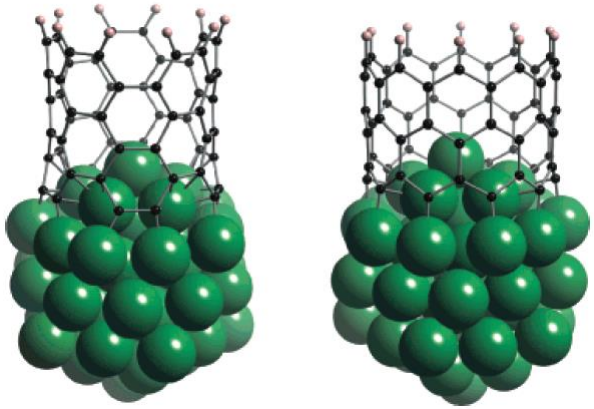
In perpendicular growth conditions …

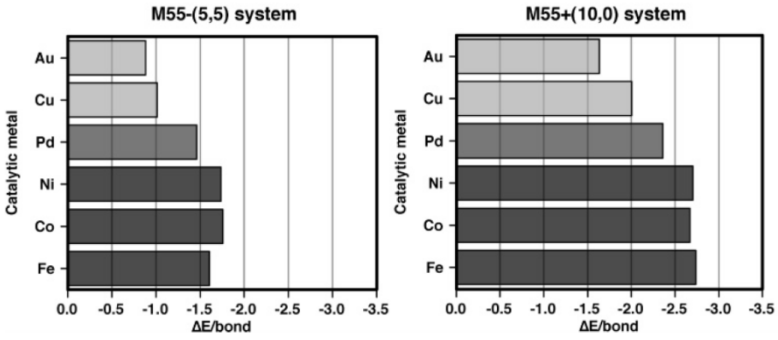
Tube / metal NP bonds are stronger for zigzag.
According to Ding/Bolton, the energy gained by reconnecting a cut tube to a metal NP is larger for Fe

Larger absolute values of (ZZ-Arm) will favor zigzag,
What would be the role of an alloy ?

Using their DFT calculations …

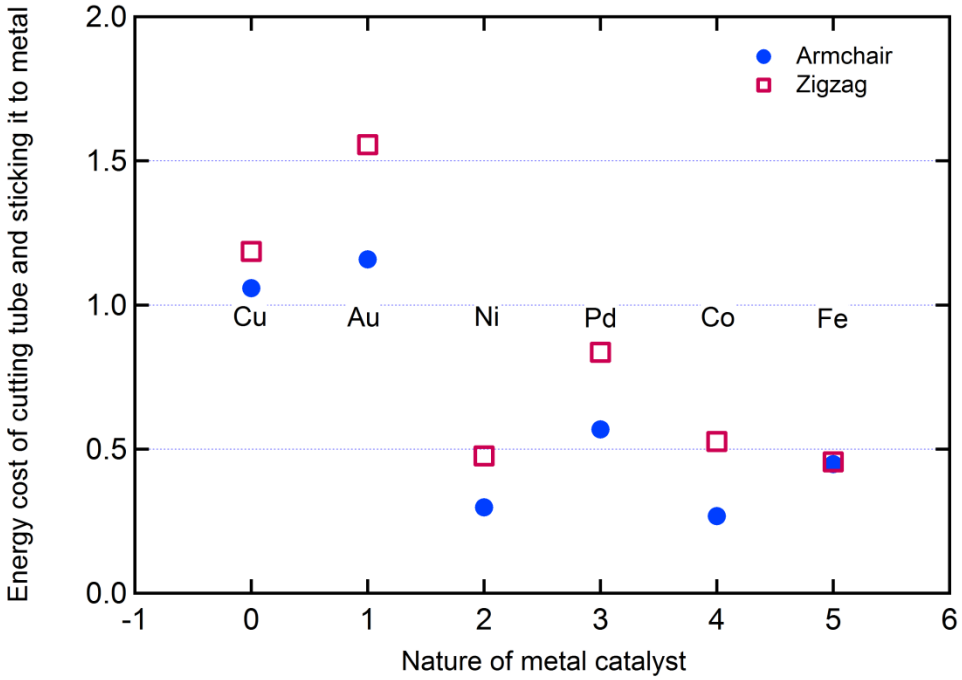
DFT calculations of edge energies





Adhesion energies calculated by :

Ding, F.*et al. Nano Lett.* **2008**, *8*, 463–468.



For Ni, Co Fe :

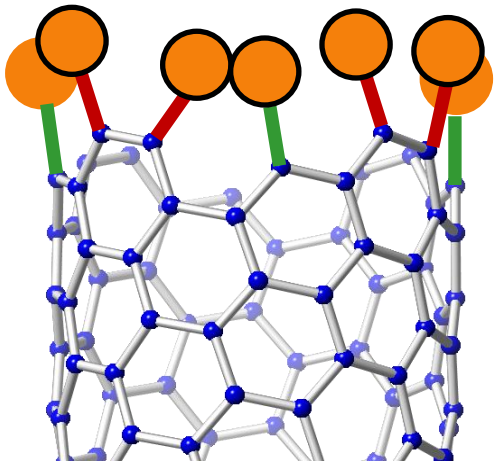
- E_A and E_Z are in 0.2-0.5 eV/bond range
- E_Z always > E_A
- Is it always like this ?

Calculation of edge energy

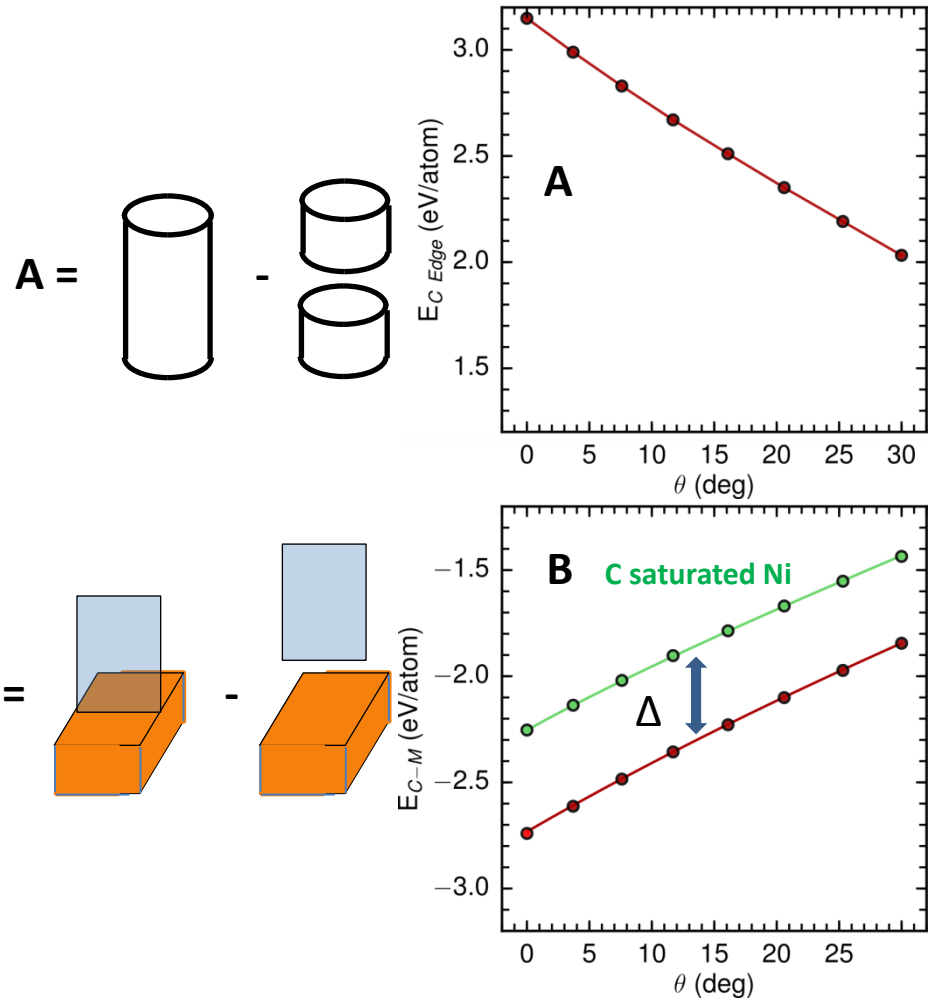
Approximation : chiral probabilility depends on :

- Edge armchair or zizgag bonds
- Tube curvature energy

Liu *et al.* Phys. Rev. Lett. **2010**, *105*, 235502.



DFT calculations C + Ni



Edge energy

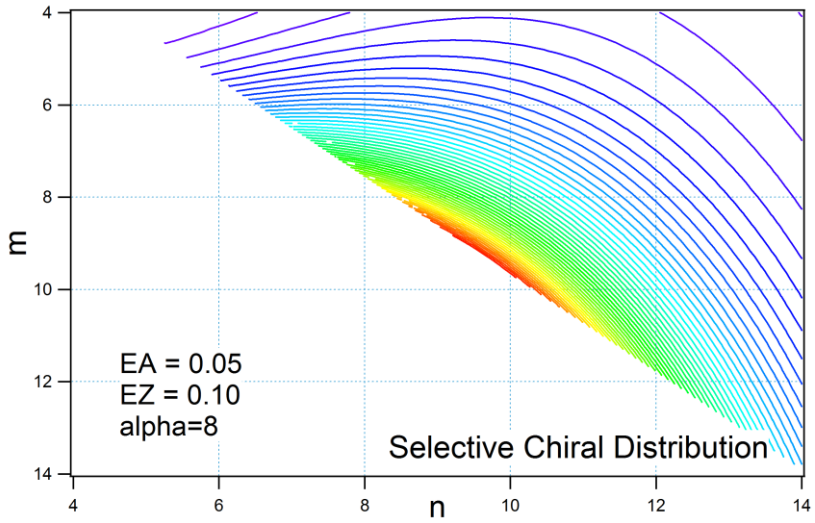
A/2 + B = Energy cost of cutting tube

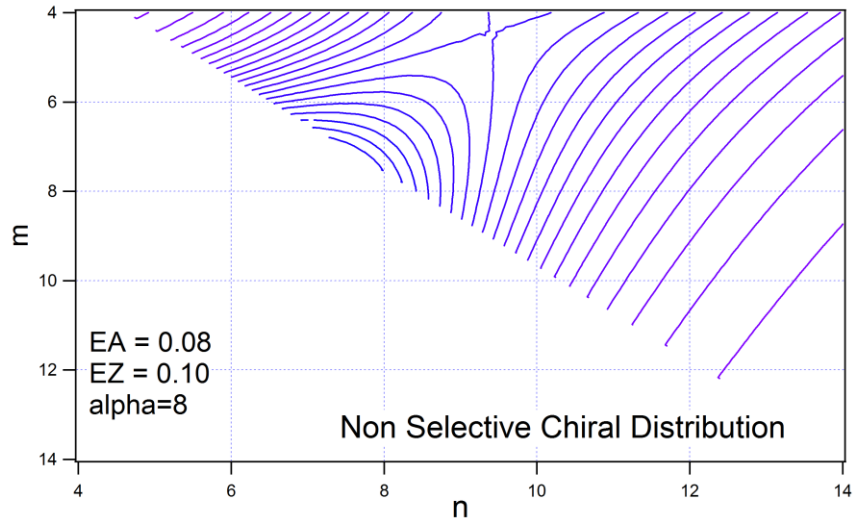
+ Energy gain by reconnecting it to metal NP + Δ = difficult to evaluate by DFT

Qualitative model for chiral selectivity in perpendicular mode

$$E_{Tot} = E_{Edge} + E_{Curv} = 2\,m\,E_A + (n-m)E_Z + \alpha\,(n+m)(n^2 + m^2 + nm)^{-1}$$

Parameters (E_A, E_Z) might be calculated by DFT, or simply used as **toy model**





We can get either :

- near armchair selectivity for reasonable (E_A, E_Z)
- no selectivity
- near zigzag selectivity for unrealistic parameters

We never get (2m, m) or single chiral tube dominant probability : so ?