Unfolding the secrets of phase stability at the nanoscale

(the 7 questions you should NOT ask in a final exam)

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AFLOW

Automatic-FLOW for Materials Discovery

Duke UNIVERSITY

***DOD-ONR,* NSF, DOE, *NIST, ISF,* CRAY**

Question 1

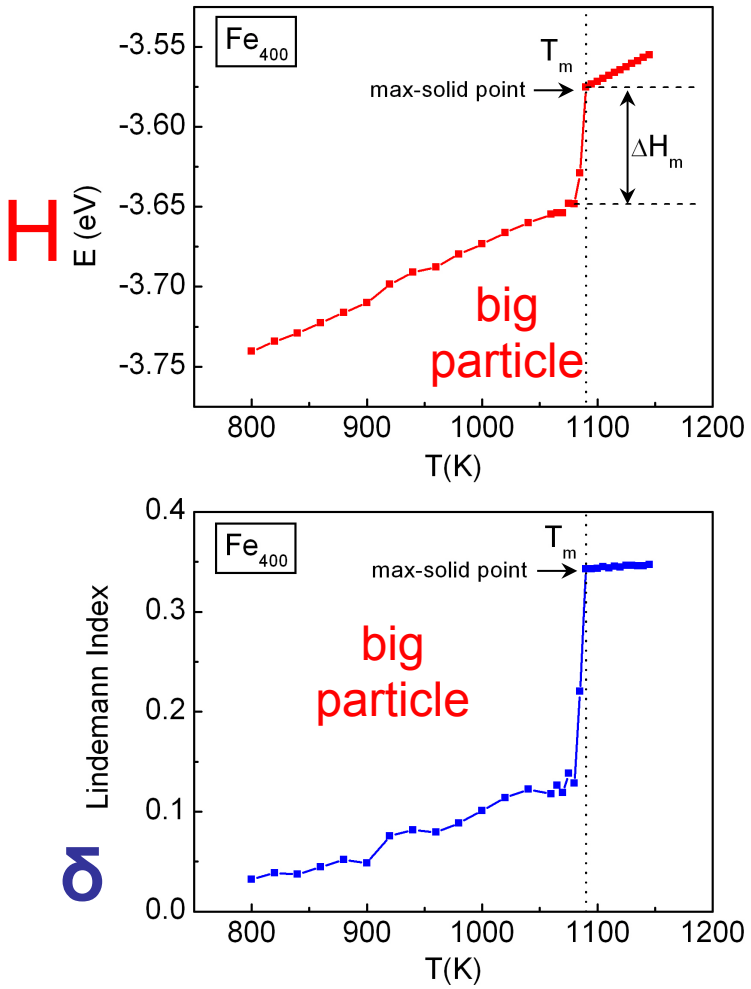
what is melting for nano-particles ?

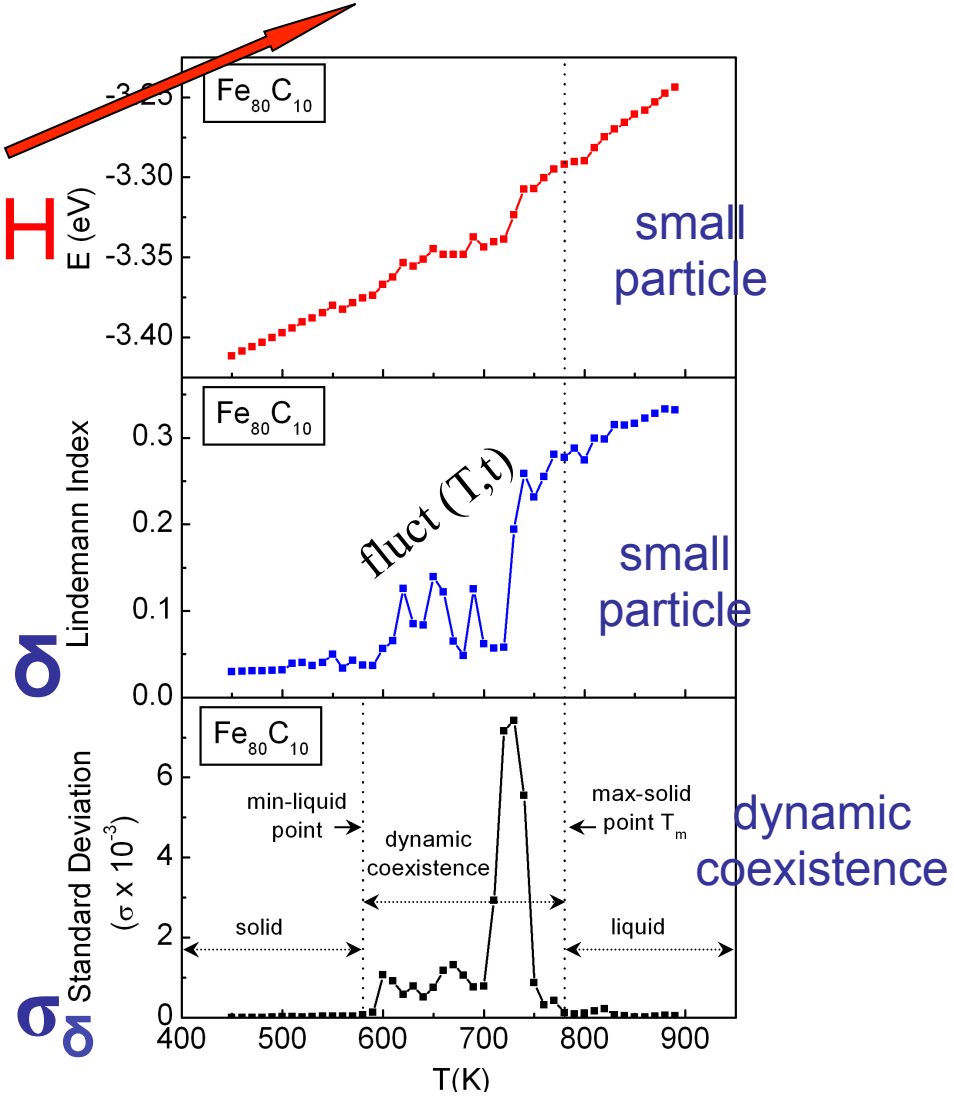
MD: Finite size: definition of T_m

Finite size melting in ΔT: max-solid (T_m)
Thermodynamics: caloric curve (ΔH_m)
Order Parameter: Lindemann Index (δ)

$$\delta \equiv \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}$$

liq~1/3,
sol<~0.1





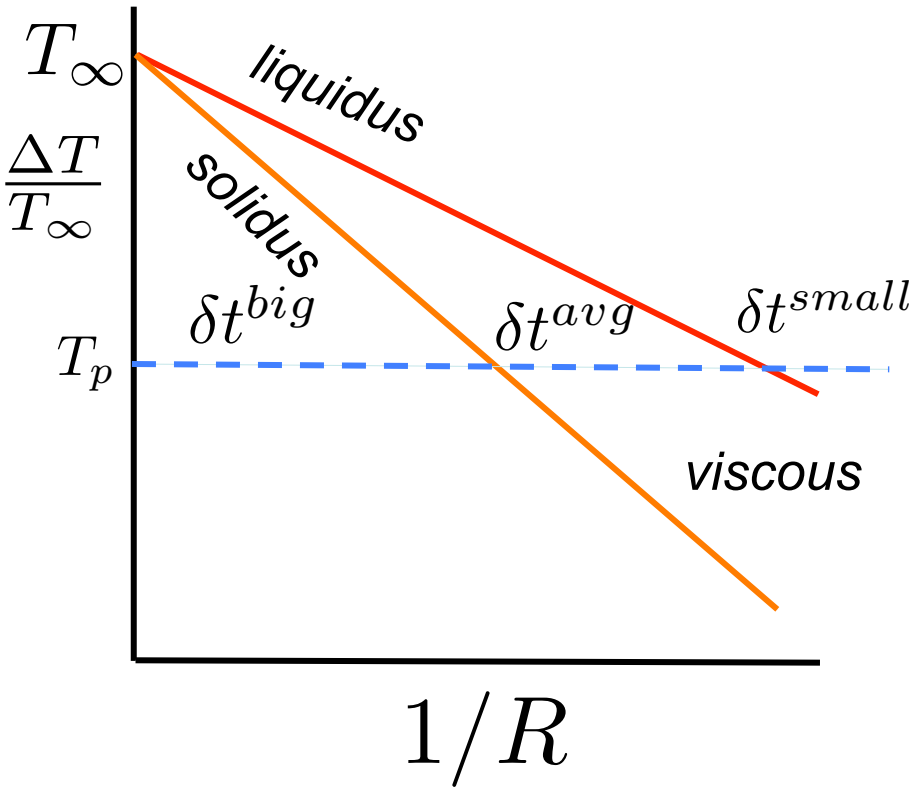
Alavi, Thompson, J. Phys. Chem. A **110**, 1518 (2006).
Jiang *et al,* Curtarolo, Phys Rev B **75**, 205426 (2007)

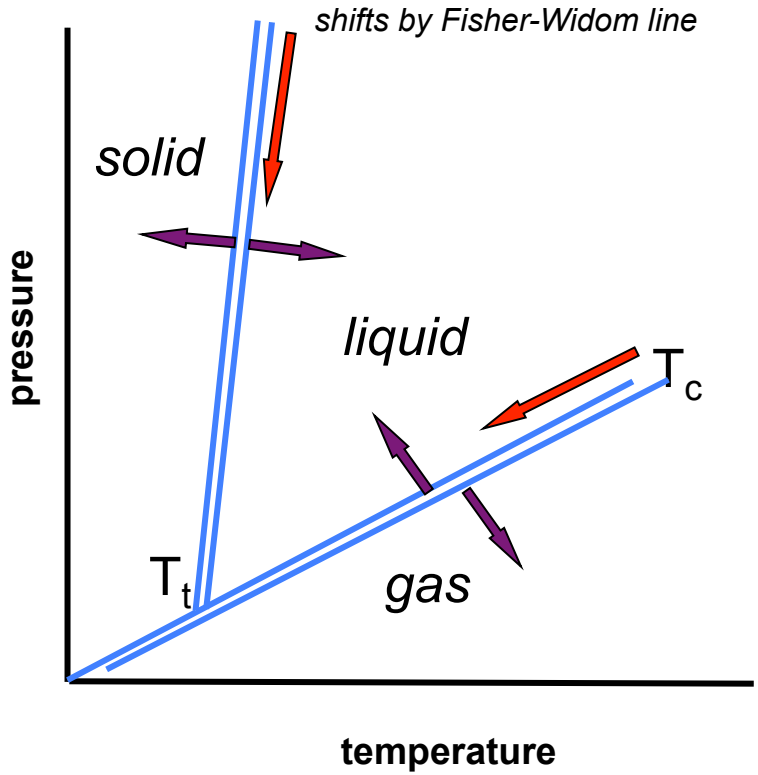
the Gibbs-Thomson tricks

$$(\delta P = 0 \rightarrow F = C - P + 1)$$

Gibbs phase rule (F=C-P+2)

- nanoscale “shape” is another degree of freedom
- *liquidus* and *solidus* also for single component systems
- two curves





min(sum)!=sum(min) => F=C-P+1 (get extra +1)

Fisher-Widom JCP 50, 3756 (1969)

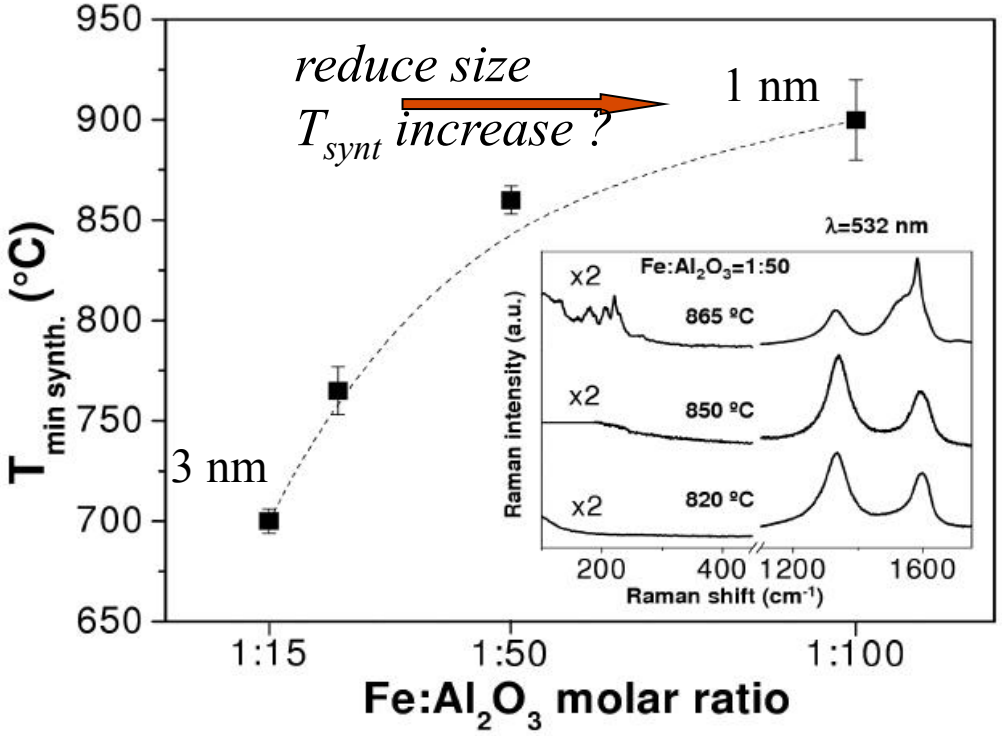
Question 2

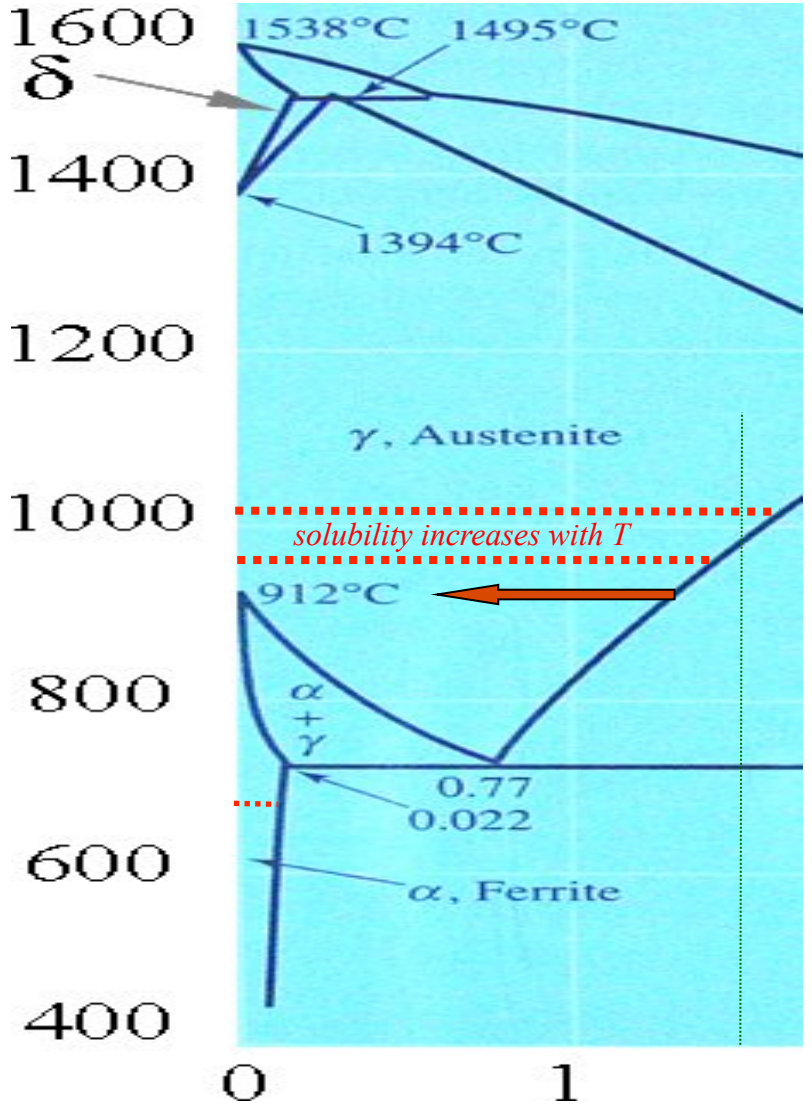
discuss an effect of phase boundaries movements at the nanoscale

HINT: catalysis of nanotubes

GIBBS-THOMSON paradox: PRL100, 195502

MIN synthesis $T_{min\text{-}synth}$ temperature of CVD nanotubes increases





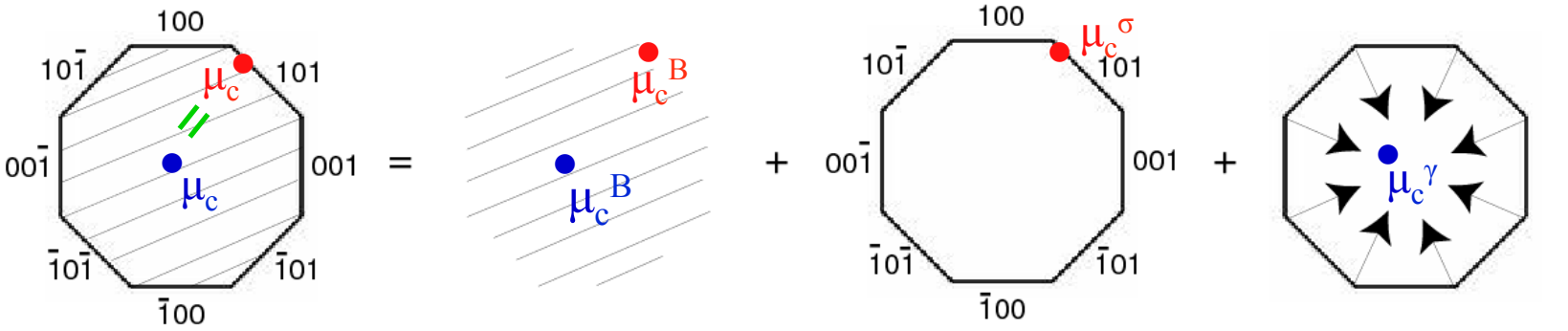
Phys. Rev. Lett. **100**, 195502 (2008)

QM-Model: assumptions

Interplay of 3 phases competing for stability active phase, poisoning phase and product.

They have energy which varies with size of particle, and temperature populates them differently!

THERMODYNAMICS



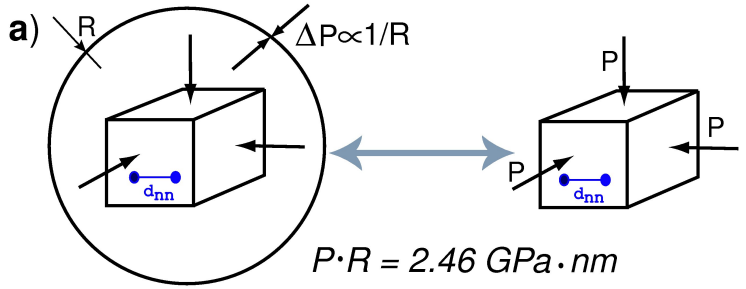
Free Energy = Bulk Energy + Surface Energy (σ) + Surface Tension (γ)

$F = \sim \int f\, d^3r + \sim \int \sigma\, d^2r + \sim \int \gamma / \langle R \rangle\, d^3r$

Stability of various competing phases as a function of size
(*size-pressure approx. similar to Young-Laplace equation)*

"Size-pressure approximation"

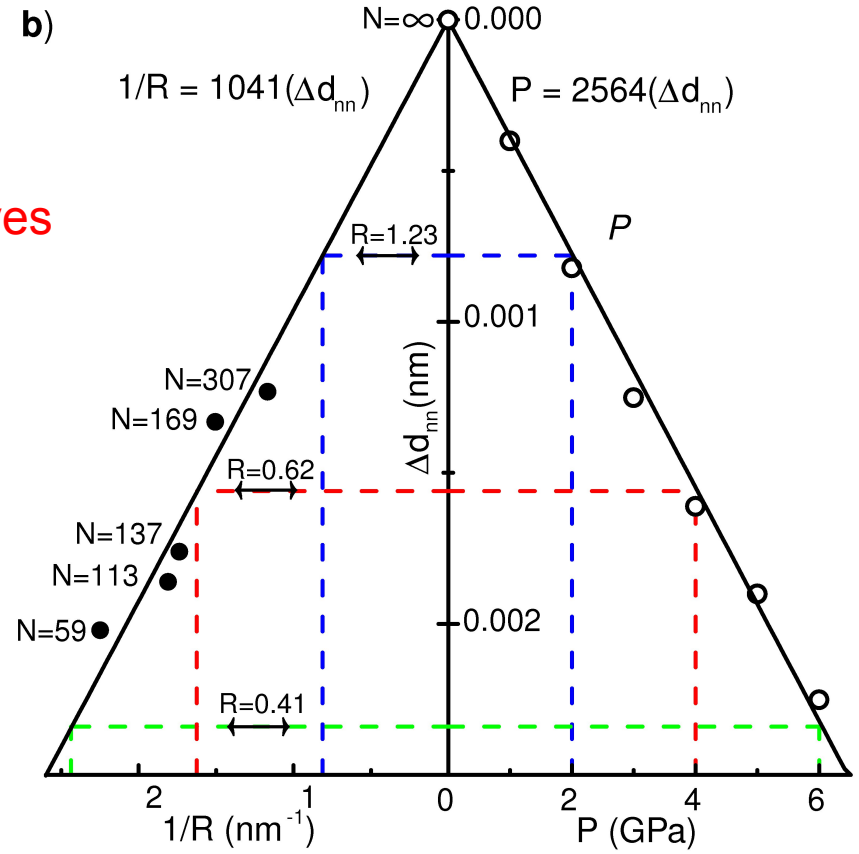
"Young-Laplace" equation
$P=2\gamma/R$

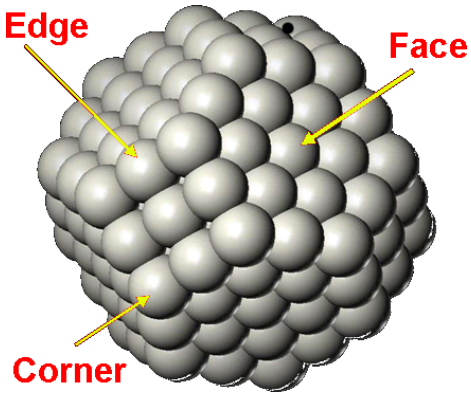


$P \cdot R = 2.46\ GPa \cdot nm$

<R> = avg(R) no
<1/R> = avg(1/R) yes

RADIUS
$$\frac{1}{R} \equiv \frac{1}{N_s} \sum_i^{N_s} \frac{1}{R_i}$$





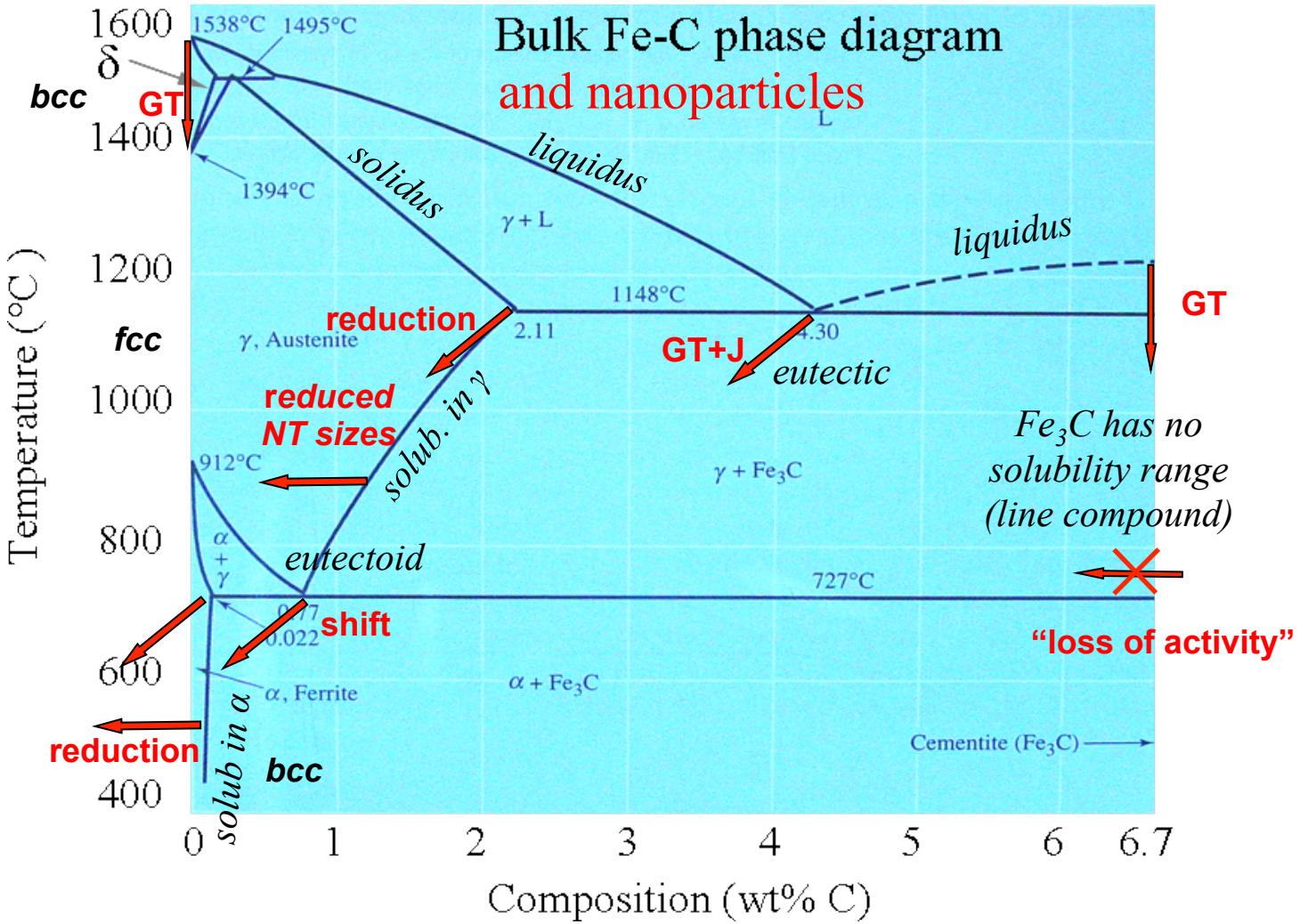
Phase diagram for spherical nanoparticles of radius R

Phase diagram for bulk system at corresponding hydrostatic pressure P

"Size-Pressure approximation" γ =1.23 J/m^2. True YL liquid Fe is γ ~1.85 J/m^2

[J. Campbell *Smithells' Metals Reference Booked*, Kim *et al.*, J. Mat. Res. **21** (6) 1399 (2006) DOI: 10.1557/JMR.2006.0171)

Reducing Size: Gibbs-Thomson Equation



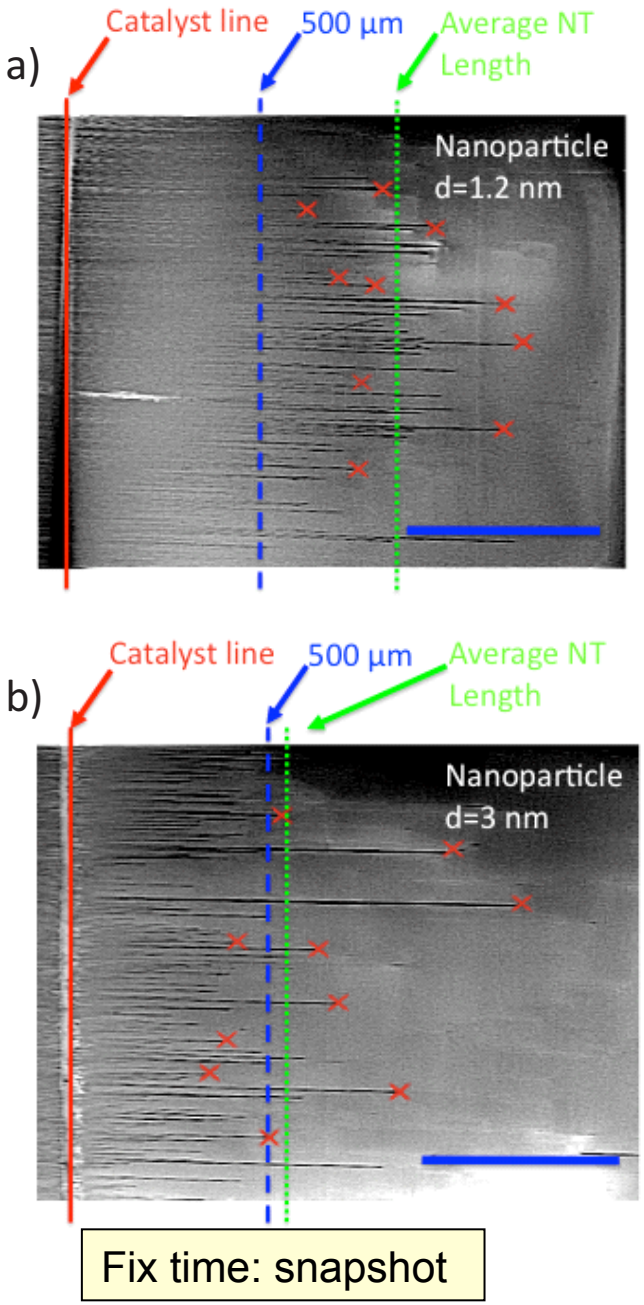
To explain shift of eutectic, there **must** be reduction of solubility !

Jiang, *et al,*, **SC**, PRB **75**, 205426 (2007)
SC *et al.,* Physics Procedia, **6**, 16-26 (2010)

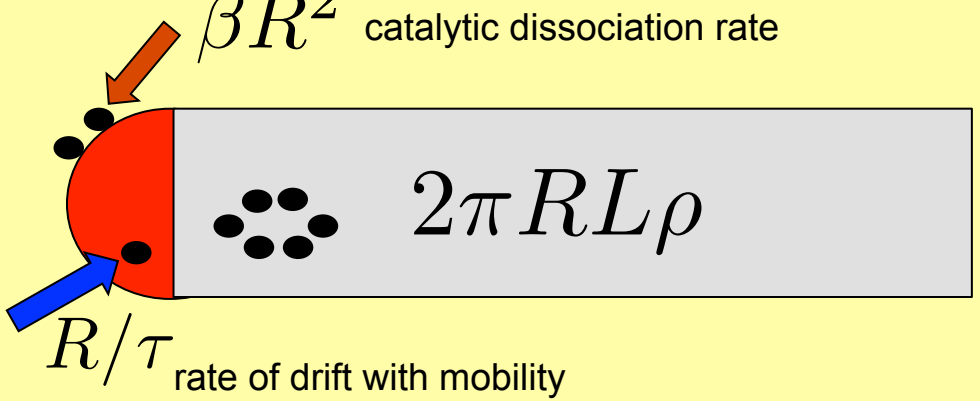
Question 3

is loss of ergodicity good or bad ?

Check this out: small particle => transforms faster ?



Fix time: snapshot



time-constant ratios

$$\frac{\tau_1}{\tau_2} = \left(\frac{R_1^2}{L_1}\right)\left(\frac{L_2}{R_2^2}\right)$$

viscous state effect

$$\frac{1}{\tau_1} > \frac{1}{\tau_2} > \frac{1}{\tau_3}$$

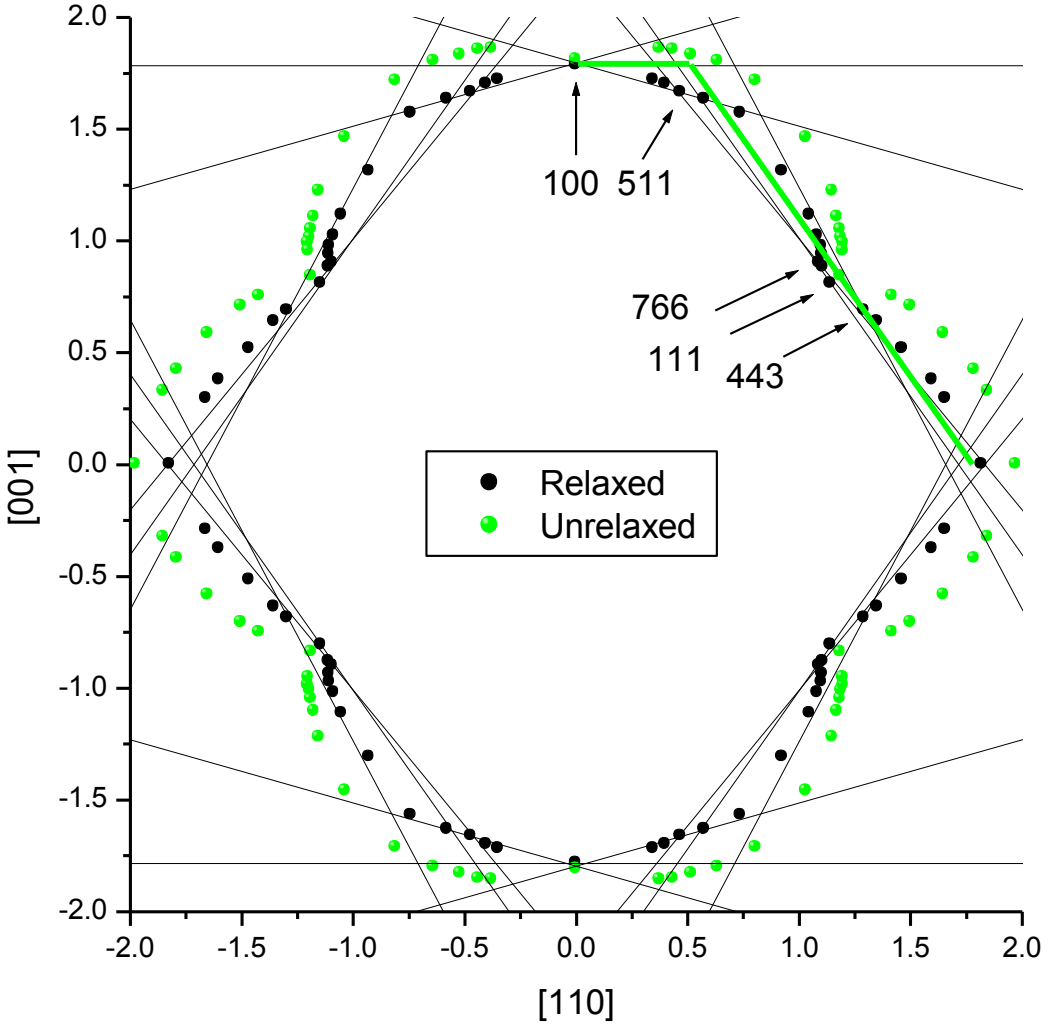
ACS NANO 4(11), 6950 (2010)

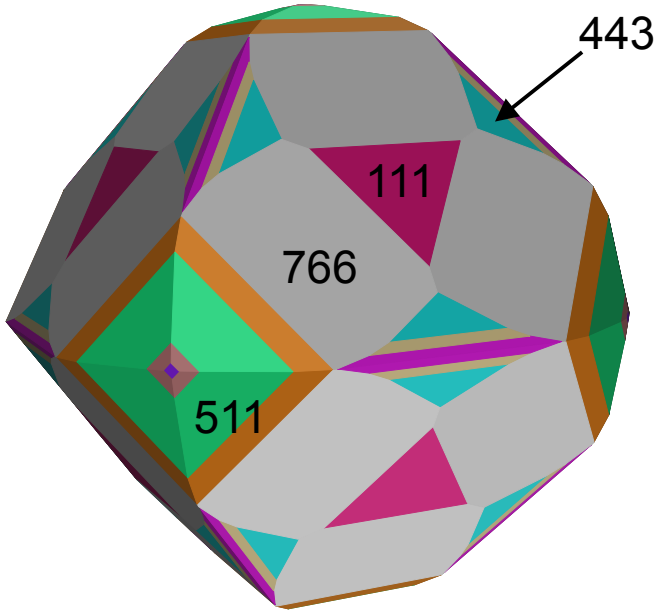
Question 4

Can you extend the Wullf construction to negative surface tensions?

Wulff construction

(110) cross section of Wulff's plot

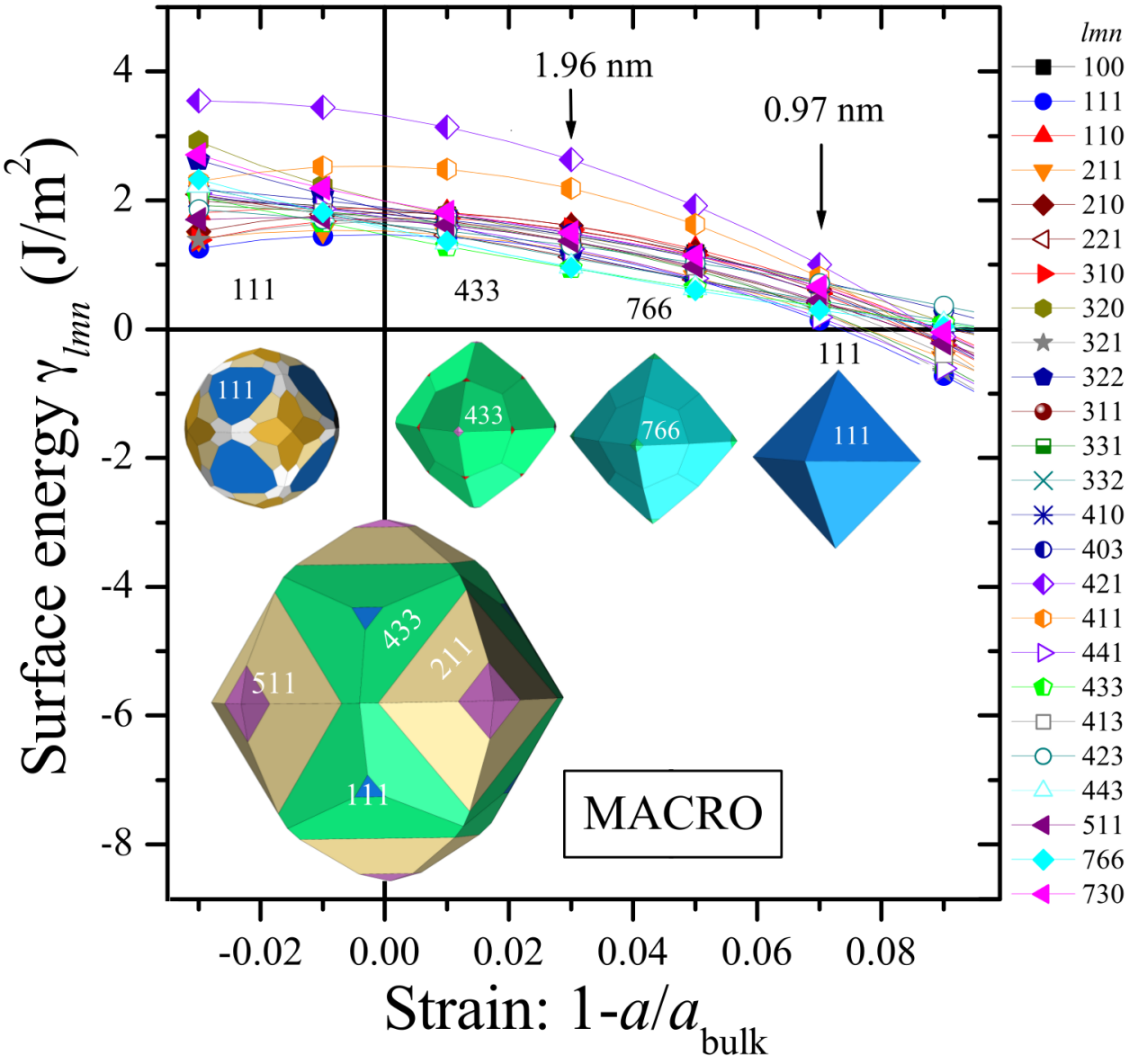




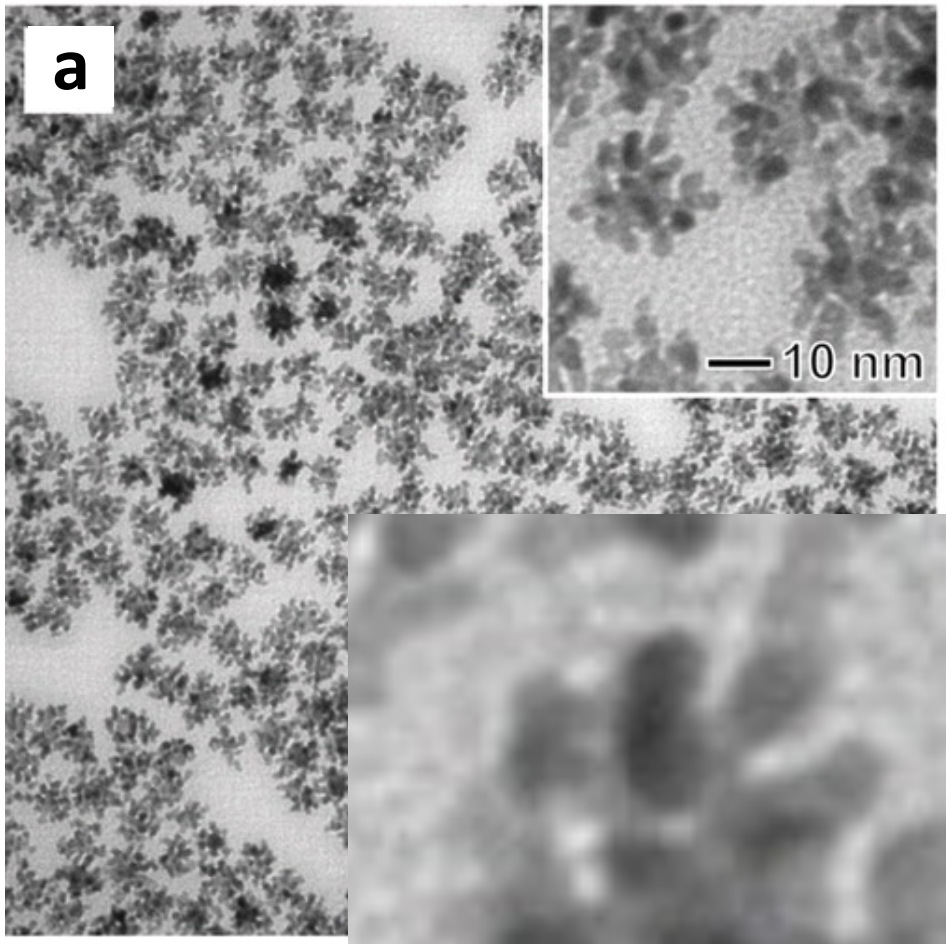
surf tension is the key quantity for very small nano-crystals.

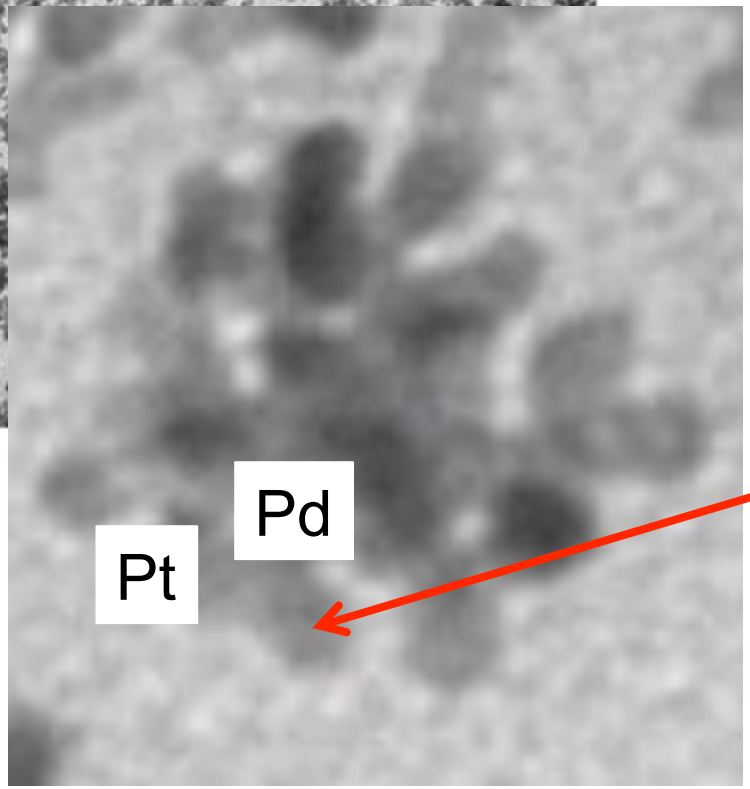
Six common shapes with (100) and (111) facets:
Peng, Yang, Nano Today **4**, 143 (2009)
Tetrahexahedron with (730) facets: Tian et al., Science **316**, 732 (2007)

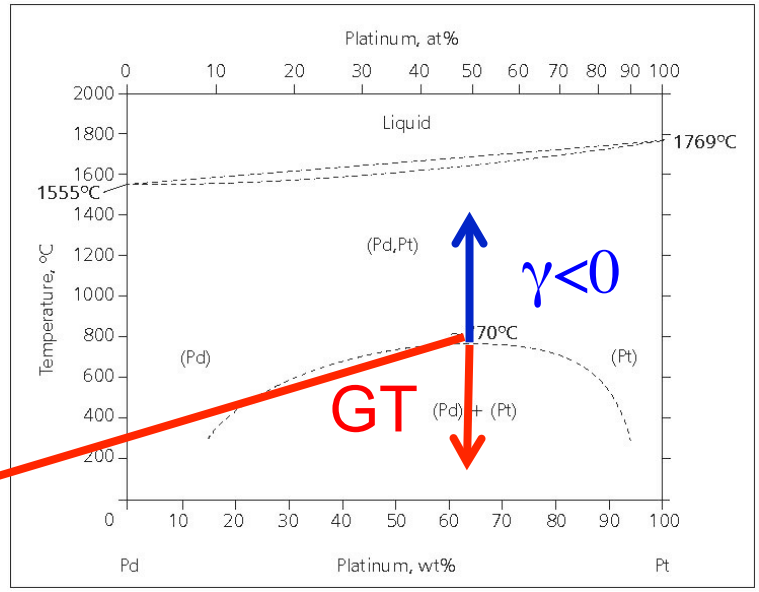
Wulff


Surface energy γ_{lmn} (J/m^2)
Strain: 1-a/a_{bulk}
1.96 nm
0.97 nm
111
433
766
111
MACRO
433
211
511
111
lmn
100
111
110
211
210
221
310
320
321
322
311
331
332
410
403
421
411
441
433
413
423
443
511
766
730

Oxygen reduction reaction on Pt surfaces, rate-determining step in a proton-exchange membrane fuel cell





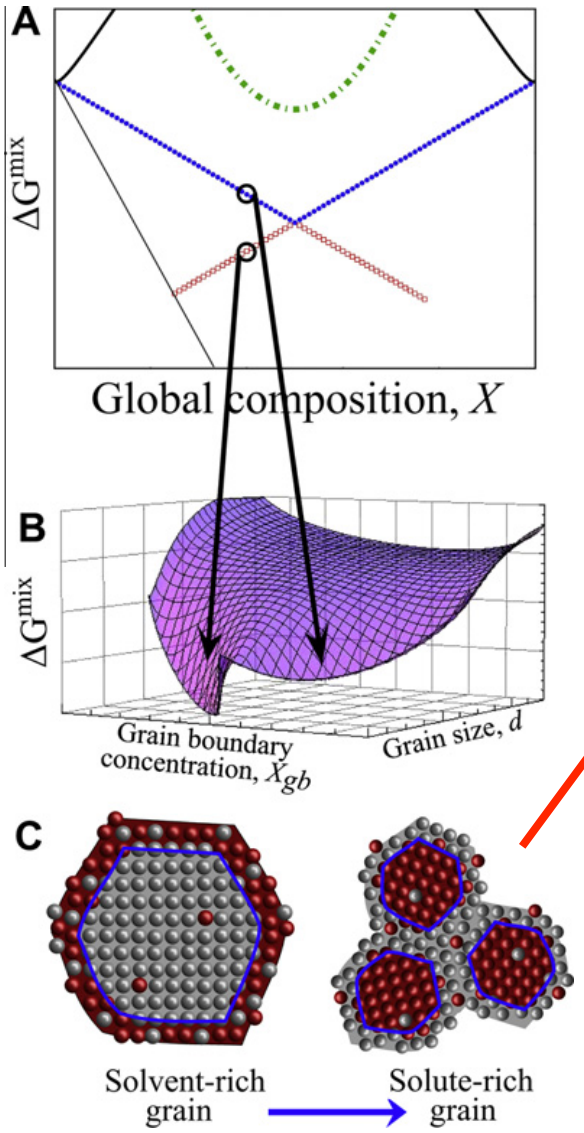


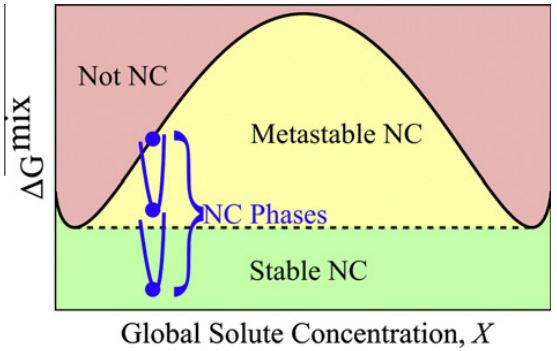
Lim et. al.. Pd-Pt bimetallic nanodendrites with high activity, Science **324**, 1302 (2009)

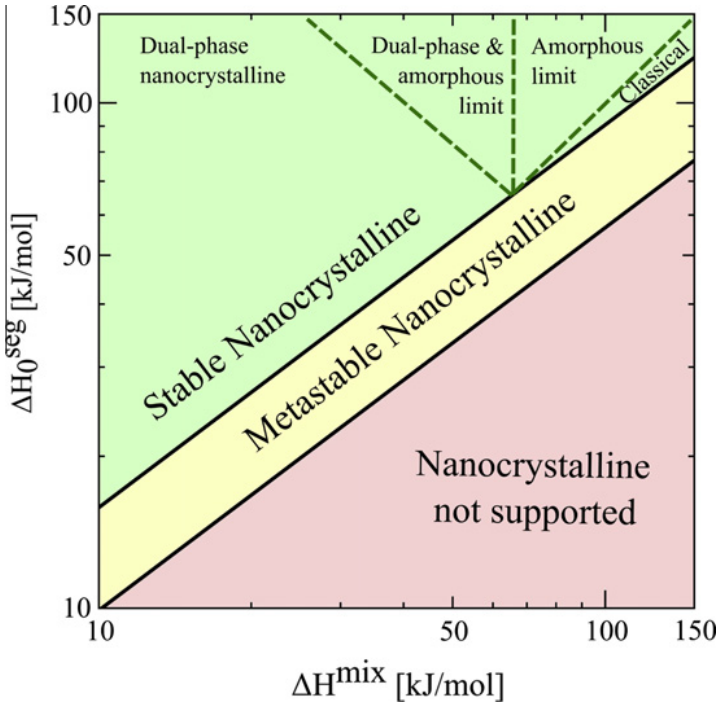
Question 5

Can you control coarsening at the nanoscale ?

Control coarsening in nanograins by alloying

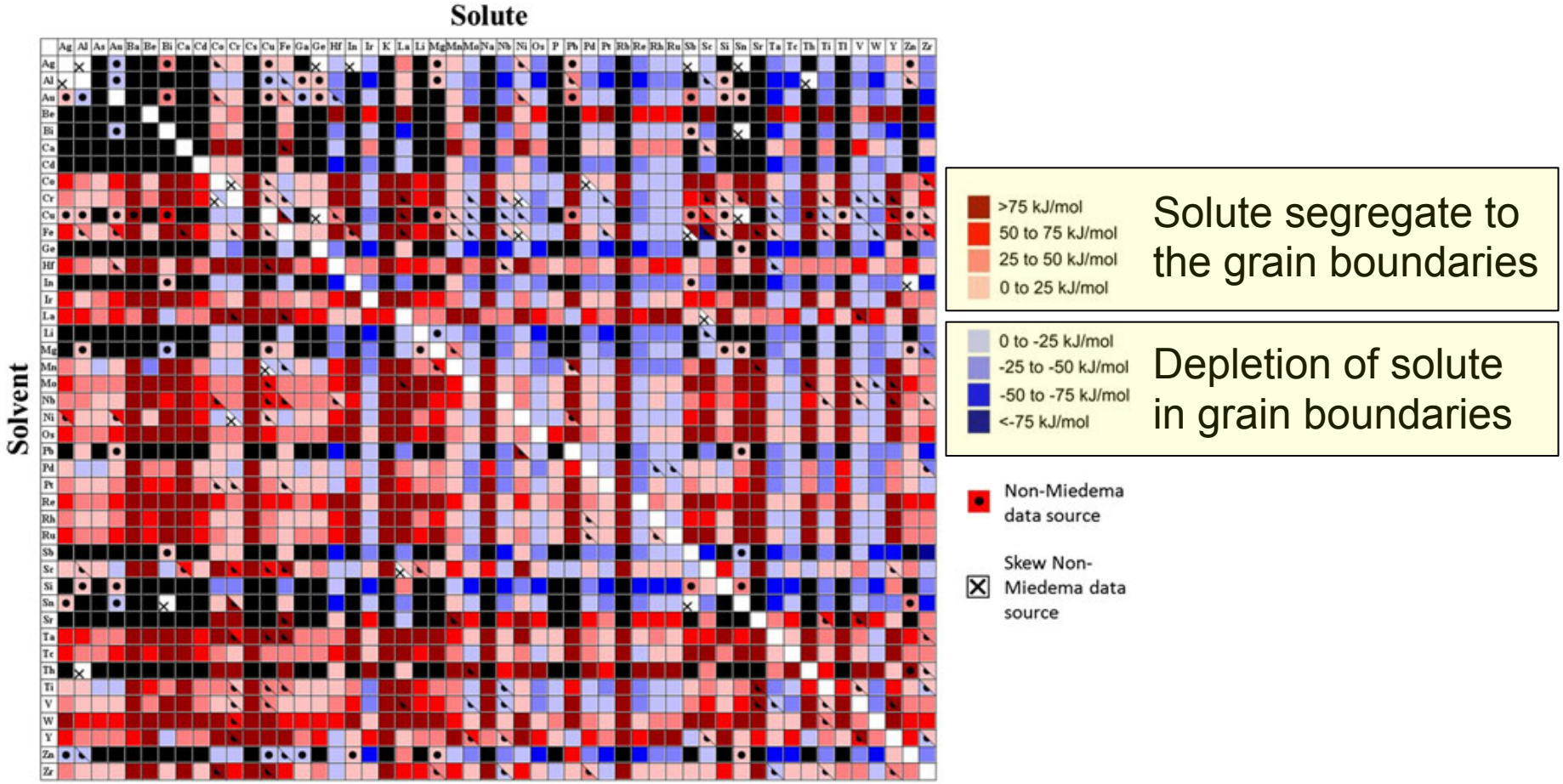






Murdoch, Schuh, *Stability nanocrystalline alloys grain growth phase separation.* Acta Mat. **61**, 2121 (2013)

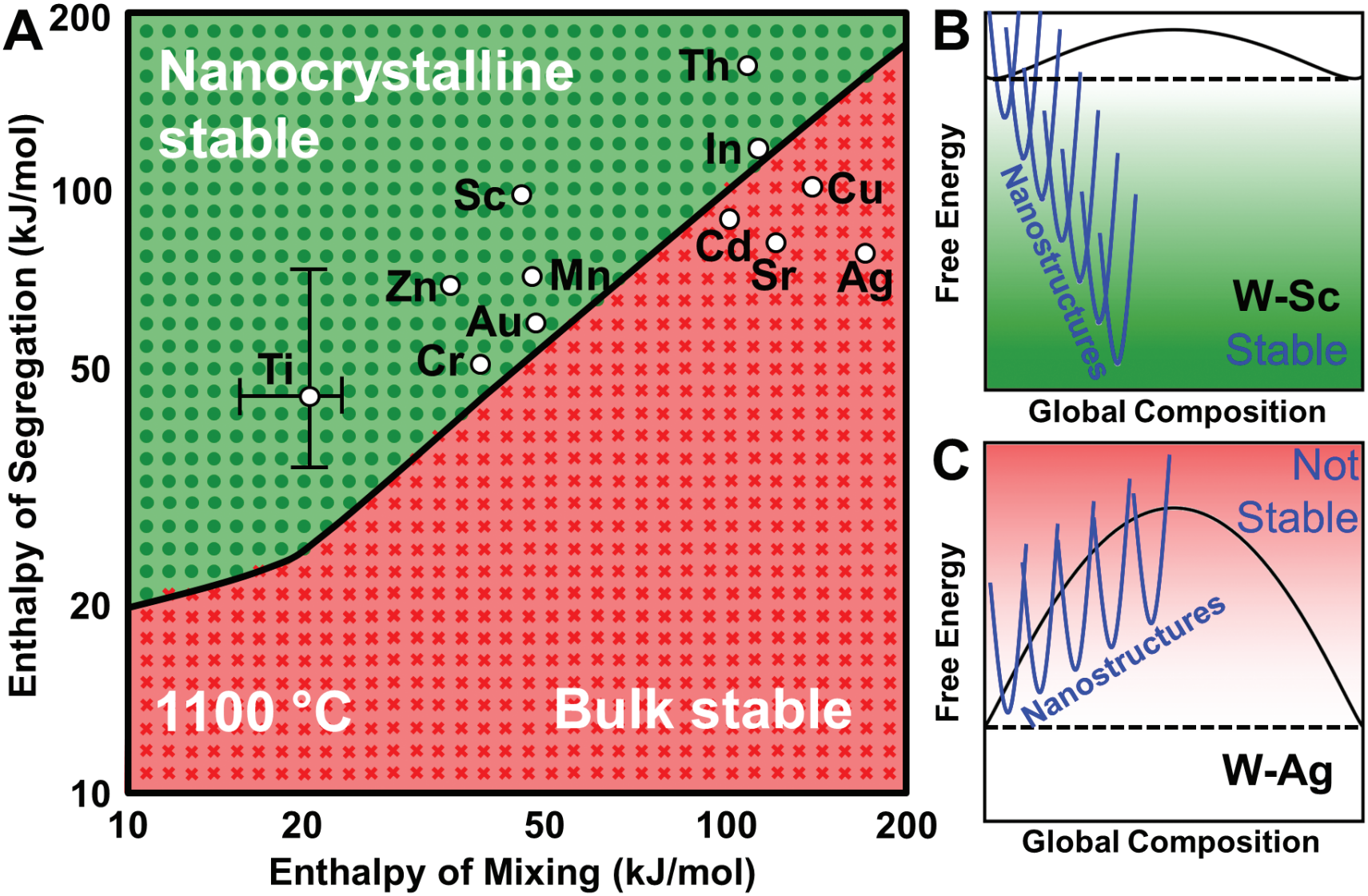
Segregation enthalpies for binary systems (estimation)



Phenomenological, Miedema and so on.

Murdoch and Schuh, J. Mater. Res. **28**, 16, Aug (2013)

Let`s see tungsten+something

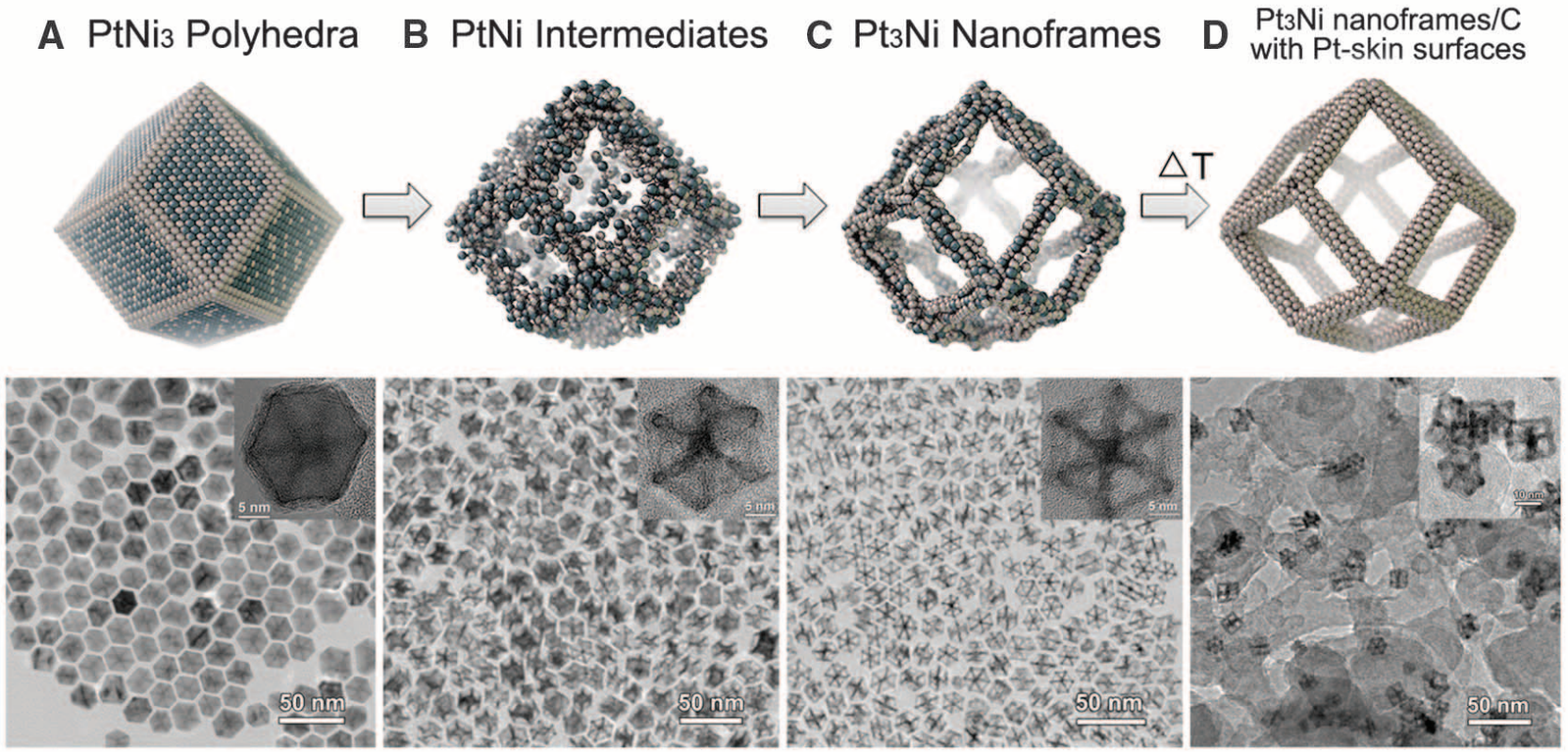


Chookajorn, Murdoch, Schuh, *Design of stable nanocrystalline alloys*. Science **337**, 951 (2012)

Question 6

What supports nanoframes ?

We like internal erosion



for OXYGEN REDUCTION REACTION

nanoframe catalysts = 36 mass activity,
22 specific activity, versus Pt-carbon catalyst

Chen et al., Highly Crystalline Nanoframes Electrocatalytic, Science **343**, 1339 (2014)

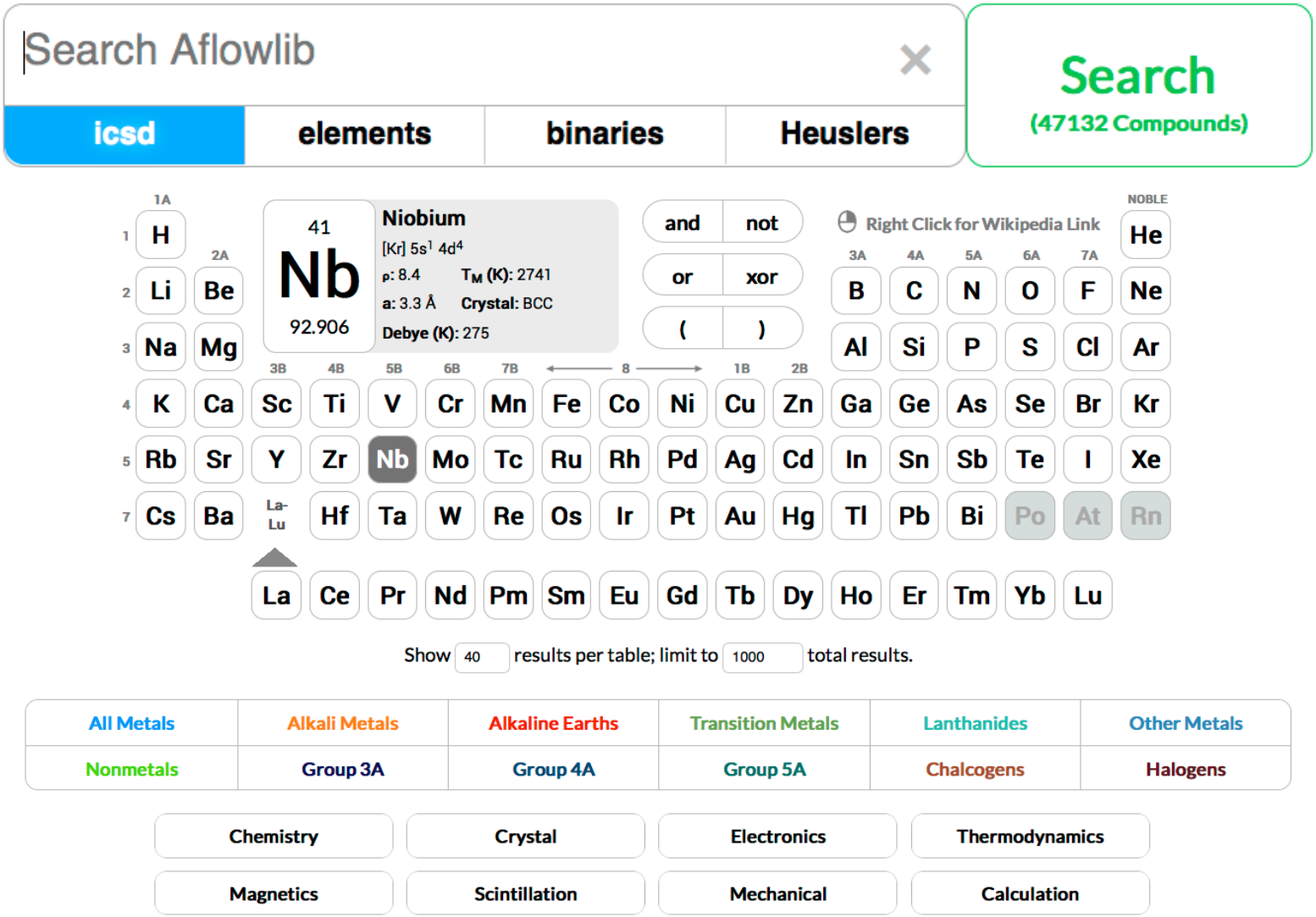
Question 7

Can you find thermodynamic data on GOOGLE-nano-materials ?

Consortium of QM calculations

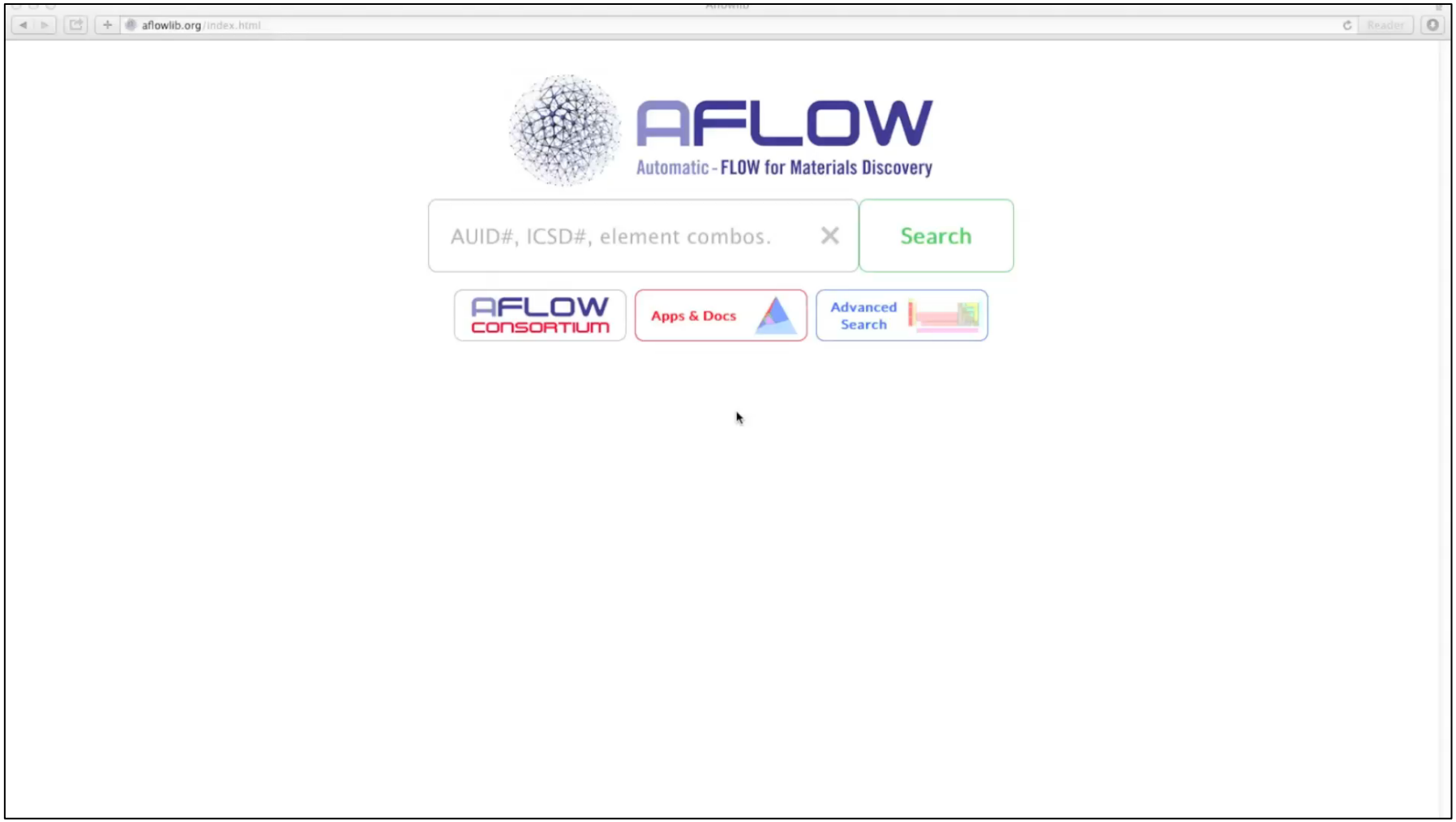
AFLOWLIB.ORG: Comp. Mat. Sci. **58**, 227 (2012)

Consortium of QM calculations



api

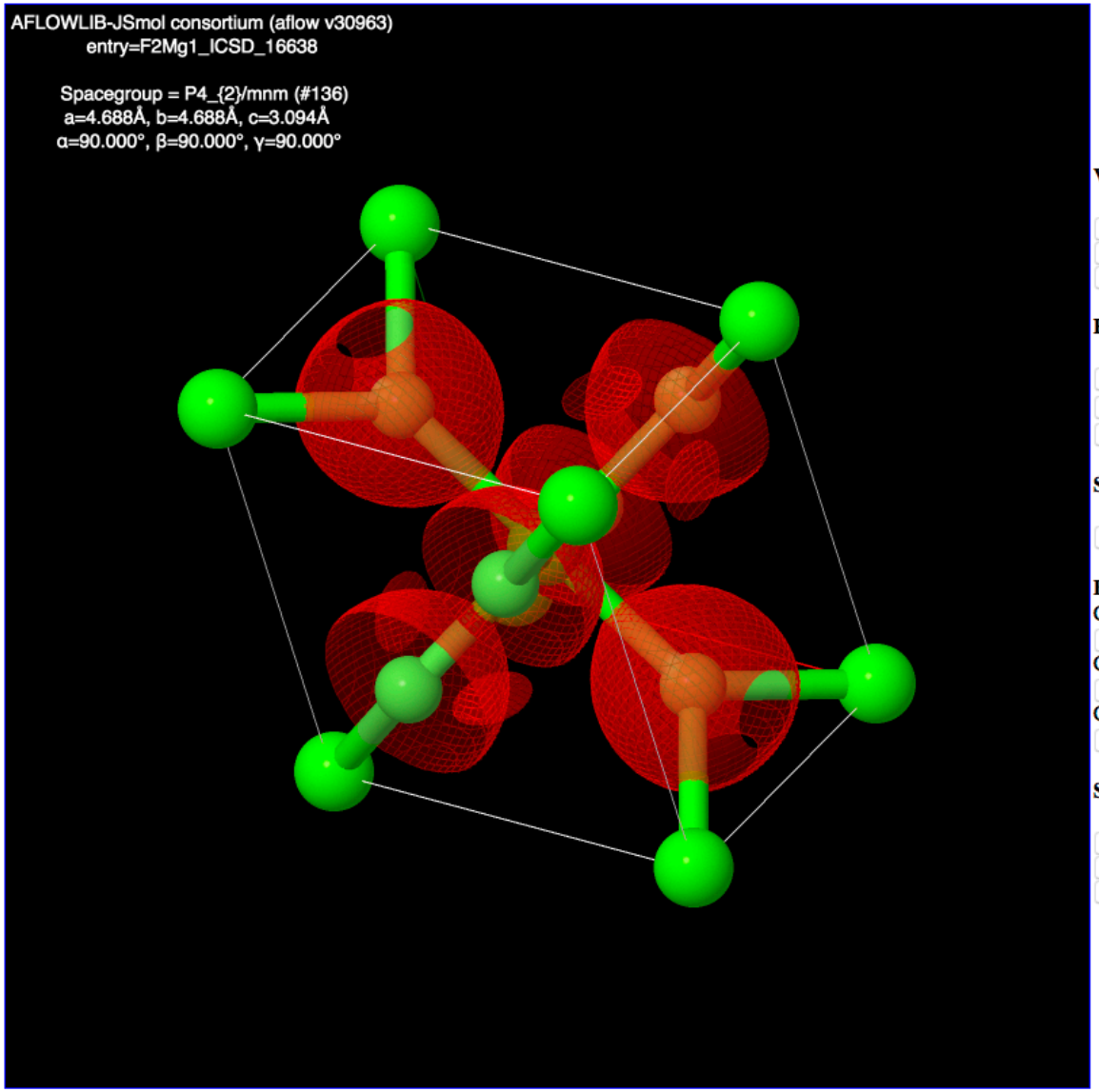
Example of QM calculation



api

See where charge is

Space Group: P4_{2}/mnm (#136)



Visualizer options:

Ball & Stick	Spacefill
Rotation On	Rotation Off
Label On	Label Off

Relaxed structure:

As calculated	
Standard conventional	[info]
Standard primitive	[info]

Supercell:

2x2x2	RESET

Bader Isosurfaces:

Cutoff = 0.25

F	Mg	All

Cutoff = 0.50

F	Mg	All

Cutoff = 0.75

F	Mg	All

Save:

Save CIF FILE	Save STATE
Save JPG	Save PNG
Save Jmol	Save PNG+Jmol

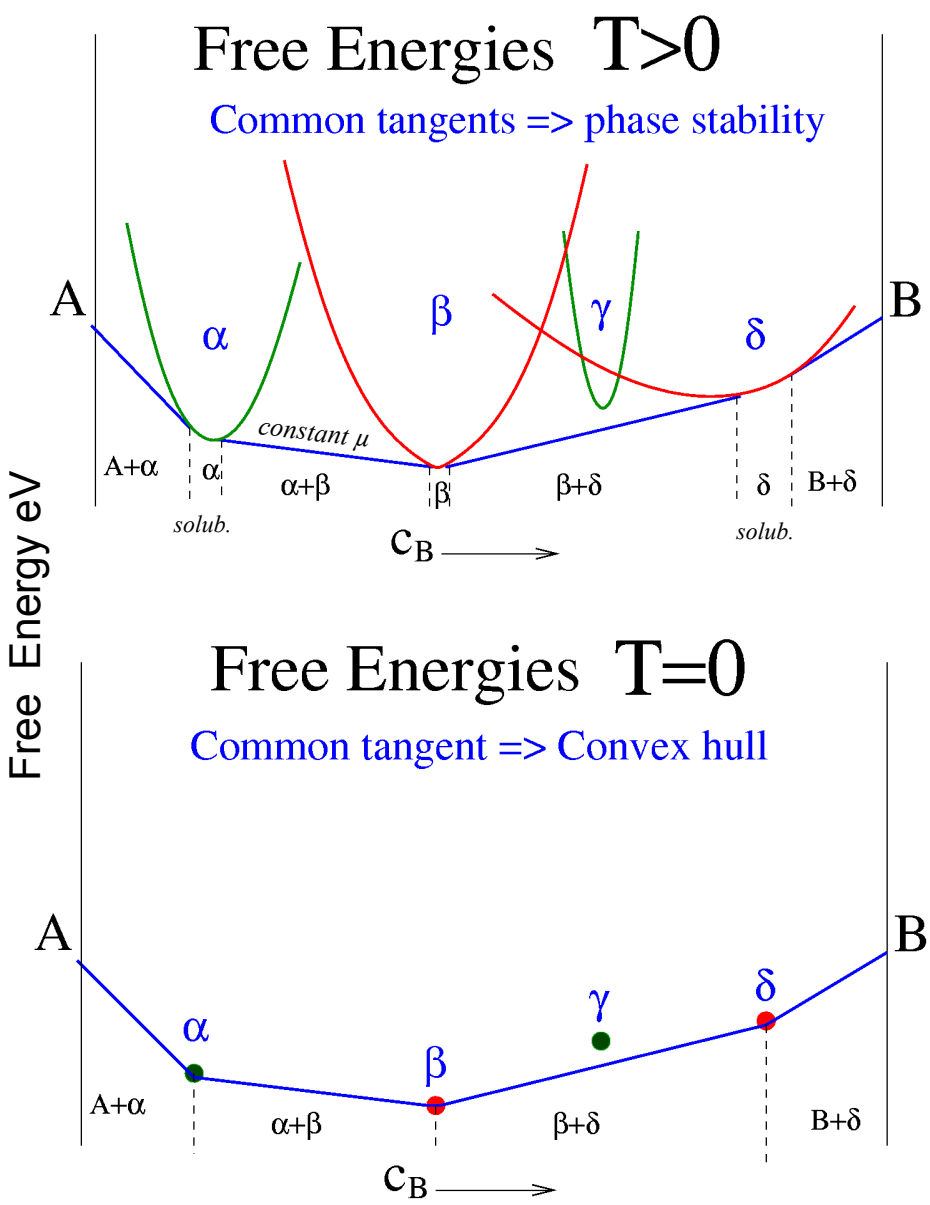
api

NANO is going CLOUD

aflowlib.org

FINISHED

Materials Thermodynamics: Phase stability



- **dE=-pdV+TdS+μdX**
- **G=E+pV-TS (for p,T,X variables)**
- **dG=Vdp-SdT+μdX**

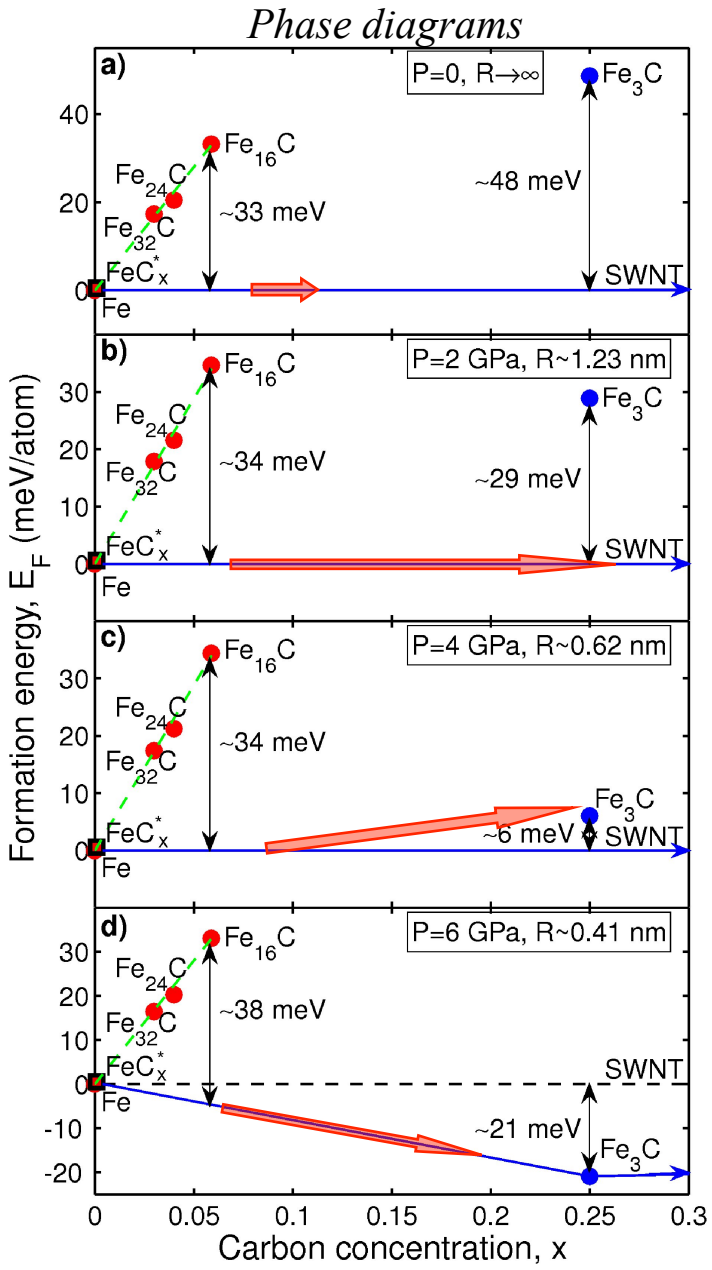
eq: μ=dG/dX (const p,T)

T>0: phase's free energies are "parabolas" because of configuration entropy: they allow out of stoichiometric composition.

T=0: phase's free energies are "energy points" (F=E-TS=E), points are minima of the "parabolas" ⇒ good approximation.

T>0: need S
big: configurational ~ –k[x logx+(1-x)log(1-x)]
small: vibrational (gas of phonons) & electrons

Reduced solubility caused by stabilization of Fe_3C



Phys. Rev. Lett. **100**, 195502 (2008)

Bulk

- C prefers to dissolve in Fe-rich environment
- Fe_3C unstable

R ~ 1.4 nm, D ~ 2.8 nm

- Less C dissolves in Fe to form random Fe-C
- Fe_3C unstable with high energy, never forms
- **STEADY STATE IS POSSIBLE** for big tubes !

R ~ 0.7 nm, D ~ 1.4 nm

- Lesser C dissolves to form random Fe-C
- Fe_3C unstable with how energy, will form with T and saturation of C.
- **STEADY STATE IMPOSSIBLE,** SWNTs will be finite.

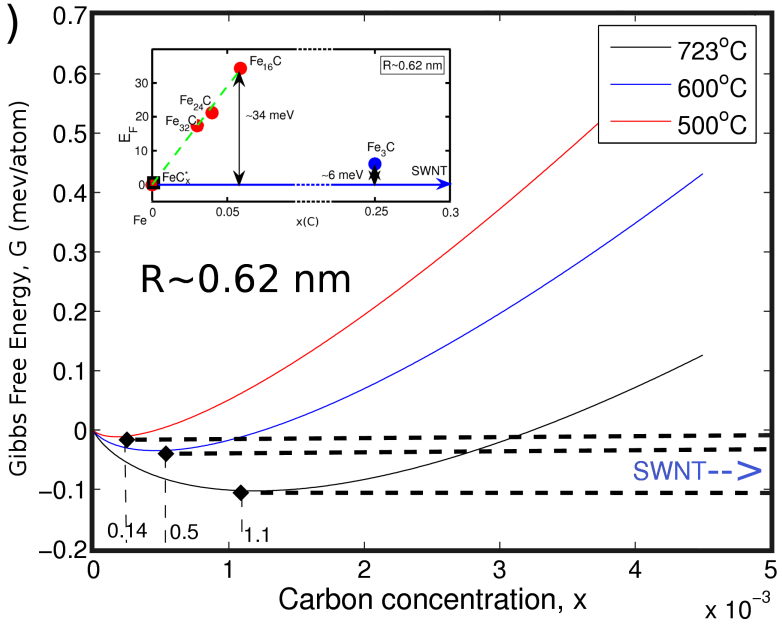
R ~ 0.5 nm, D ~ 1.0 nm

- Fe_3C is stable
- No production, just nucleation of Fe_3C.

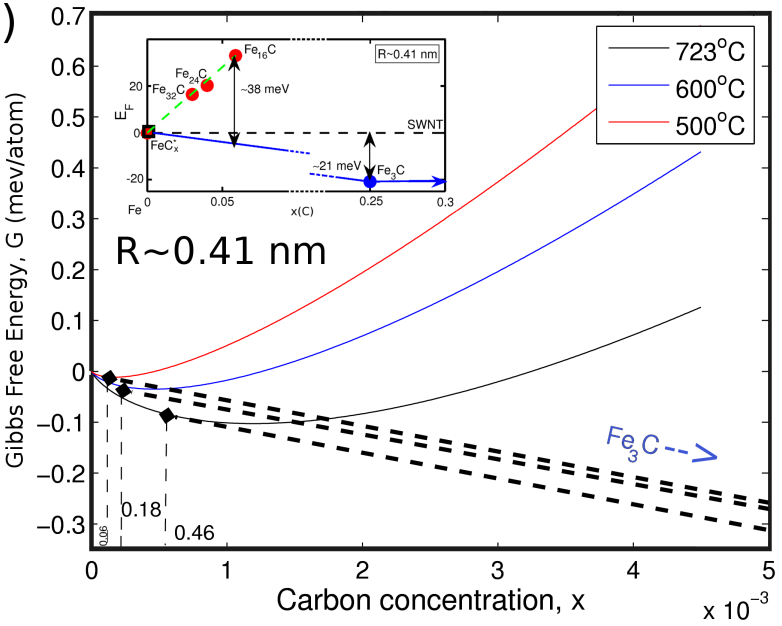
SWNTs with D<1.2nm CAN NOT be grown with Fe and CVD

Real calculation: thermodynamics

a)



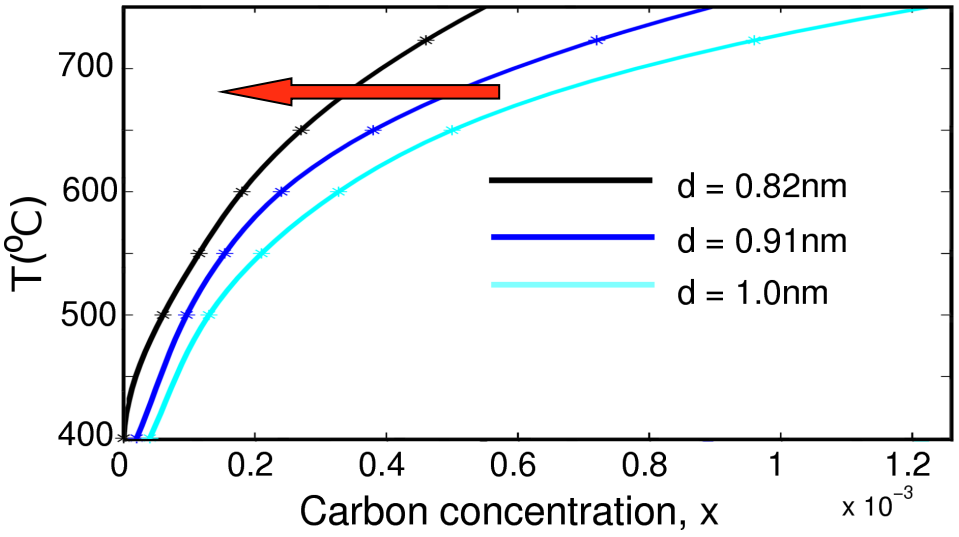
b)



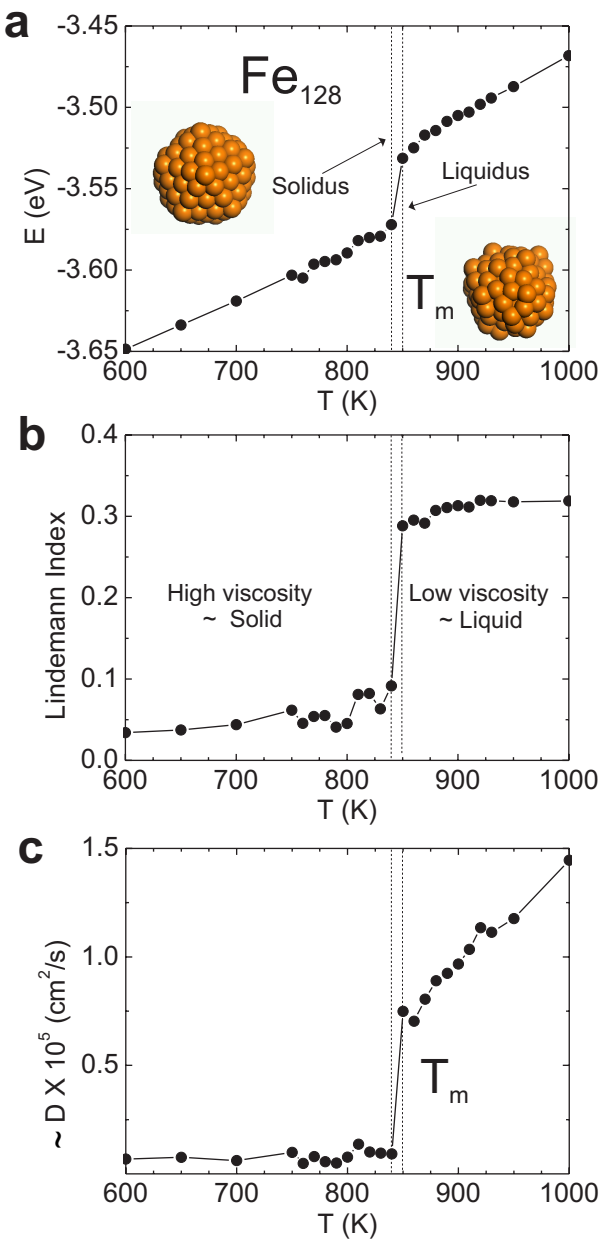
dE=-pdV+TdS+μdX
Gibbs : G=E+pV-TS (for p,T,X variables)
dG=Vdp-SdT+μdX
eq: μ=dG/dX (const p,T) *tangents*

S= Configurational (ideal max ΔS~0.7 kB/atom) –k[x.logx+(1-x).log(1-x)]
vibrational (ΔS~0.1-0.2k_B/atom) and electronic neglected

Solubility as a function of D !

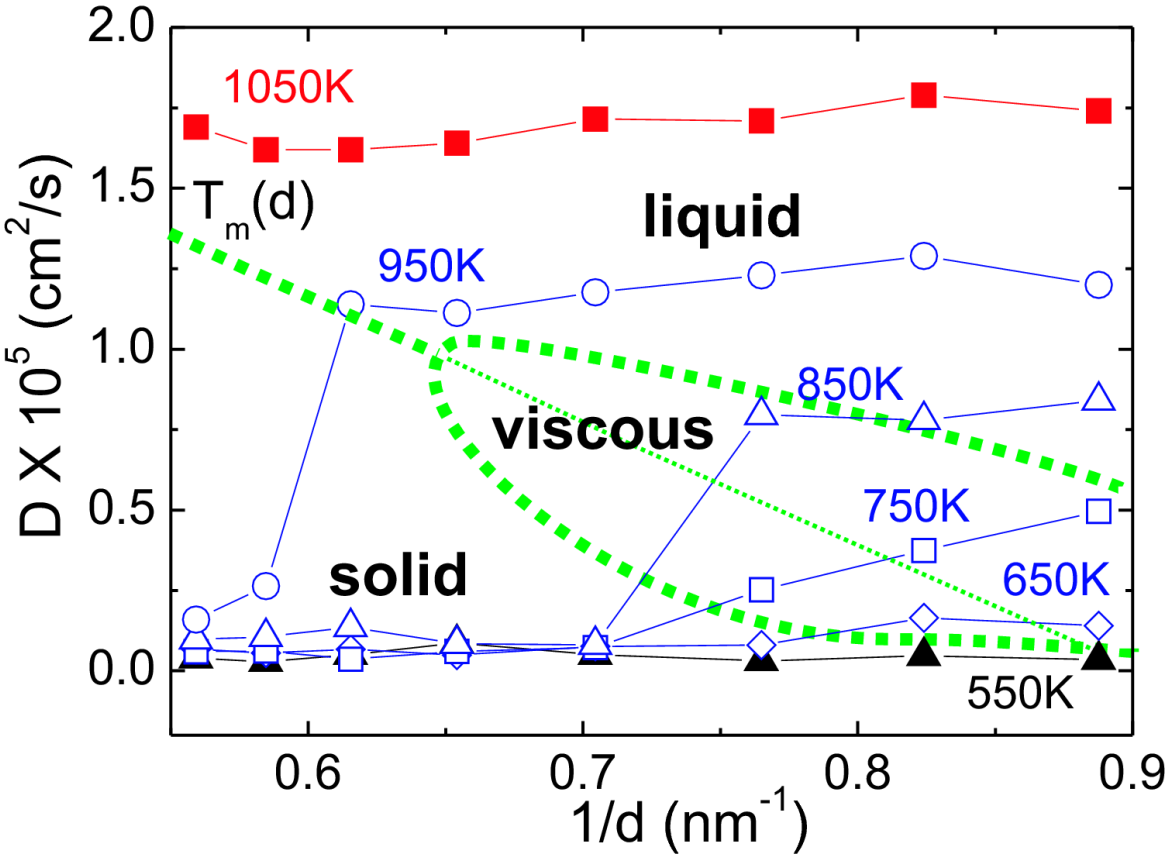


What about kinetics ? (viscous state effect on the activity)



quasi-SELF-DIFFUSION

(Green-Kubo, autocorrelation function)



T=fixed: small particle => more "fluid" => transforms faster ?

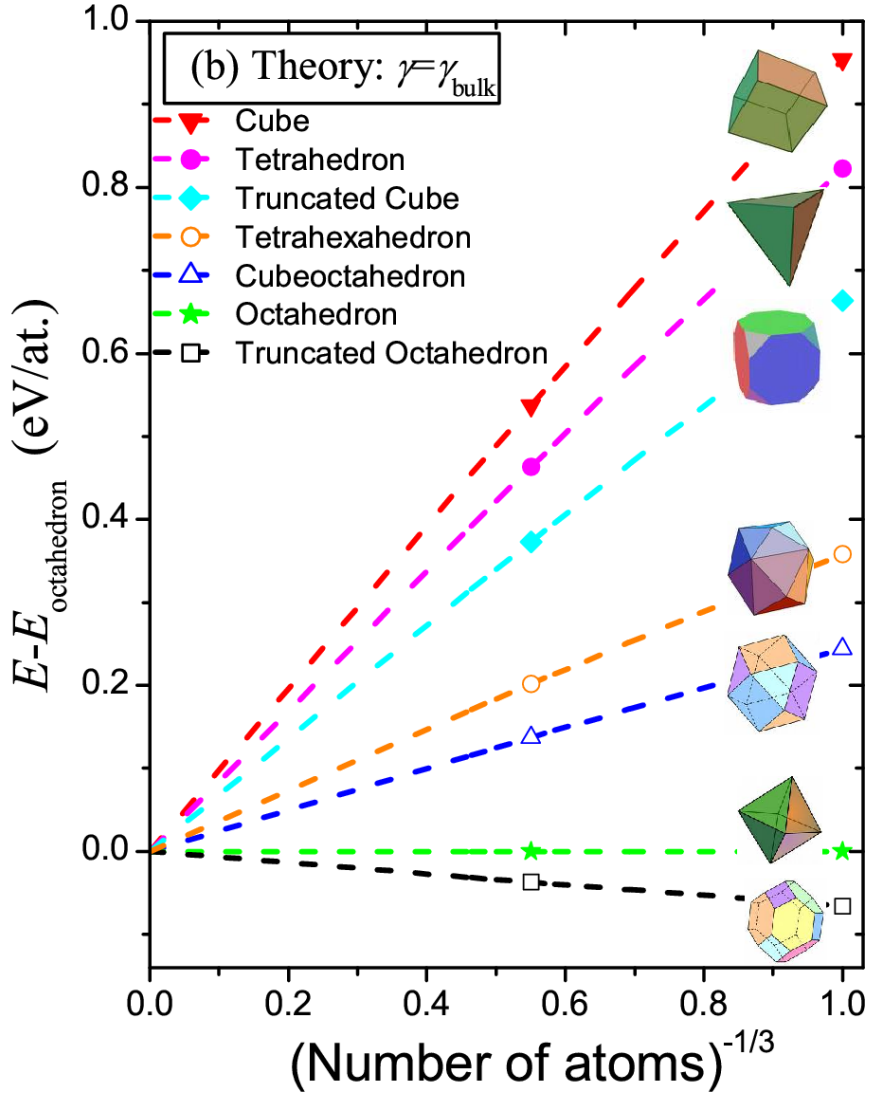
ACS-NANO **4**(11), 6950-6956 (2010)

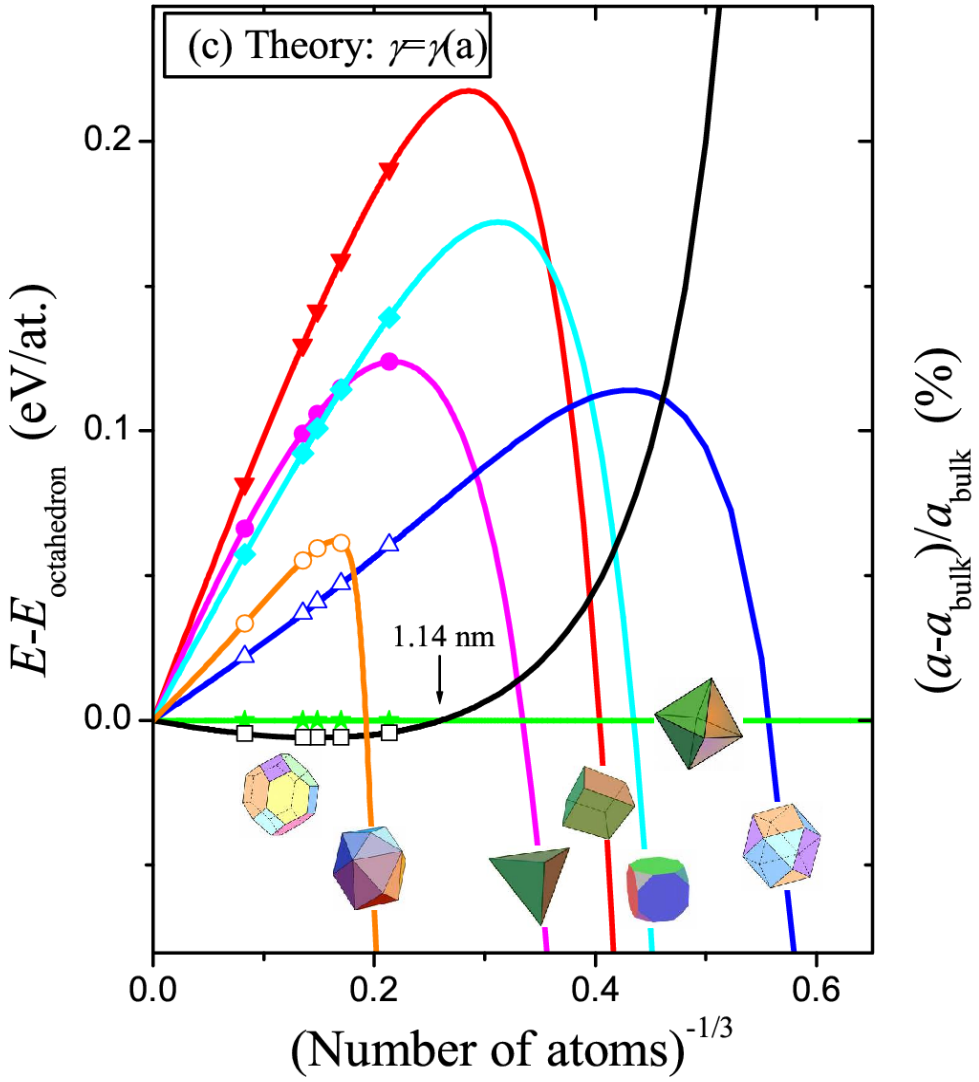
Question 4

Explaining weird shapes?

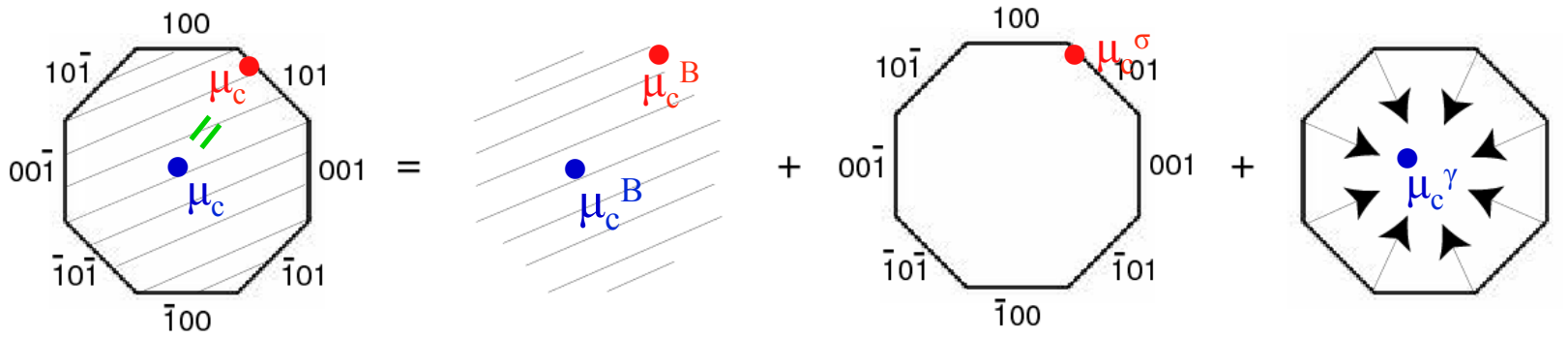
Variational Description of surface tension contribution: Pt

Six common shapes with (100) and (111) facets: Peng, Yang, Nano Today **4**, 143 (2009)
Tetrahexahedron with (730) facets: Tian et al., Science **316**, 732 (2007)





Variational Description of surface tension contribution: Pt



Free Energy = Bulk Energy + Surface Energy (σ) + Surface Tension (γ)

$$F = \sim\int f\, d^3r + \sim\int \sigma\, d^2r + \sim\int \gamma/\langle R\rangle\, d^3r$$

Stability of competing phases as function of size (size-pressure ~ Young-Laplace)

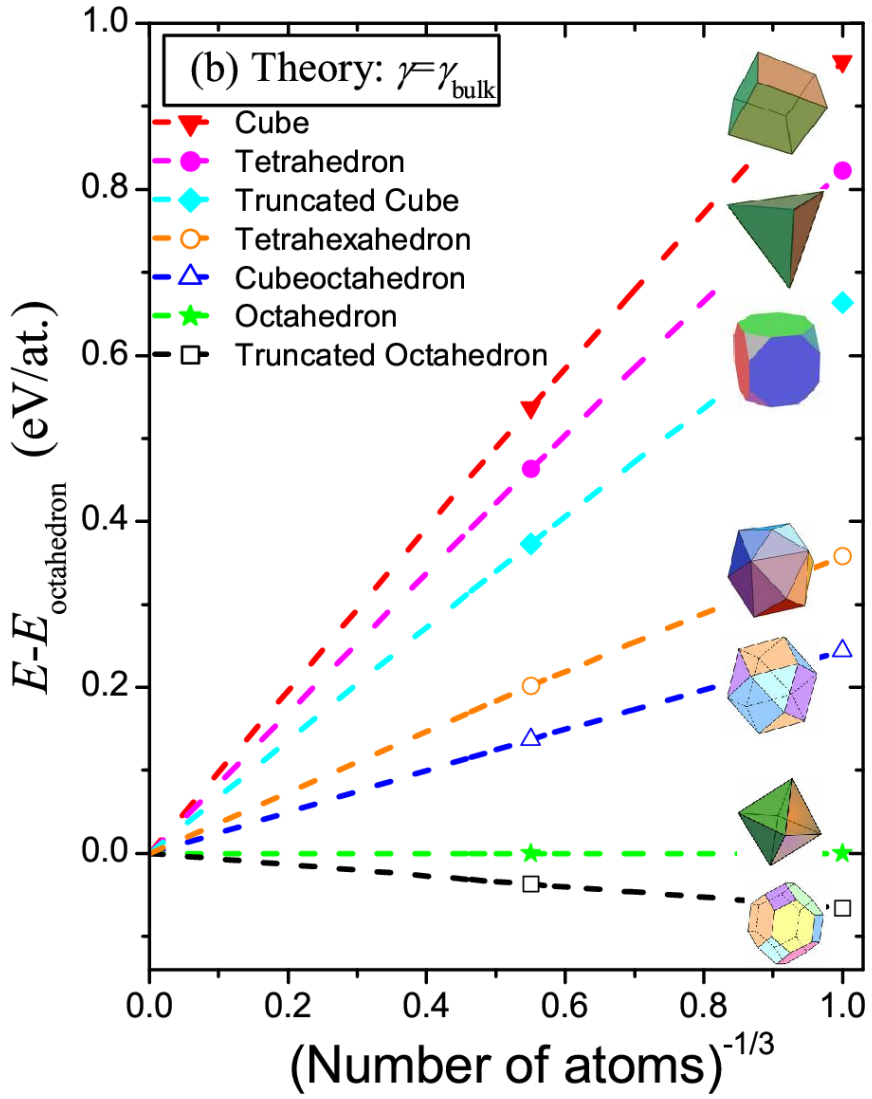
$$E(a) = E_{\mathtt{bulk}}(a) + \sum_{lmn} \sigma_{lmn}(a) S_{lmn}(a)$$

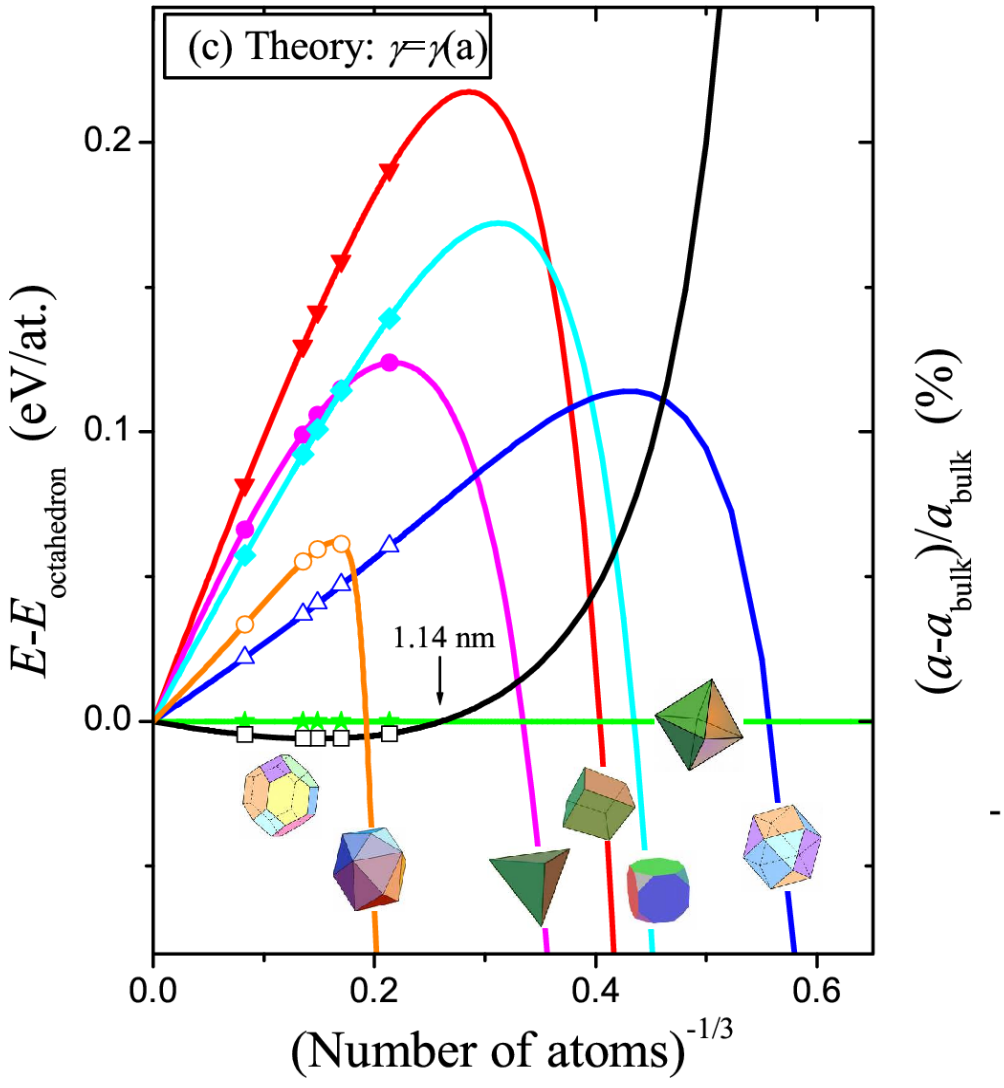
$$E = E(a)\big|_{\frac{\delta E}{\delta a}=0}$$

We chose Platinum: ***unexplained experiments***

Ab Initio Insights on the Shapes of Pt nano-catalysts, ACS-NANO **5**(1), 247-254 (2011)

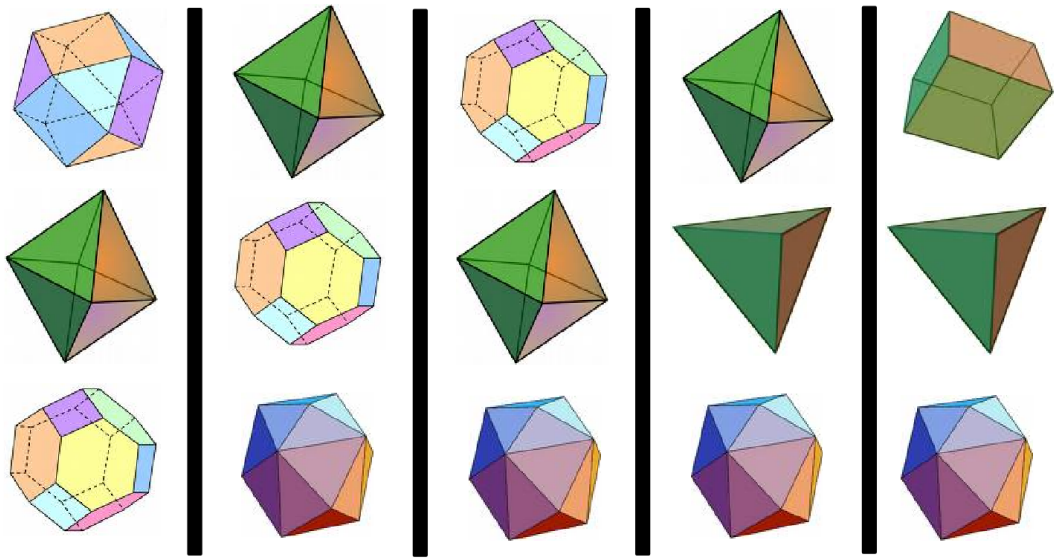
Six common shapes with (100) and (111) facets: Peng, Yang, Nano Today **4**, 143 (2009)
Tetrahexahedron with (730) facets: Tian et al., Science **316**, 732 (2007)





Size-dependent stability of Pt nanocatalysts

Pt three most stable nanocrystals



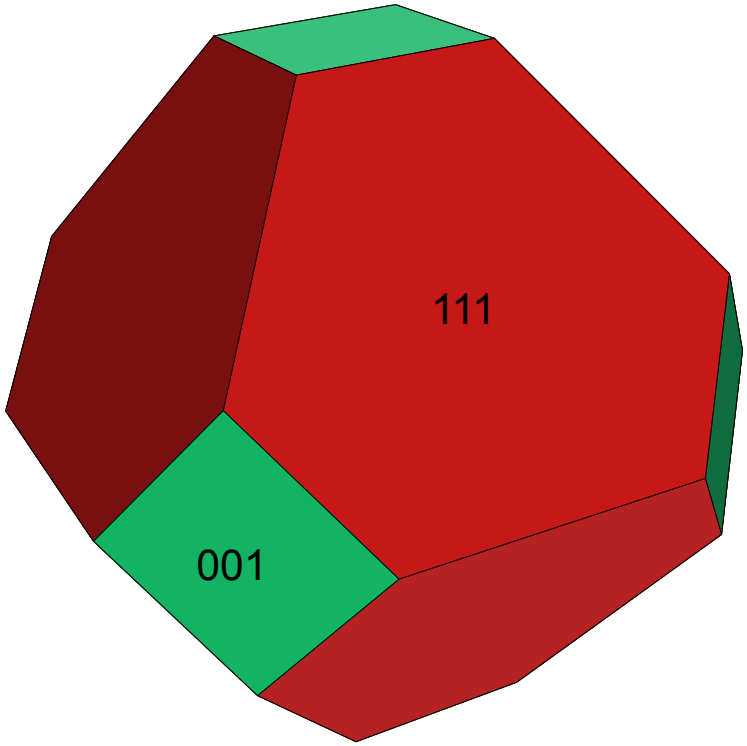
We underestimate the thresholds a little because we neglect variational contribution of free energy of edges, corner (with respect to order parameter).

Beyond previous state of the art: Barmard, Zapol, J. Chem. Phys. **121**, 4276 (2004)

Ab Initio Insights on the Shapes of Pt nano-catalysts, ACS-NANO **5**(1), 247-254 (2011)

Wulff's plot of Pt equilibrium shape

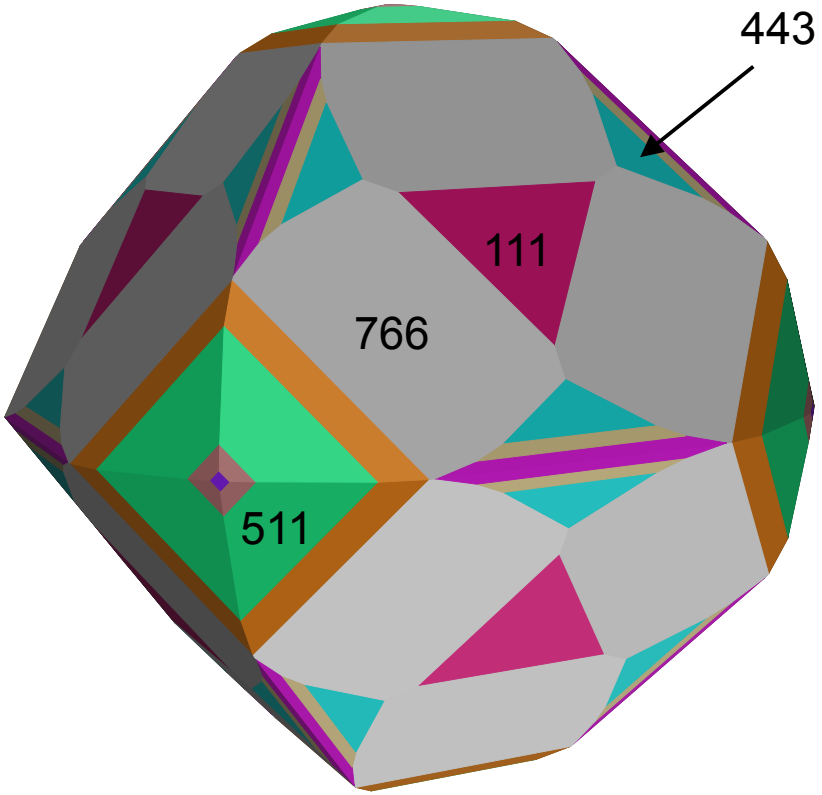
~ unrelaxed



$\gamma_{(lmn)}(a_0)$

surface energy

~ relaxed

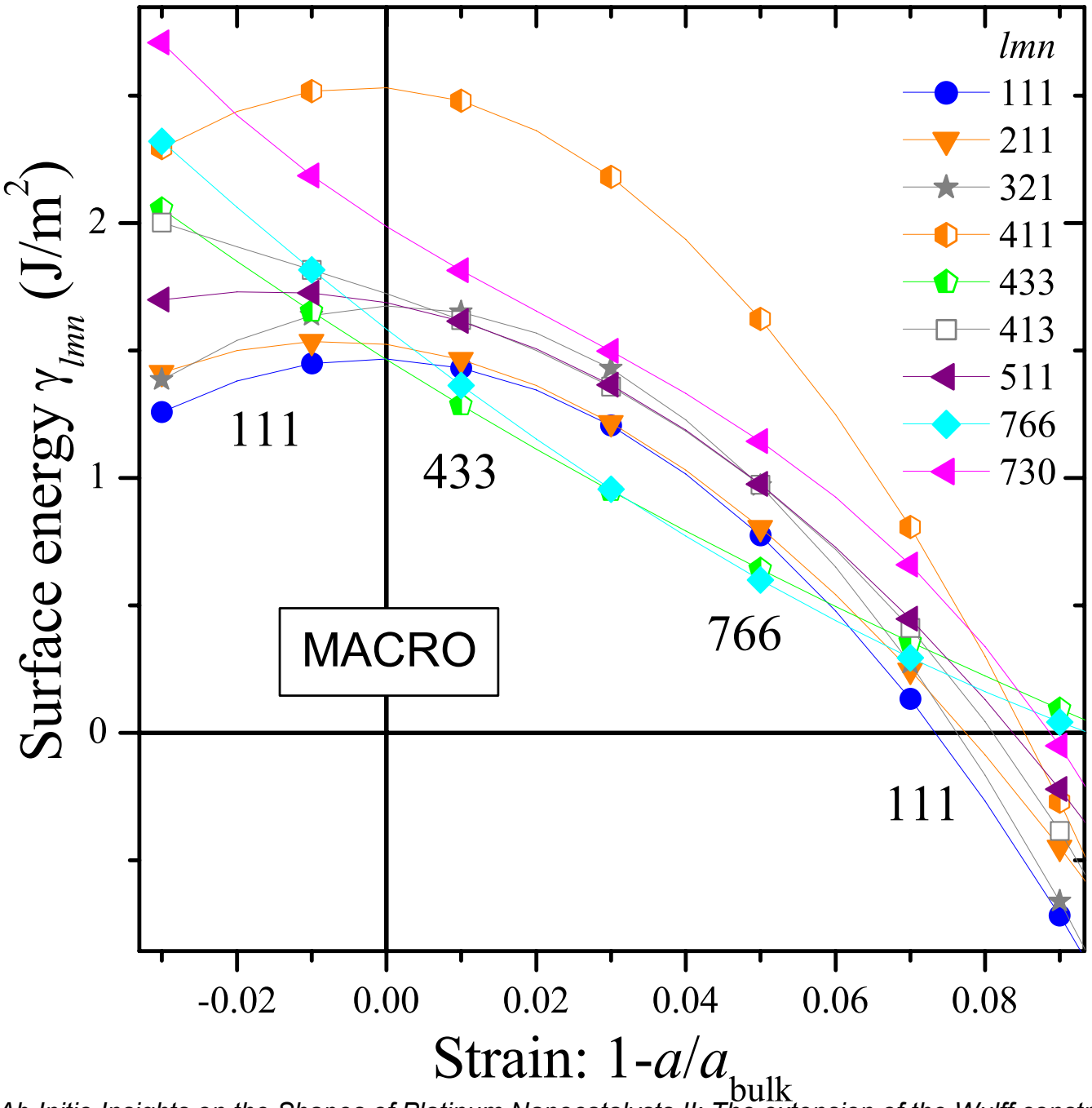


$$\gamma(a) = \gamma(a_0) + \underbrace{\left.\frac{\partial \gamma(a)}{\partial a}\right|_{a_0} (a - a_0)}_{\text{surf tension}} + \cdots$$

surf energy

Variational approach to shapes, surfaces and Wulff plots for nanoparticles, submitted (2011)

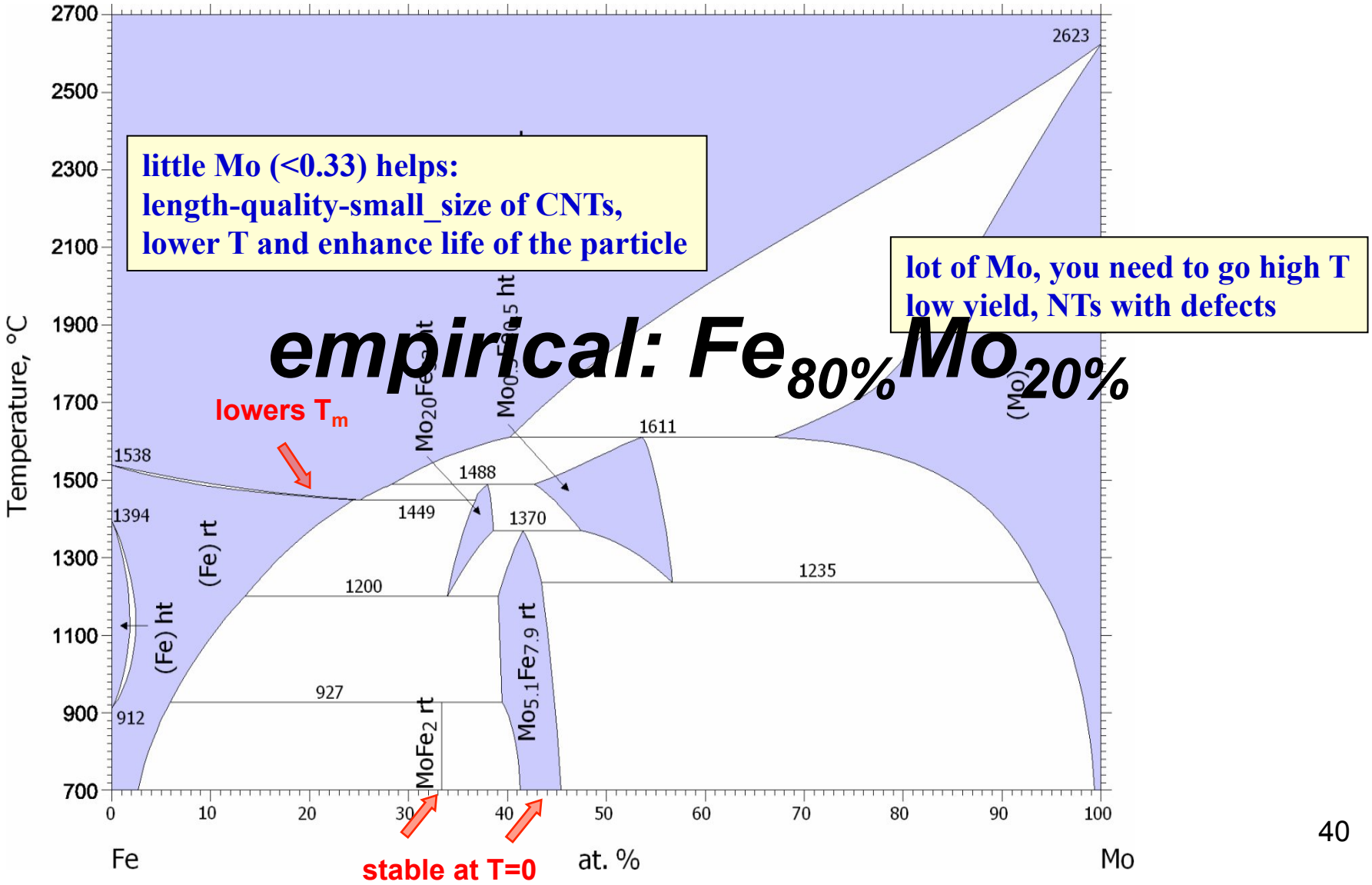
Wulff


Surface energy γ_{lmn} (J/m^2)
Strain: 1-a/a_{bulk}
lmn
111
211
321
411
433
413
511
766
730
MACRO
111
433
766
111
-0.02
0.00
0.02
0.04
0.06
0.08
0
1
2

Alloying ? Experiments 3

Why Mo? Mo was chosen because it lowers T_m of FeMo.
And to reduce sintering of particles (Co, Resasco *et al.*).

APL **90**, 163120 (2007)



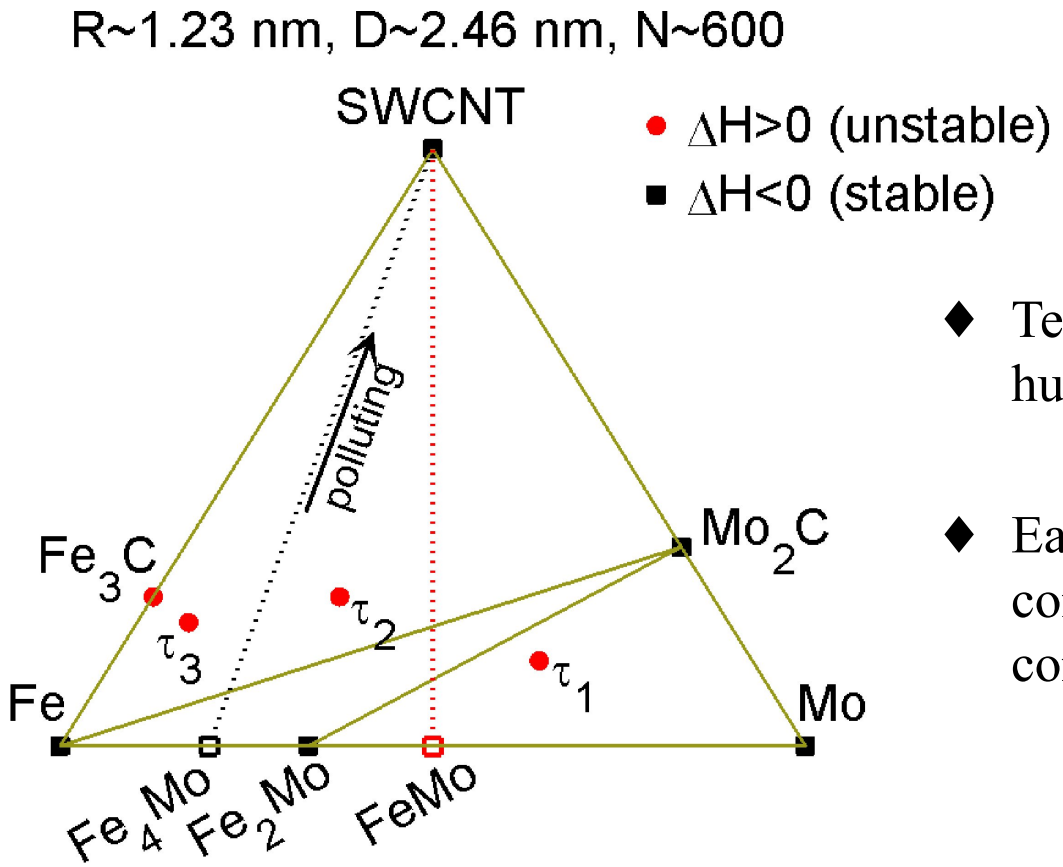
Ternary phase diagram for Fe-Mo-C

"Size-pressure approximation"

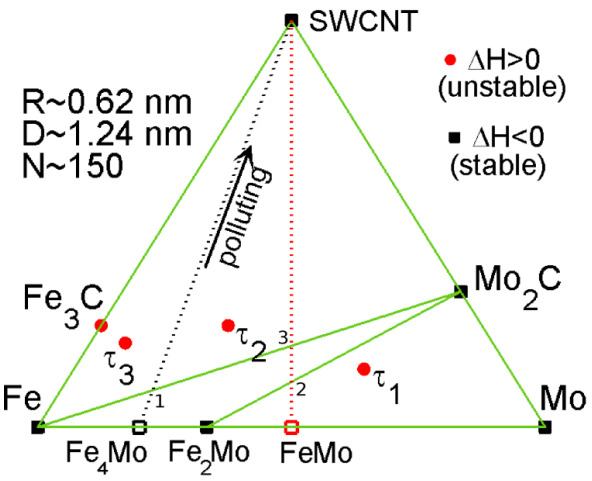
Fe-Mo-C phase diagram (with all competing phases)

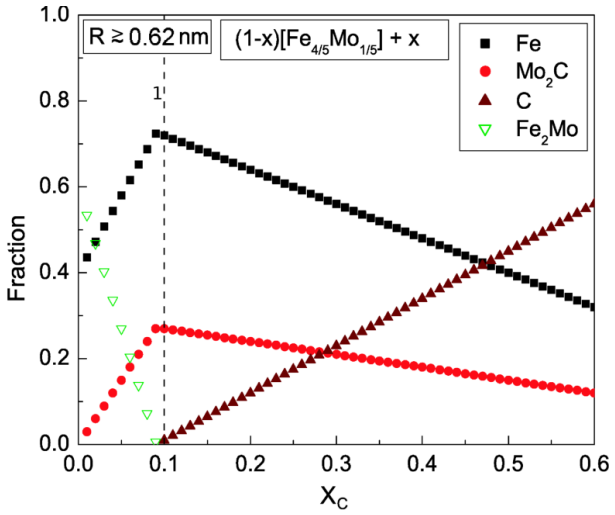
- Binary phases: Fe_3C, Fe_2Mo, Mo_2C and Fe_4Mo ($Fe_{0.8}Mo_{0.2}$ my **RND** particle)
- Ternary phases: Fe_2Mo_4C (τ_1), Fe_2MoC (τ_2), and $Fe_{21}Mo_2C_6$ (τ_3).

References: Fe (bcc), Mo (bcc), and C (SWNTs)



- Ternary convex hull is a *"pyramid"* hull with triangular facets.
- Each point can be expanded as linear combinations of the three vertices containing it.



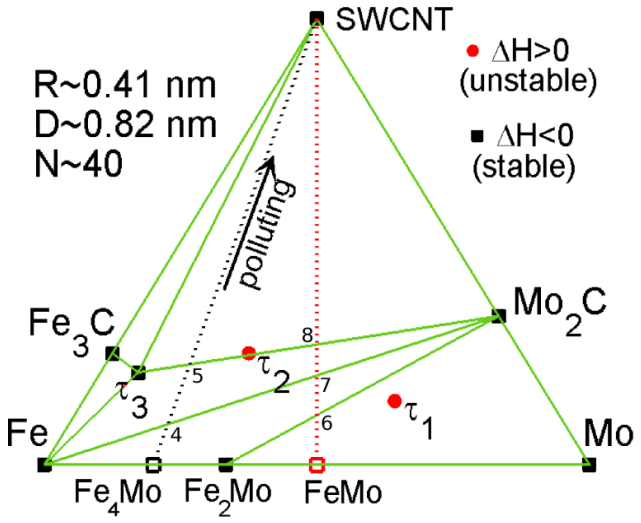


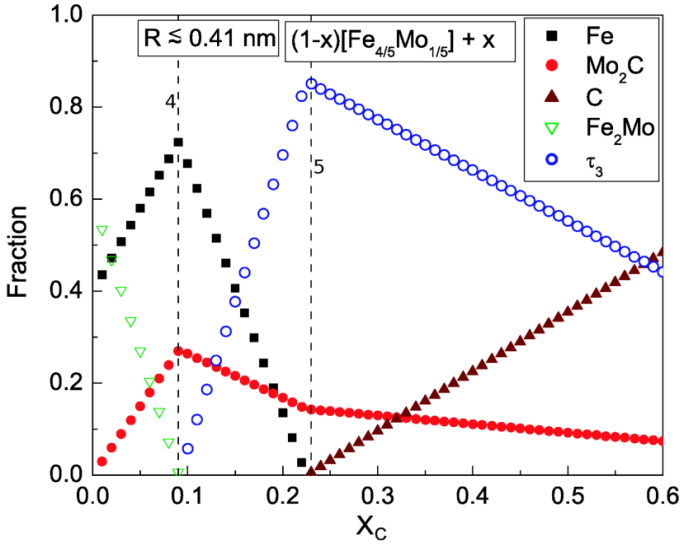
little Mo (<0.33) helps

big

STEADY STATE:
Free Fe never dies
stays in surface

Fe_2Mo decomposes in free Fe+Mo_2C: Mo prefers C, nucleated Mo_2C is segregated inside ($\gamma_{Fe} < \gamma_{Fe2Mo} < \gamma_{FeMo\_rnd}$)

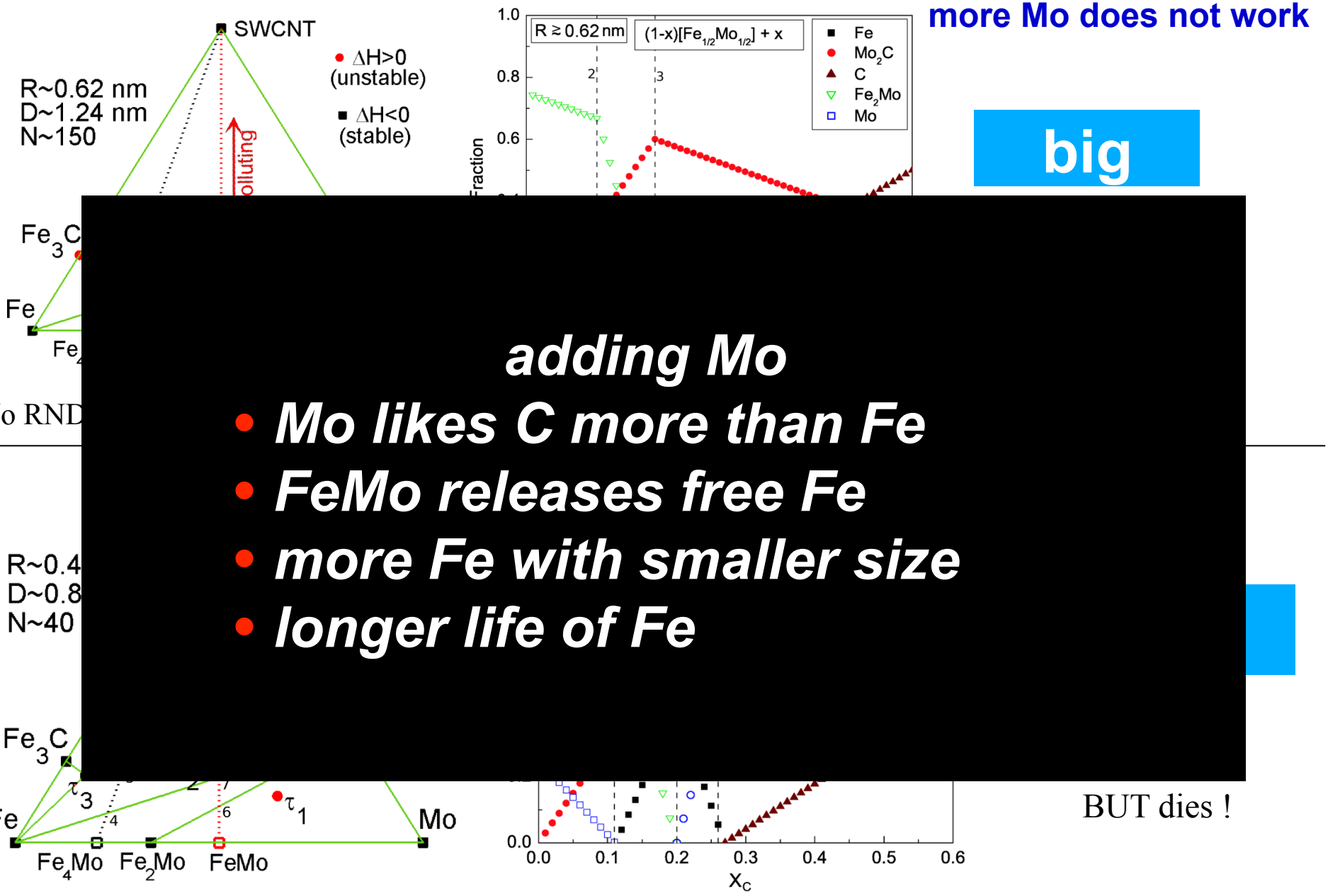




small

Fe lives free
BUT dies !

Free Fe is released **even in tiny particles**
(**NO STEADY STATE**, but FeMo CNTs can be smaller than Fe CNTs)



more Mo does not work

big

BUT dies !

PRB **78**, 054105 (2008)

Even worse, you also form a stiff ternary carbide τ_3.

Conclusions

***THERMODYNAMICS* rules nano-catalysts pollution.**

***SIZE-PRESSURE* approximation to get trends, SOLUBILITY.**

***STEADY-STATE* for big D (Fe and FeMo).**

***RULES* for nano-catalysts design.**

PRL**100** 195502 (2008); PRB **78** 054105 (2008); PRB **75** 205426 (2007)
APL **90** 163120 (2007); PRB **77** 115450 (2008); APL **88** 133110 (2006)

Acknowledgements

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TERAGRID: TACC and SDSC

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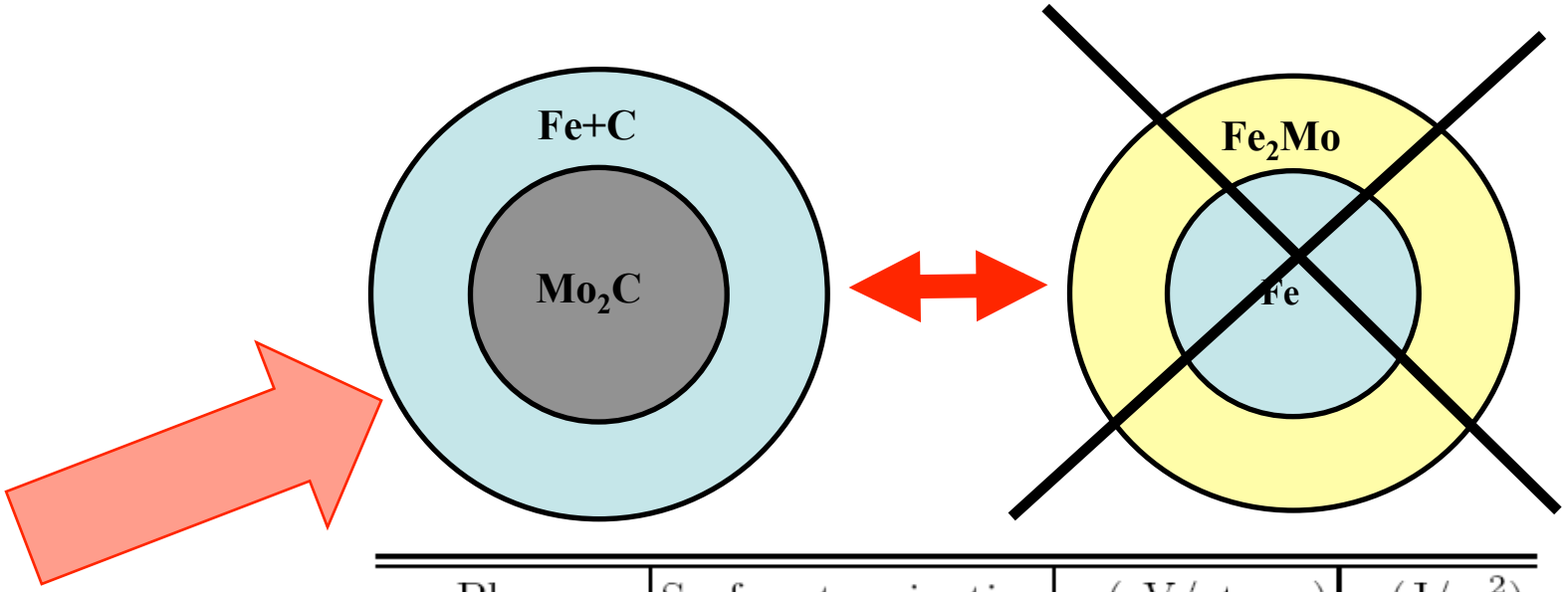
Multiple postdoc openings

Where are Mo and Fe ?



Phase	Surface termination	σ (eV/atom)	γ (J/m^2)
Fe-bcc	(1 1 0)	0.85	2.44
$Fe_{71}Mo_1$ mid	(1 1 0)	12.89	4.03
$Fe_{71}Mo_1$ out	(1 1 0)	13.28	4.16
Fe_2Mo	(0 0 4)	3.68	3.12

$$\gamma_{Fe} < \gamma_{Fe_2Mo} < \gamma_{FeMo}$$