Multiscale Studies of Catalyst-Assisted Carbon Nanotube Growth

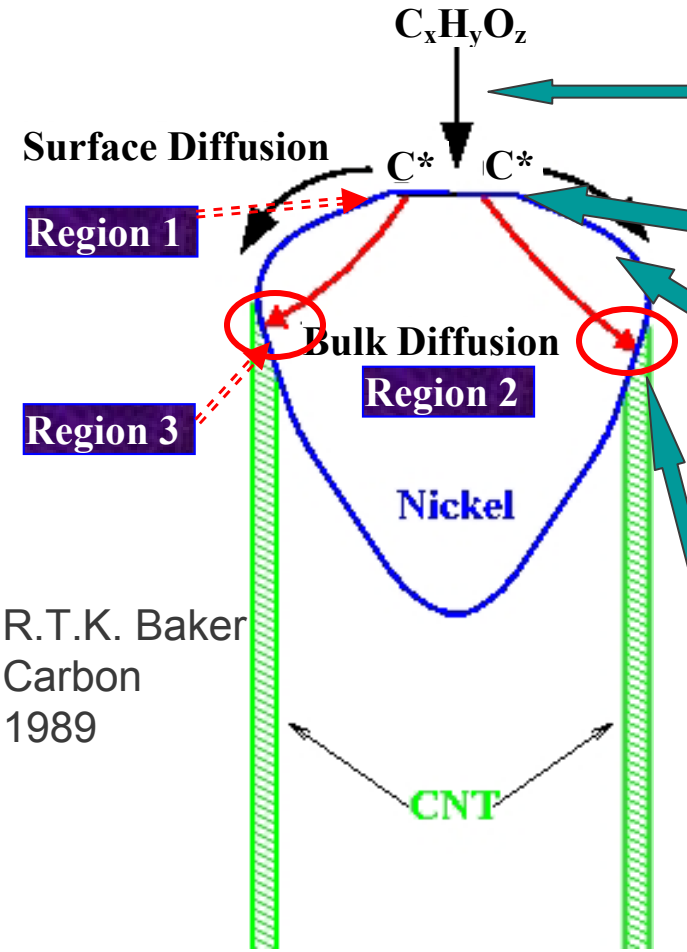
J.C. Wells[1], S. Pannala[1], B.G. Sumpter[1], Q.-M. Zhang[3], and Z. Zhang[2] , and R.F. Wood[2]

[1]Computer Science and Mathematics Division, ORNL
[2]Condensed Matter Sciences Division, ORNL
[3]Department of Physics, University of Texas at Arlington

DOE-NSET Workshop "Artificially Structured Nanomaterials: Formation And Properties", Gatlinburg, TN, October 13-15, 2003

*Research sponsored by the Material Sciences and Engineering Division Program of the DOE Office of Science and the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

"*Standard*" CNT Tip-growth Mechanism



R.T.K. Baker
Carbon
1989

Decomposition Rates: Dependence on Concentration, Temperature, Composition?

Surface Carbide formation? How stable is it?

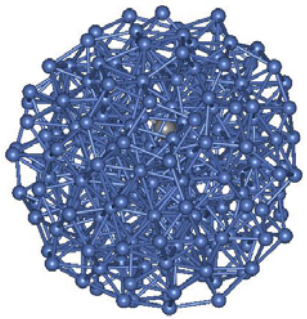
Diffusion pathways? Surface vs. Bulk?
Implications on growth? Catalyst clogging?
Is diffusion the growth rate-limiting step?

Barriers for precipitation of carbon into CNT?
How does the precipitation start?
Is precipitation the rate limiting step?
What dictates the chirality, diameter, length?

Multiscale in time and space:
- **Time (pico secs. to secs.)**
- **Length (Angstroms to mm)**

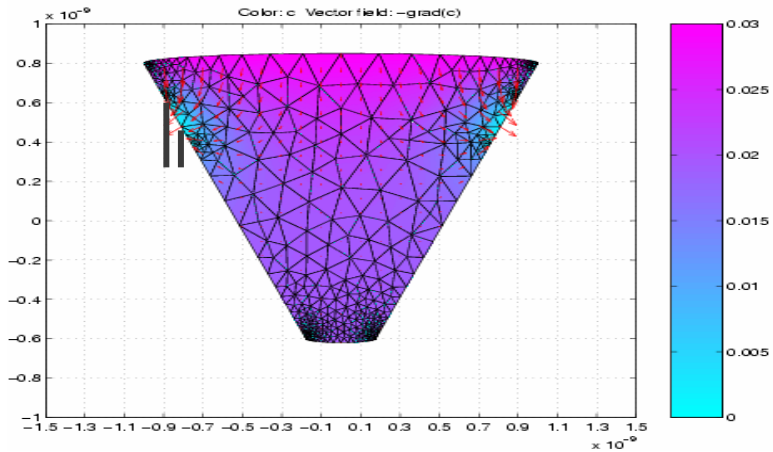
→ **Plausible, but difficult, way to solve this multiscale problem is by integrating DFT/MD and Continuum.**

Multiscale Modeling (Overview)

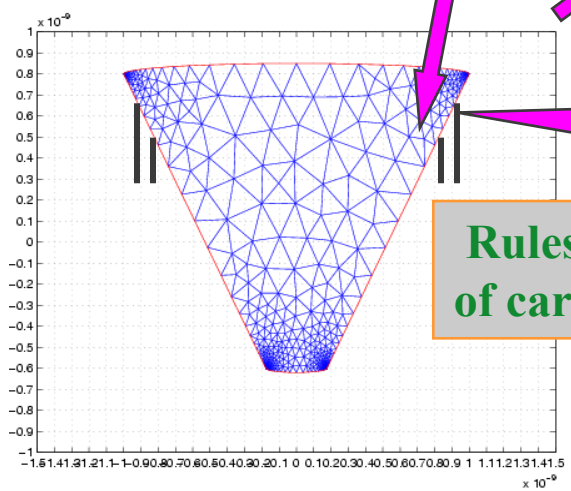


MD Simulations (Dynamic)
Time Scale ~ pico s, Length ~ nm

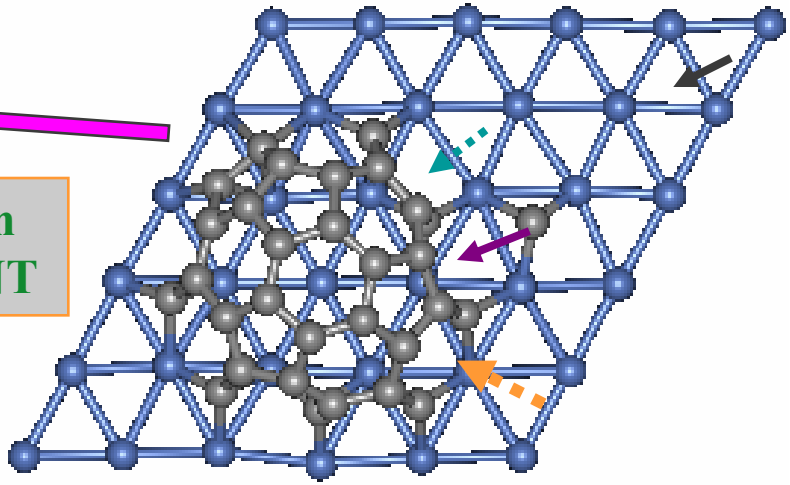
Time and space evolution of carbon concentration in the catalyst



Mass Diffusion Rates



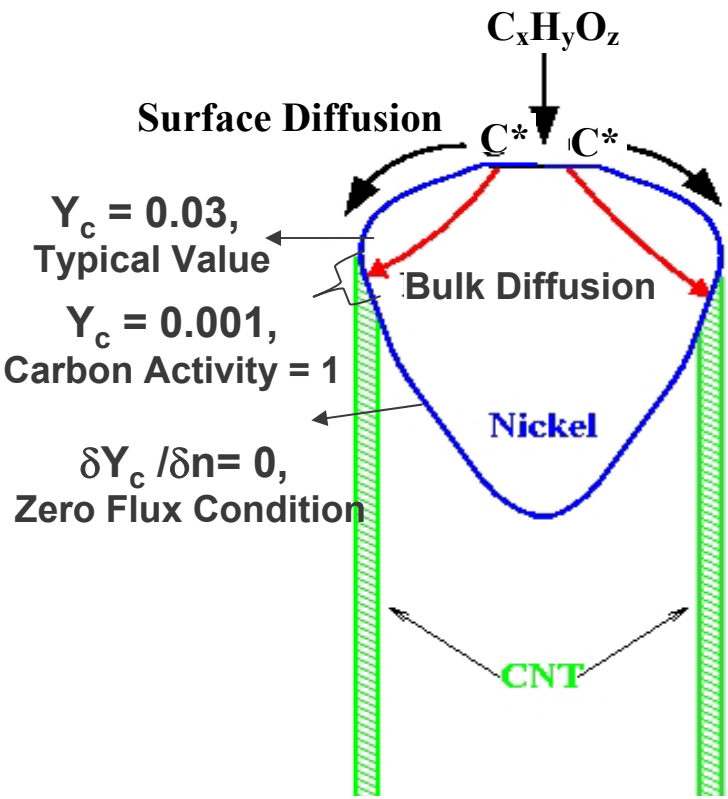
Rules for Segregation of carbon into the CNT



2D Continuum Simulations
Time Scale ~ µs-s, Length ~ mm

Single Carbon Atom Addition
(DFT Calculations)

2D Continuum Growth Model: Tip Growth



Schematic

Model

$$\frac{\partial Y_c}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(rD(T,Y_c)\frac{\partial Y_c}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial z}\left(rD(T,Y_c)\frac{\partial Y_c}{\partial z}\right) = 0$$

$$\frac{\partial T}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(rk(T)\frac{\partial T}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial z}\left(rk(T)\frac{\partial T}{\partial z}\right) = 0$$

Inputs to the Model
Diffusion Rates, *D(T,Ye)*, Thermal Conductivity, *k(T)*
Temperature, *T*
Inlet Composition
Shape of Catalyst Particle
Location of CNT formation
Size of Catalyst

Predictions
Spatio-temporal distribution of Carbon
Growth Rates
Inner Diameter of NT
Single Vs. Double Vs. Multi-wall NTs
Insight into growth and control of NTs

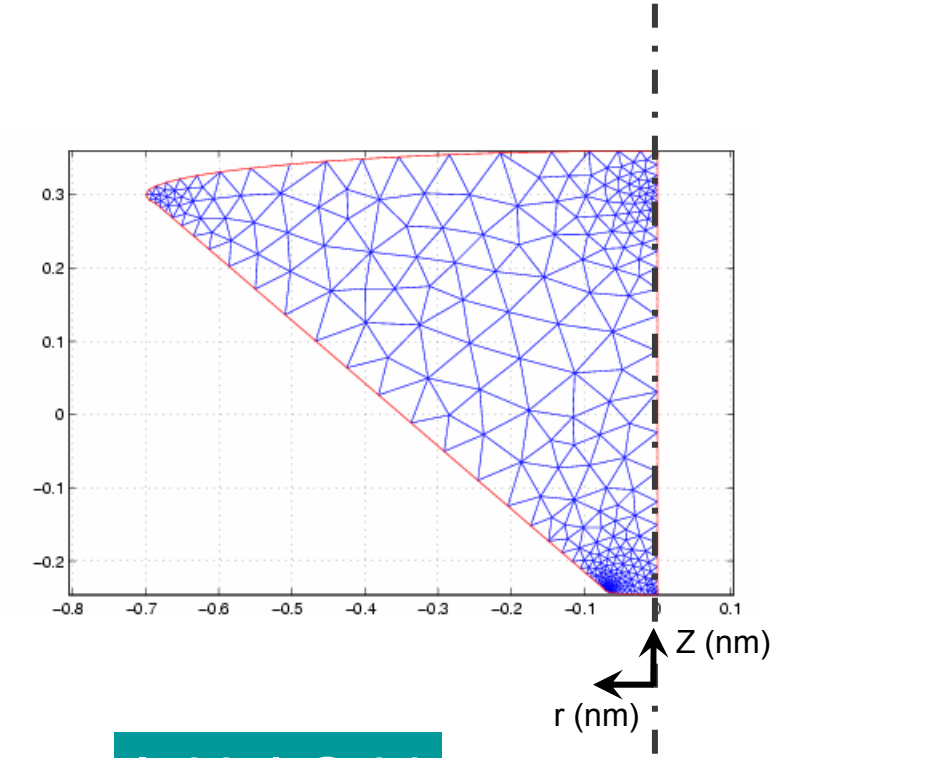
Simplifying Assumptions

- Neglect carbon concentration dependence of diffusion, i.e., $D(T,Ye) = D(T)$.
  - $D(T)=D_0\exp[-\Delta E/kT]$
  - $D_0=0.012\ cm^2sec^{-1}$; $\Delta E=1.46\ eV/atom$
- Uniform temperature field within nanoparticle.

$$\frac{\partial Y_c}{\partial t}+\frac{1}{r}\frac{\partial}{\partial r}\left(rD(T)\frac{\partial Y_c}{\partial r}\right)+\frac{1}{r}\frac{\partial}{\partial z}\left(rD(T)\frac{\partial Y_c}{\partial z}\right)=0$$

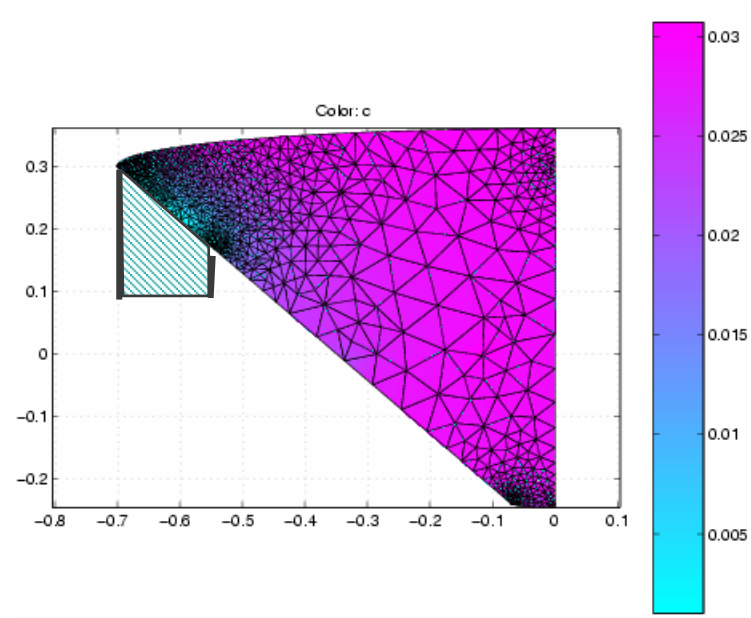
SWNT: Typical Geometry and Grid

- FEM w/ unstructured grids and Adaptive Mesh Refinement.



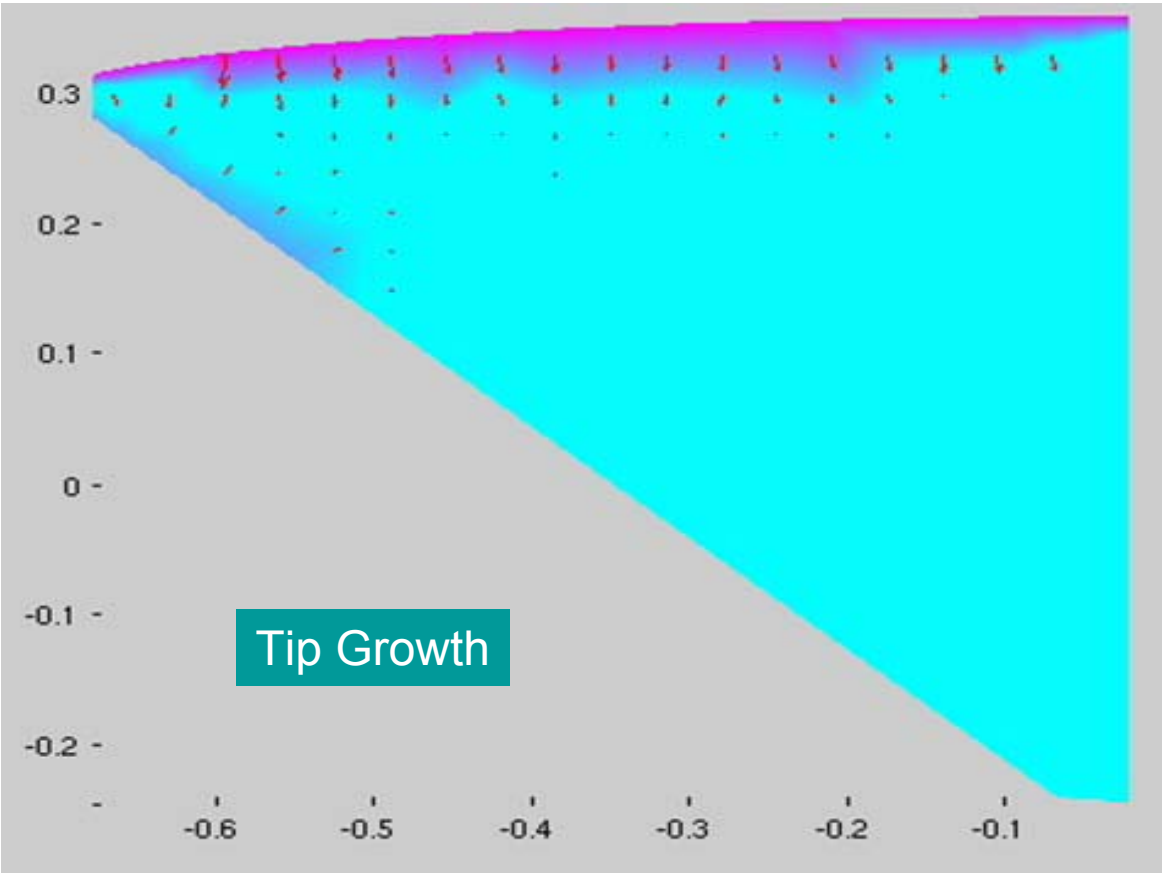
Initial Grid

Axis of Symmetry



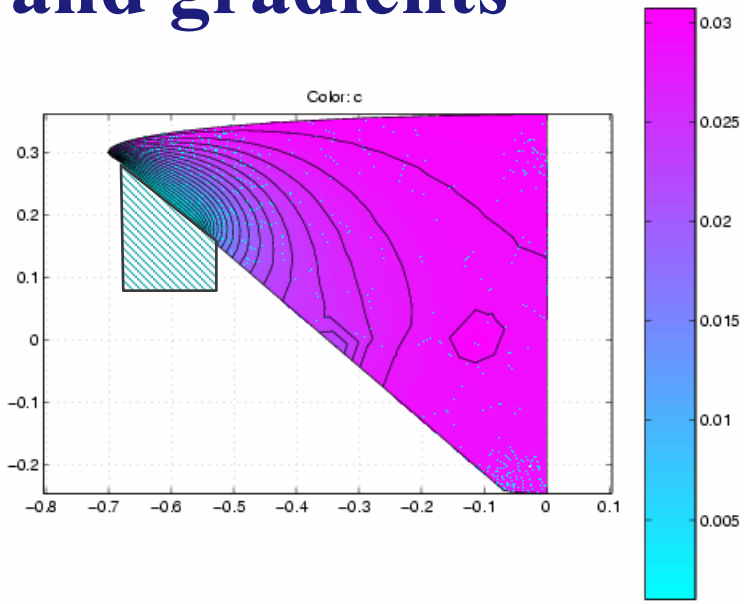
Final Grid (after AMR based on relative error)

SWNT: Transient simulation of first 300 ns

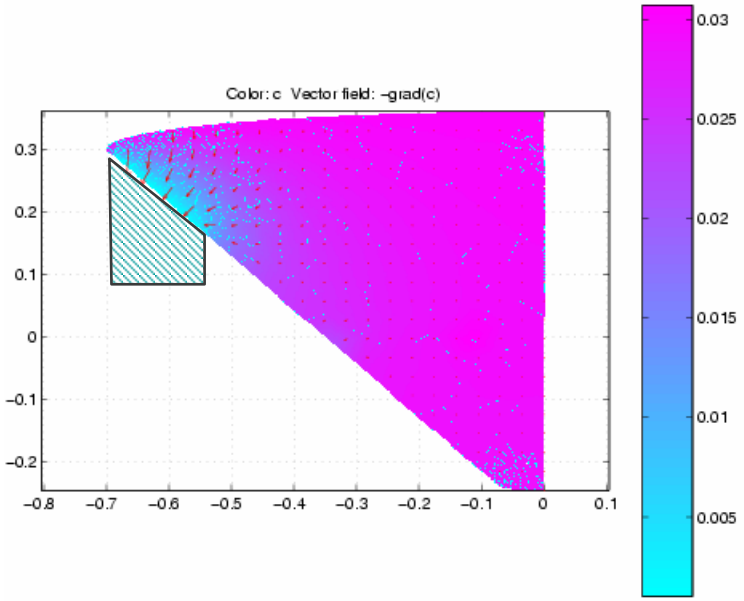


- Carbon diffuses into NP
- NT precipitates as sufficient carbon reaches interface.
- Steady-state Carbon concentration in particle bulk is quite uniform.
- The NP serves as a reservoir for carbon.

SWNT: Steady-state Concentration profiles and gradients



Carbon concentration

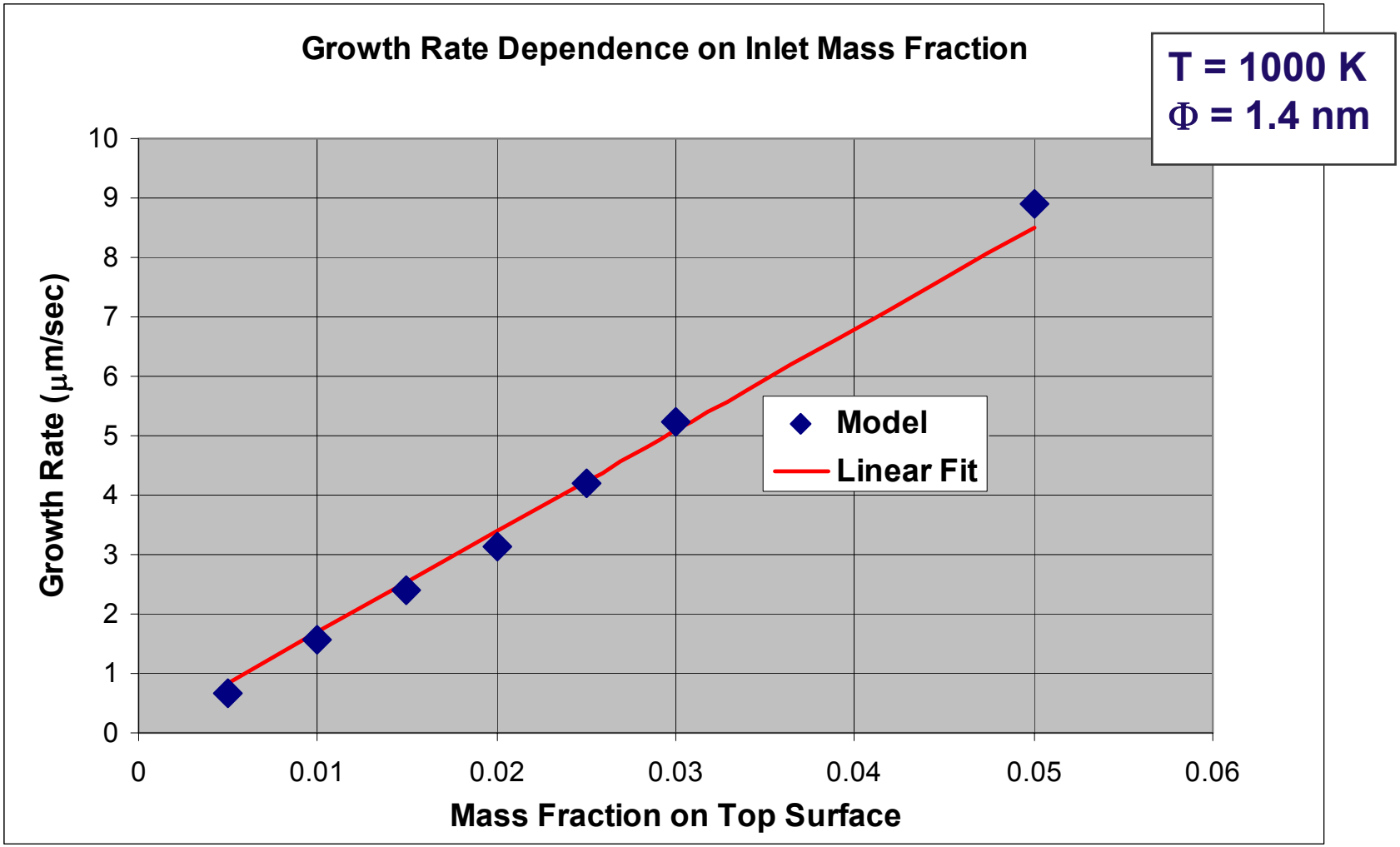


Carbon concentration gradients

- Local gradients at Ni/NT interface are integrated to yield the effective growth rate for the tube.
- Parameters varied: Inlet mass fraction, temperature of NP, diameter of the nanoparticle.

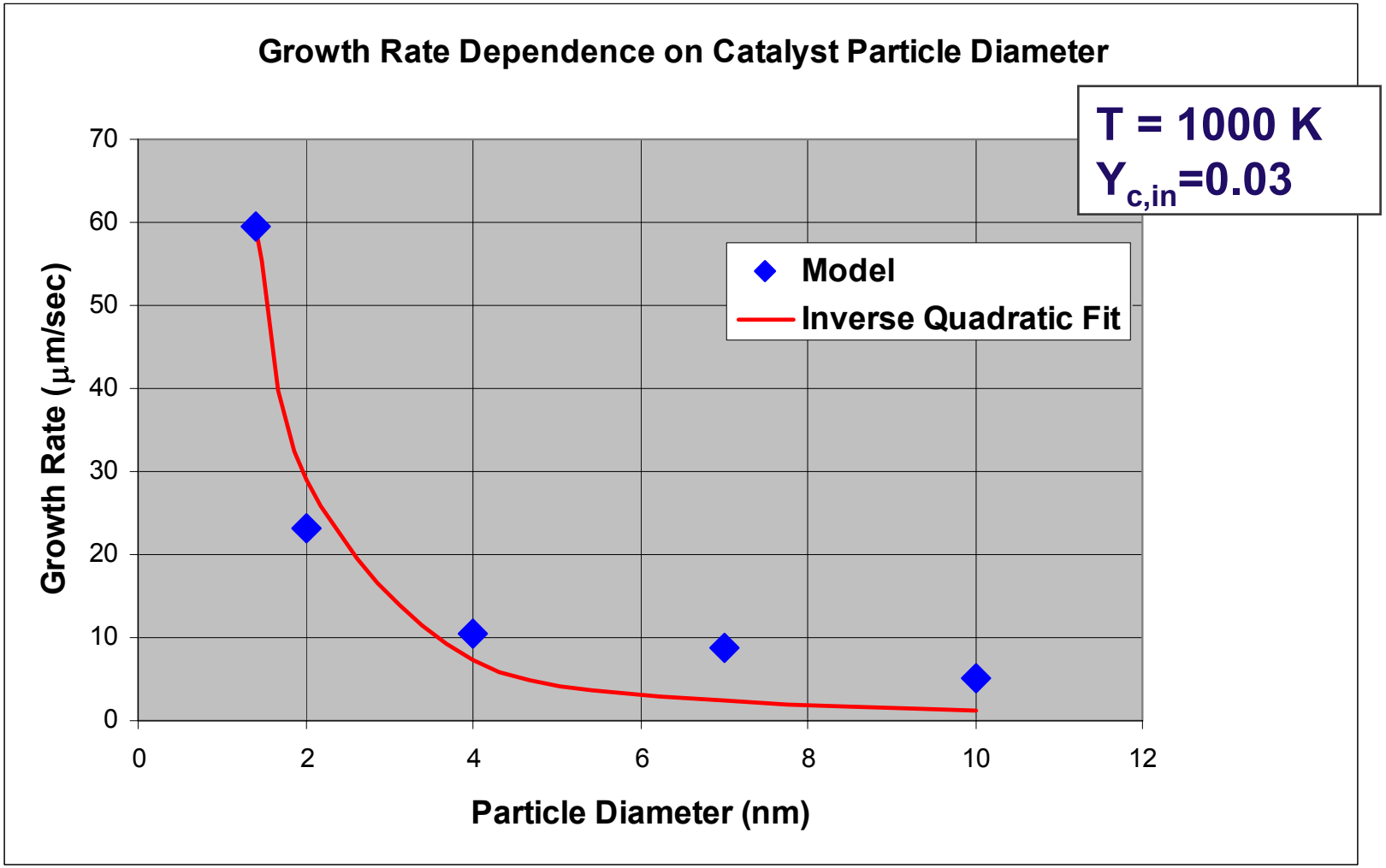
SWNT Parametric Studies:

Growth Rate Dependence on Inlet Mass Fraction



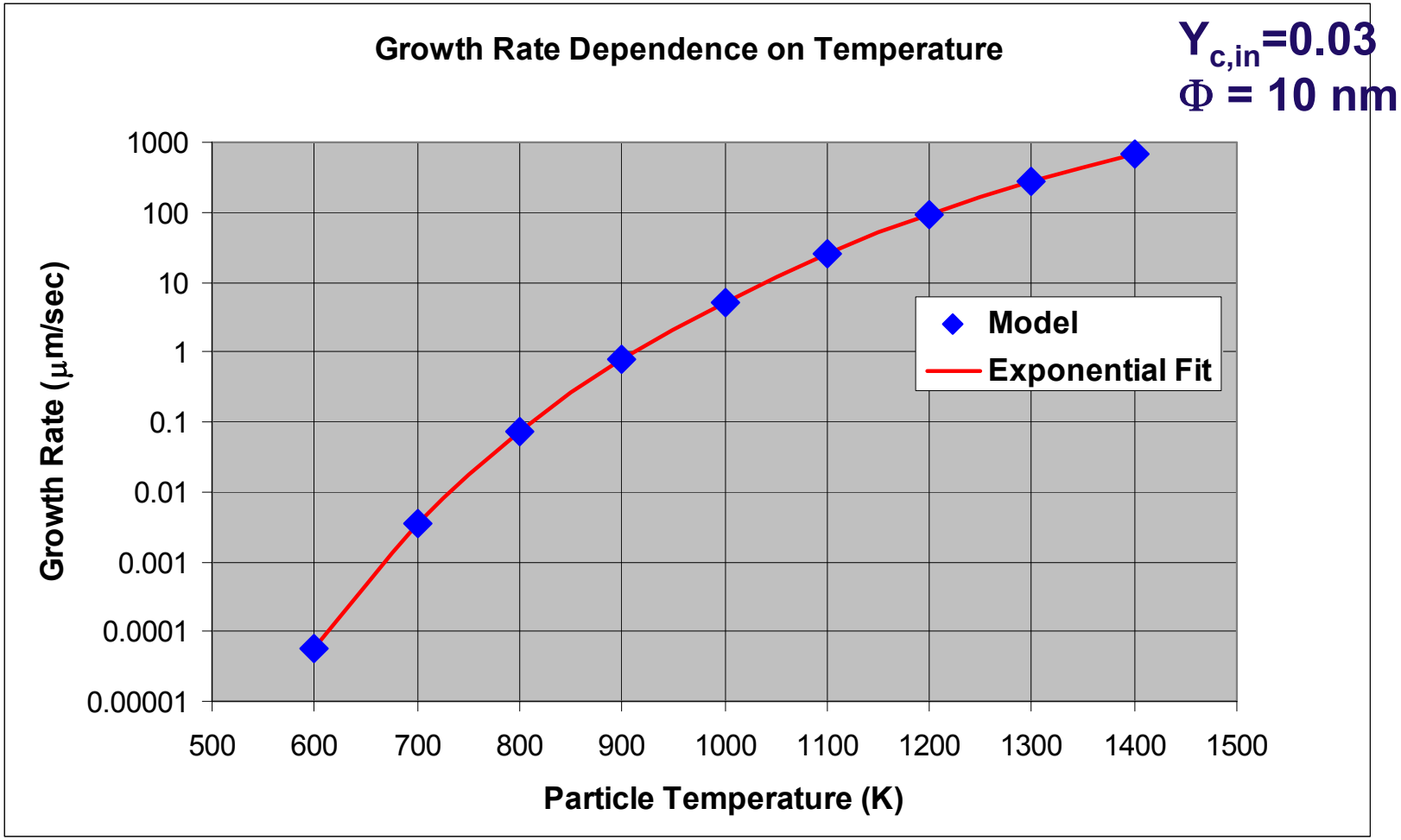
SWNT Parametric Studies:

Growth Rate Dependence on Particle Size



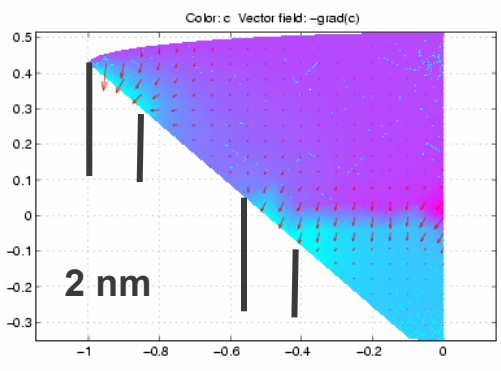
SWNT Parametric Studies:

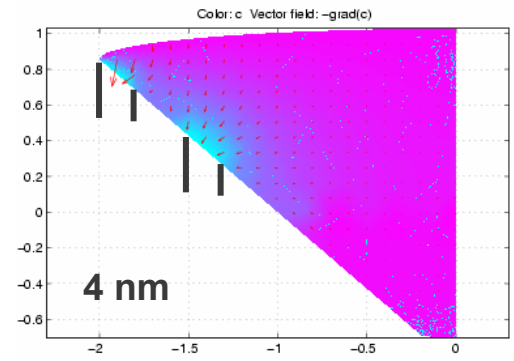
Growth Rate Dependence on Particle Temperature

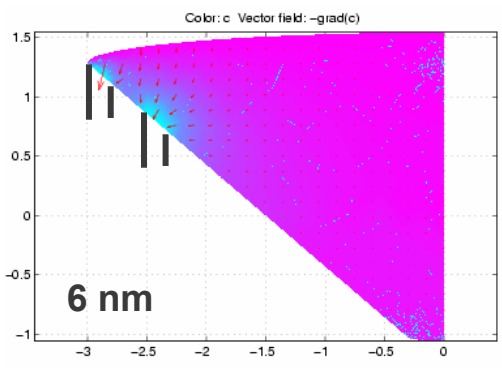


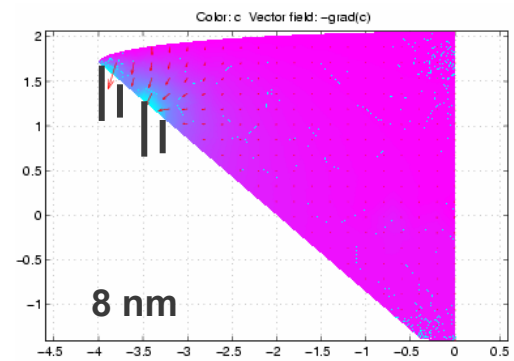
Double-wall Nanotubes (DWNT)

Steady-state carbon concentration and gradients









Question: Is it possible to have a double-wall NT with a small size catalyst particle?

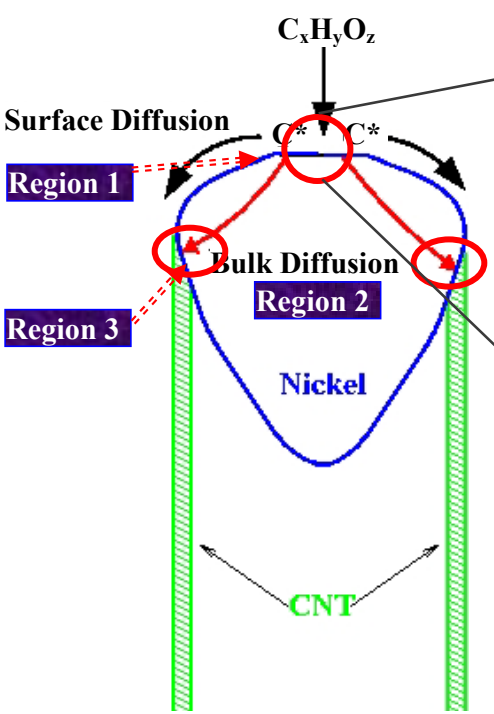
Might not be possible! Not enough Carbon flux to the inner wall.

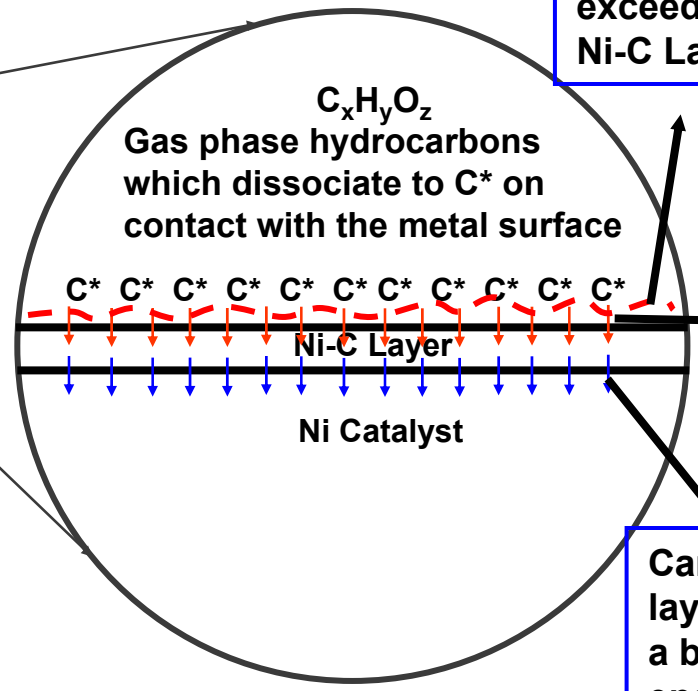
Initial Comparisons with Experiment

- Computed rates >> Time-averaged experimental rates (~0.001 to 0.01 microns/sec, Milne *et al.*).
- Geohegan and co-workers have directly measured growth rates (~0.01 to 0.3 microns/sec).
  - At 1000K, measured growth rate of 0.2 microns/sec.
  - Model predicts 2 microns/sec with $Y_c = 0.01$.
- Future studies will compare rates for MWNT growth.
- Significant Current Limitations:
  - Considered only diffusion
    - NT growth is reaction limited under specific conditions. (Hafner, et al., 1998).
  - Concentration dependence of diffusion: ***D(T) ≠ D(T,Ye).***
  - Knowledge of the precipitation process.
  - Surface carbide formation "chokes" the carbon supply.

Next Step

Carbide layer (Region 1) needs incorporation of physics





Catalyst clogging/poisoning happens when decomposition rate exceeds the carbon diffusion into Ni-C Layer/Ni particle

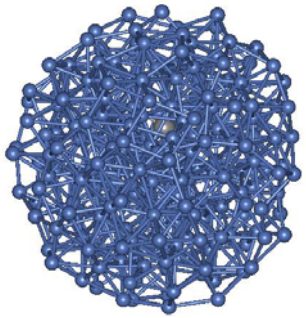
Carbon Diffusion from Surface layer to Ni-C – To be modeled as a barrier with an activation energy and pre-exponent

Carbon Diffusion from Ni-C layer to Ni – To be modeled as a barrier with an activation energy and pre-exponent

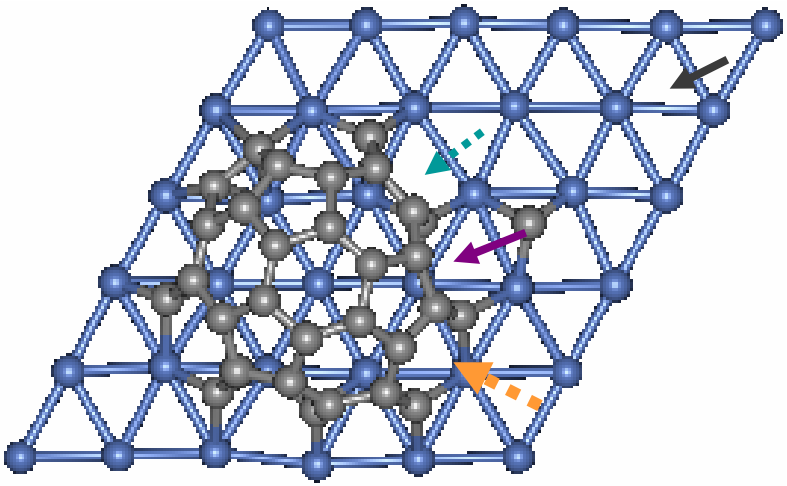
=> This input will feed into the earlier calculations as a time varying BC.

Integration of Atomistic Simulations

- Concentration dependence of $D(T,Y_c)$ for C in TM nanoparticles
  - Difficult to measure experimentally.
  - Computational challenge.
- Size-dependent solubility of carbon in TM nanoparticle.
- Interfacial transition rates.
  - Atomistic structure of the interface.
  - Transition state.
- Mechanisms for carbon layer formation on TM nanoparticle.
- Mechanisms and concentration dependence for carbon ring formation.



MD Simulations (Dynamic)
Time Scale ~ pico s, Length ~ nm



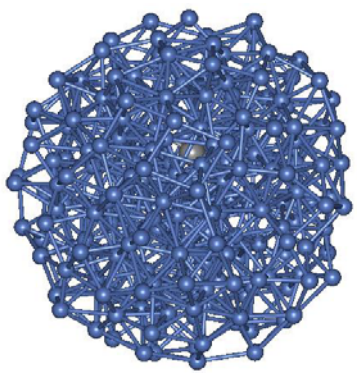
Single Carbon Atom Addition
(DFT Calculations)

Bulk Diffusion of C in Ni Clusters:

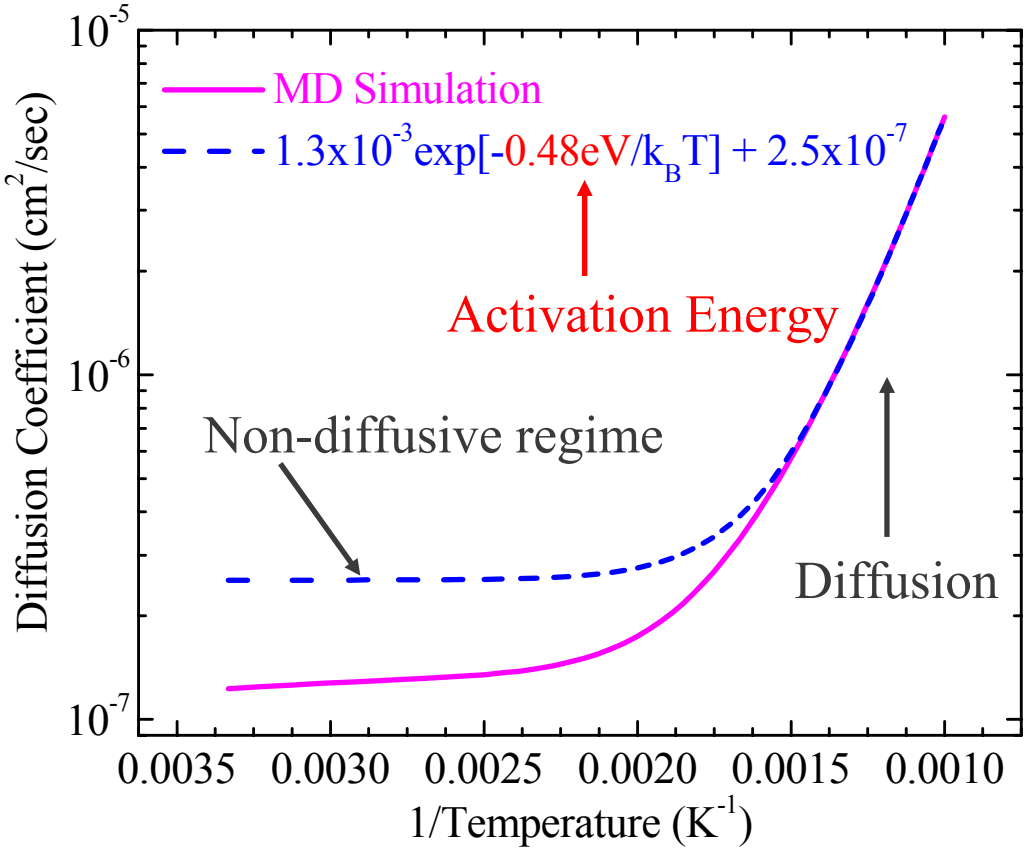
Classical MD Simulations

- Determine ***D(T,Ye)*** for C in Ni_xC_y clusters vs. temperature and cluster size
  - Non-exponential function of cluster size. Approaching bulk for large clusters.
  - Input into continuum calculations.

$Ni_{257}C_1$



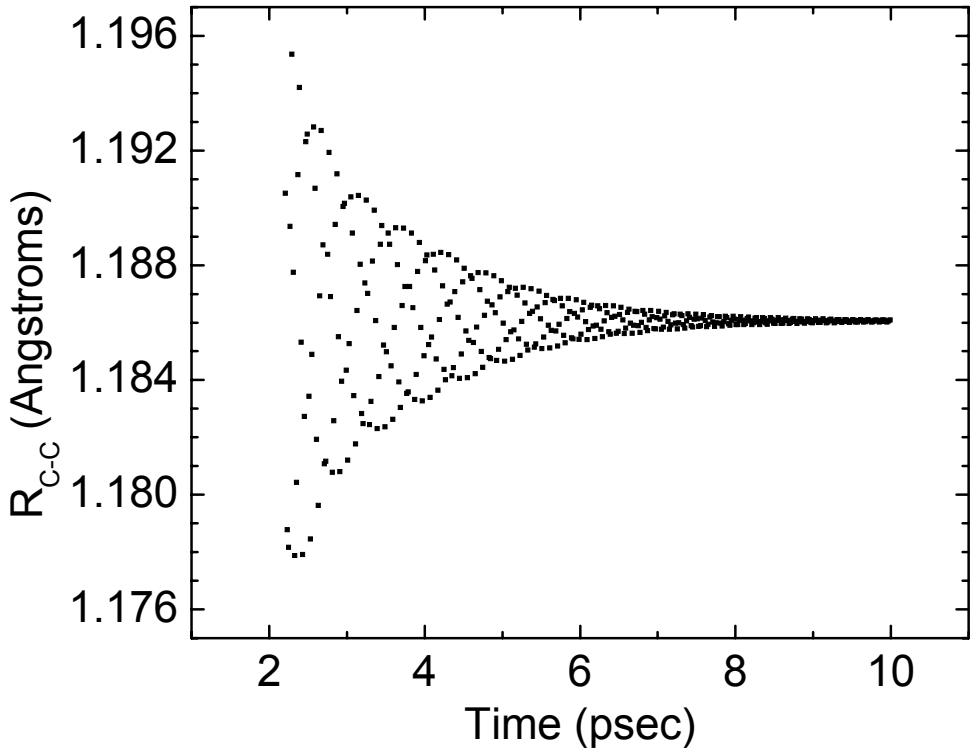
2-body TB potentials derived from DFT electronic structure and experimental results.



Bulk Diffusion of C in Ni Clusters:

Semi-empirical QM Calculations

- Studied only Ni_{38} with this technique.
- Diffusion is function of Y_c:
  - Decreases with larger Y_c.
  - Independent of temperature.
- Mechanism for diffusion of multiple C atoms.
  - Dimmer, trimer formation.



Electronic Structure Calculations

- **Carbon adsorption on Ni surfaces.**
- **Obtain insight into why Fe, Co, and Ni are good catalysts and Cu and Au are not.**
- **Calculate strain energy due to curvature and relate to pentagons.**
- **Determine energy of dangling bonds and relate to edge free energy.**
- **Use results from foregoing to calculate radius of critical nucleus via classical nucleation theory and compare to elasticity results.**

Computational Approach:

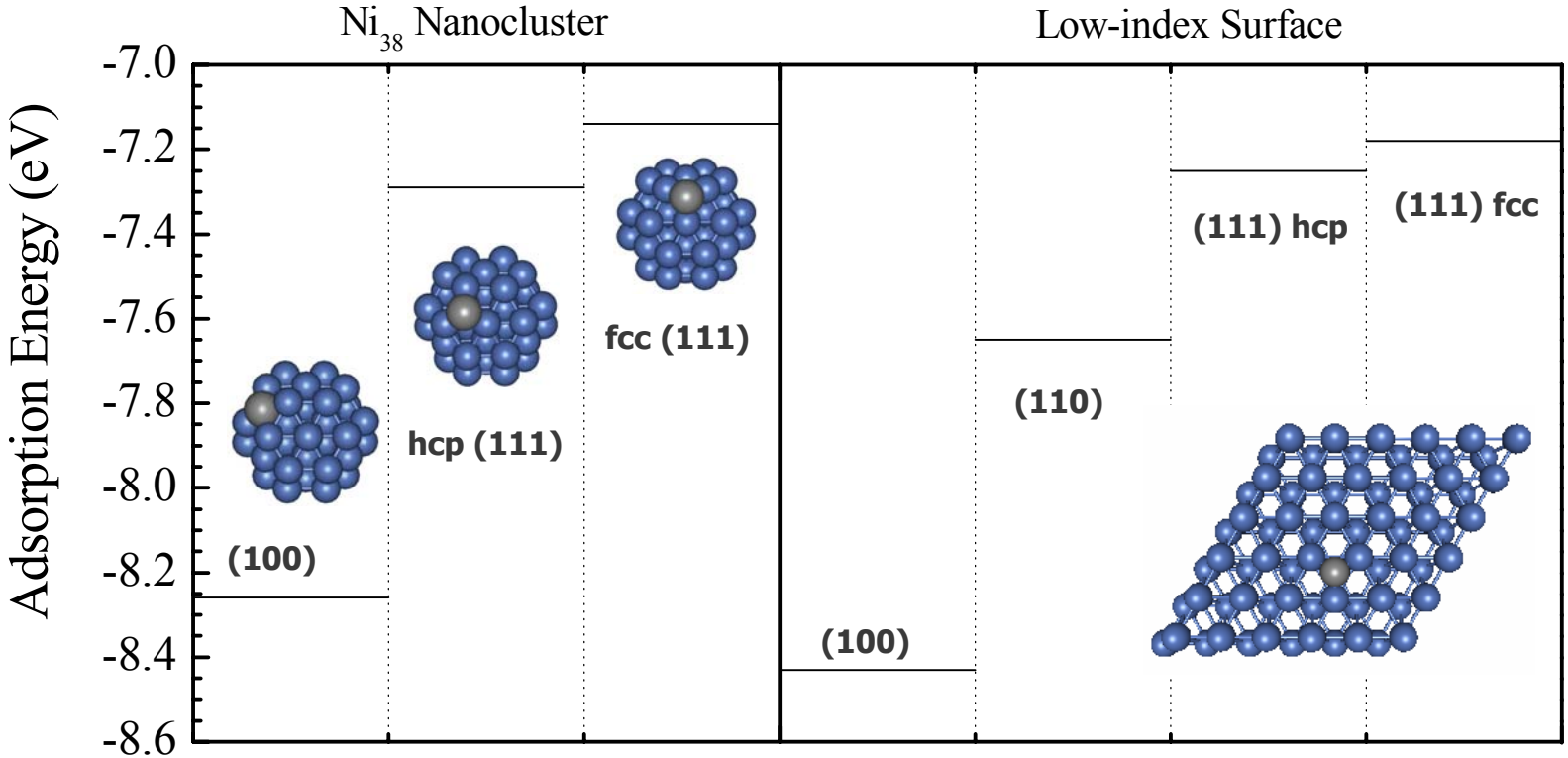
Plane-wave Pseudopotential DFT

- VASP code
- DFT + GGA(PW91)
- Plane wave (PW) basis
- Super cell geometry
- Vanderbilt ultrasoft pseudopotentials
- Valence electrons: 2s2p for C, 3d4s for Ni
- Closed-shell calculation.
  - Neglect spin.

- Ni as a paradigm
- PW Cut-off:
  - 20 Ry for wave functions.
  - 150 Ry for augmented electronic charge density.

Carbon Adsorption on Ni_{38} and low-index Surfaces

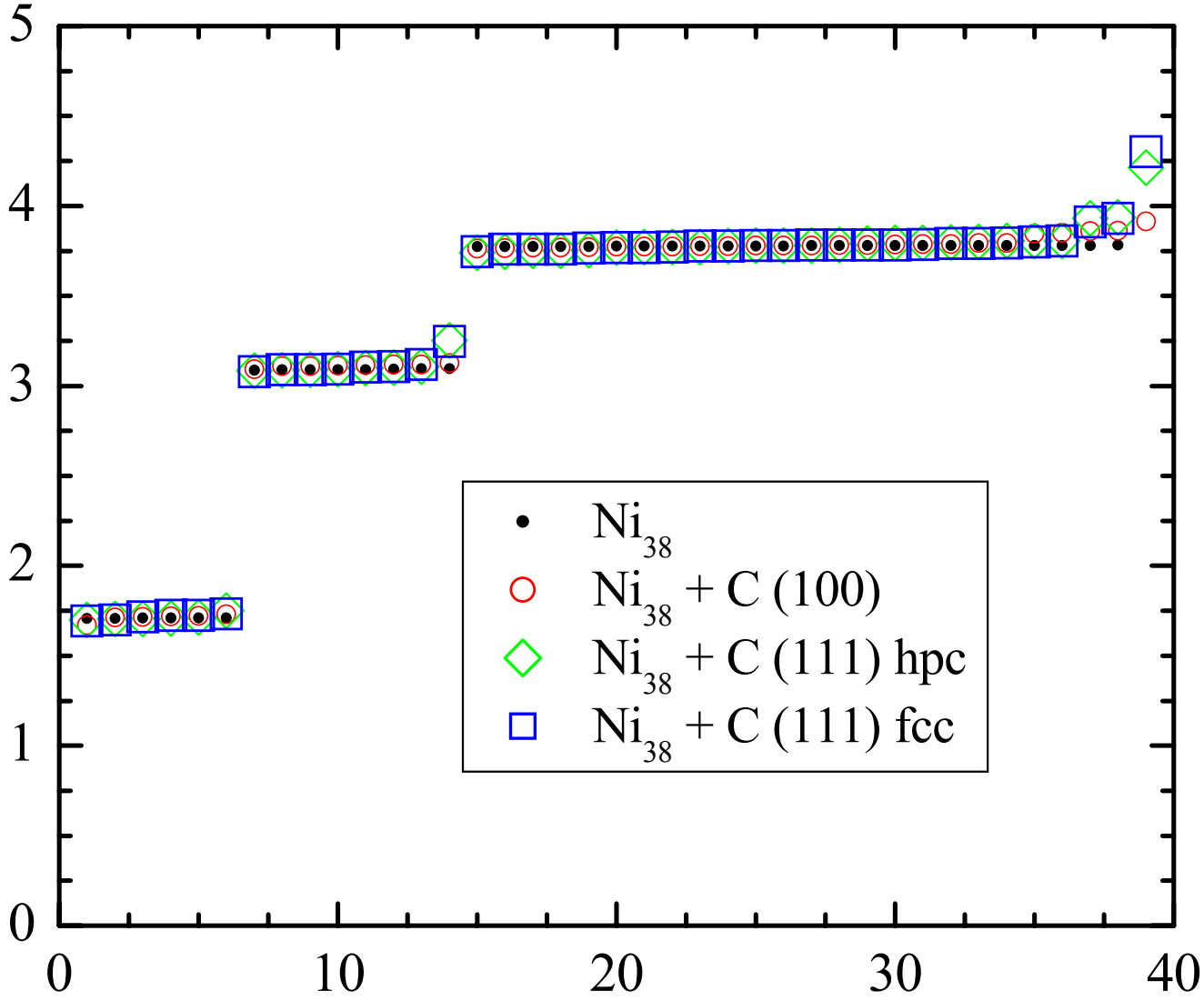
- Insight into carbon-layer formation, NT nucleation CVD growth.
- Electronic structure of TM nanocluster is a challenge.



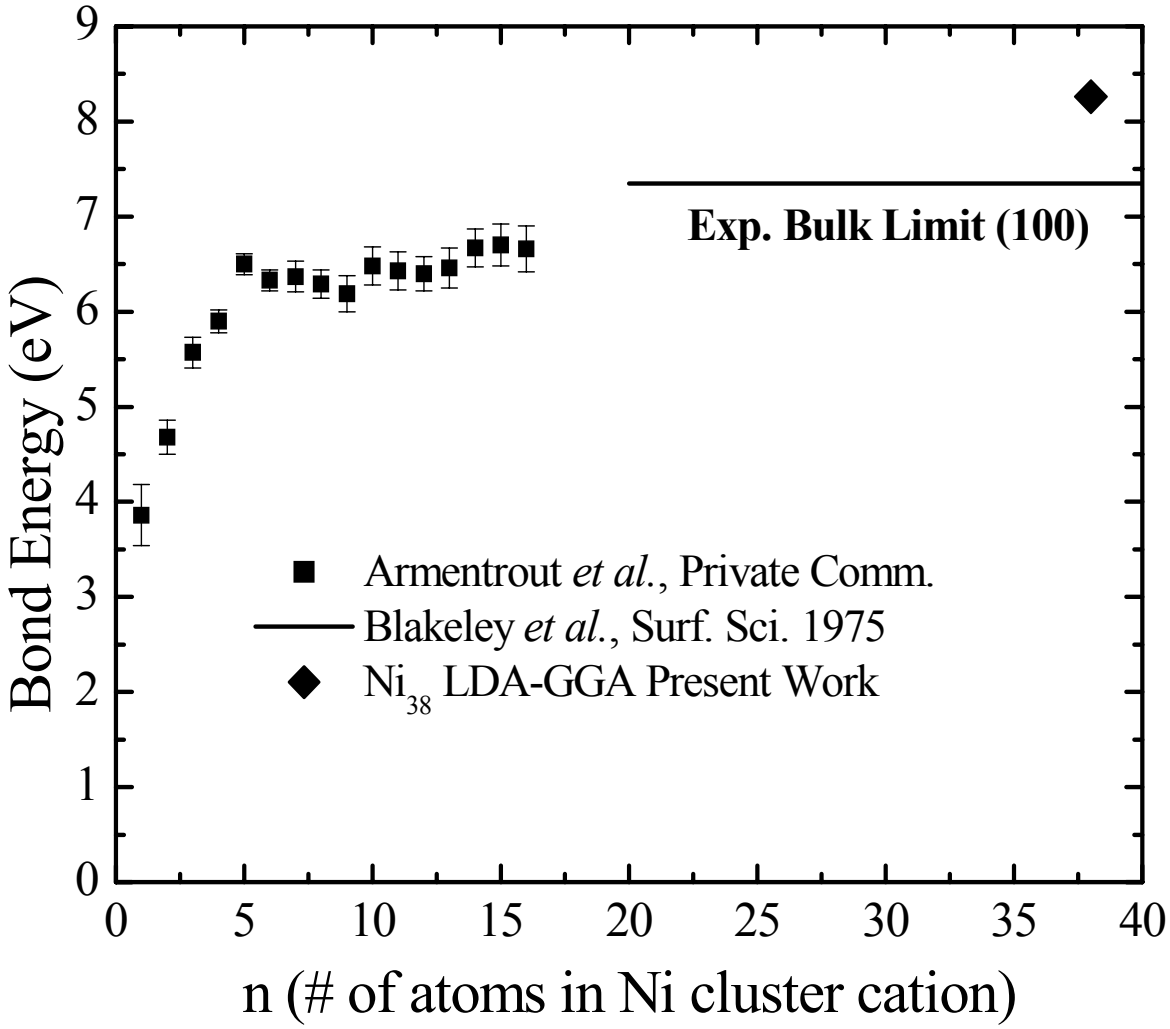
- **3 sites for adsorption on Ni_{38}.**
  - **(100), (111) hcp, and (111) fcc.**
- **Localized relaxation of Ni_{38} at site.**
- **C will remain on cluster surface.**

- **Stable sites:**
  - **(100), (110), (111) hcp and fcc.**
- **Adsorption Energetics order in same sequence on surface and Ni_{38}.**

Localized Relaxation at Adsorption Site



Carbon Adsorption on Ni Clusters: Experiment



Comparison with Theory and Experiment

	Ni Surface	Present Work Ni_{38}	DFT-GGA Surface	Present Work Surface	Experiment
E_{ads} (eV)	(100)	8.26		8.43	7.35 [11,12] 7.37 [9] 7.55 [13]
	(110)			7.65	
	(111)fcc	7.14	6.68 [39] 6.35 [40]	7.18	< 6.94 [12] 6.9 [14*]
	(111)hcp	7.29	5.97 [39]	7.25	< 6.94 [12] 6.9 [14*]
$R_{C\text{-}Ni}$ (Å)	(100)	1.83		1.85	1.80±0.015[23] 1.82±0.05[24] 1.89±0.05[25] 1.85±0.06[26] 1.79±0.03[27]
	(110)			1.90	
	(111)fcc	1.77	1.79 [39] 1.76 [40]	1.77	1.90[28**]
	(111)hcp	1.76	1.89 [39]	1.77	

Computational Approach:
Gaussian Orbitals

- NWChem
- Local Spin-Density (LSD) Approximation
  - Slater Exchange Functional
  - VWN-V Correlation Functional
- Gaussian-type orbitals
  - 6-311G for C
- Effective-Core Potentials (CRENBL)
  - Core Electrons Cu(10), Au(60), Ni(10), Co(10), Fe(10)
- Isolated system

Pentagon Binding Energies

Definitions: E (A) - energy of isolated A atom

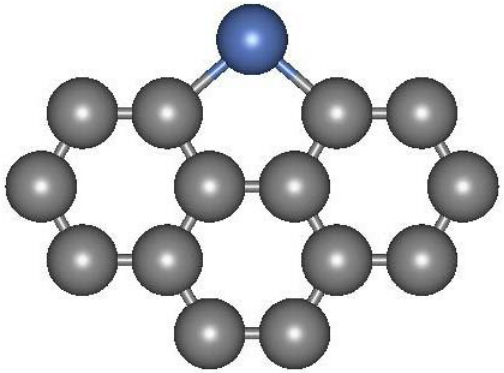
$E(C_N)$ - energy a "flake" with N carbon atoms

$E(C_N + A)$ - energy of C_N flake plus 1 A atom

Binding energy of A atom(s) to carbon flake;

$E_b(A, N) = E(C_N + A) - \{E(C_N) + E(A)\}$

Atom A	$E_b(A,14)$ (eV)
C	6.33
Fe	5.86
Co	5.94
Ni	5.87
Cu	5.05
Au	4.84

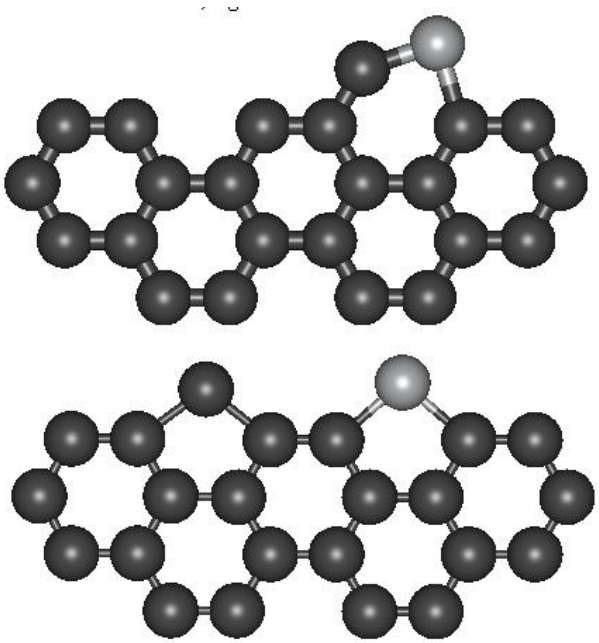


14 C atoms + 1 atom (A)

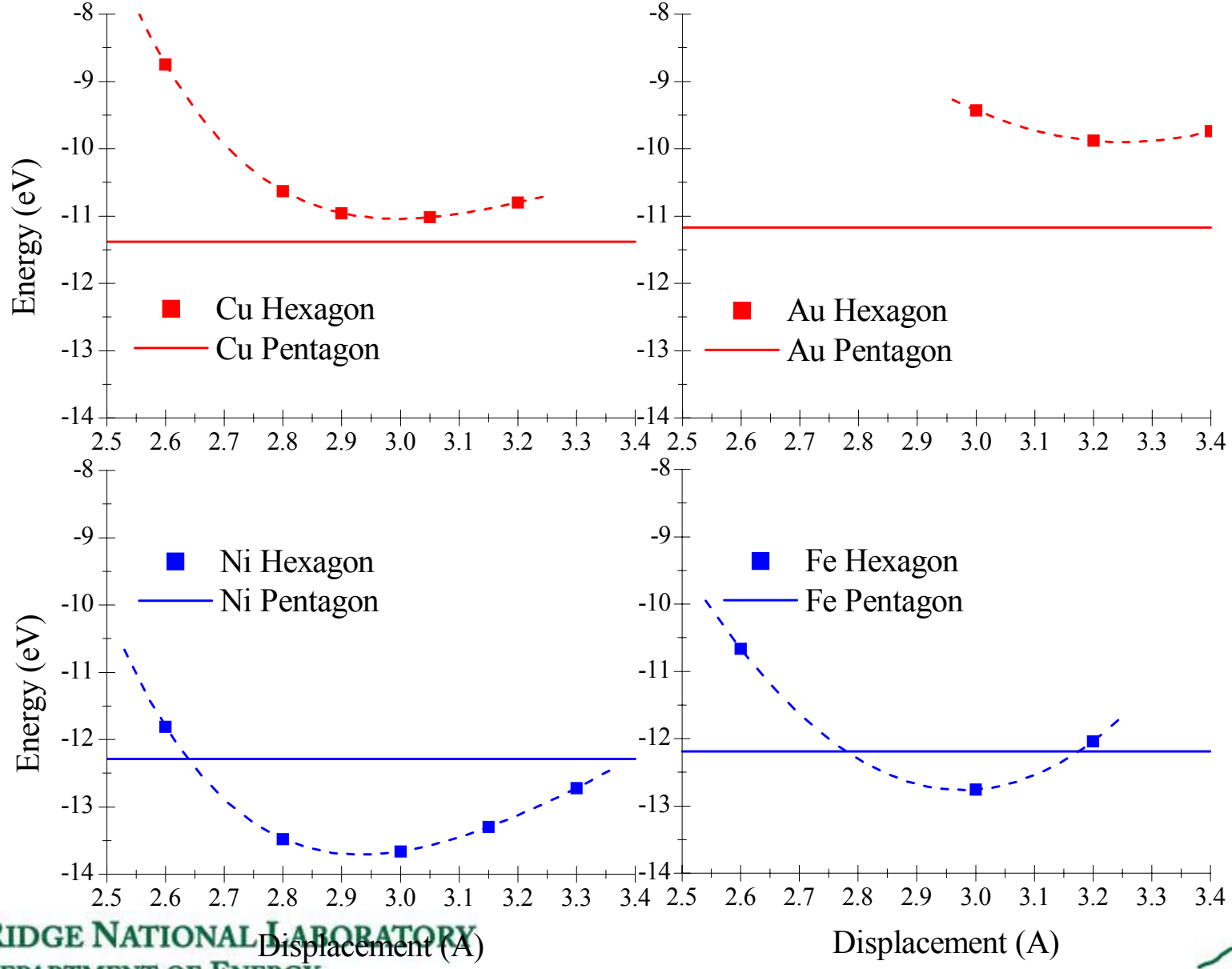
Carbon +Metal Hexagon Binding

Compare binding energies of a carbon and a metal atom in a hexagon to the binding energies in separated pentagons. ΔE > 0 means C-M hexagon is stable against break-up into two pentagons.

	C+M hexagon (eV)	C+M pentagons	ΔE
C	-15.75	-12.66	+3.09
Cu	-10.96	-11.38	- 0.42
Au	-9.88	-11.17	-1.29
Ni	-13.66	-12.29	+1.37
Co	-13.64	-12.27	+1.37
Fe	-12.76	-12.19	+ 0.57



Comparison of Hexagons and Pentagons



Conclusions and Future Work

- Lot of insight can be obtained from simple continuum calculations (with input from Experiment & DFT/MD).
  - Role of carbon diffusion and concentration.
  - Size & shape of catalytic particle.
- Inlet chemistry composition needs to be modeled.
- Carbide layer information needs to be incorporated (more on this on next slide).
- Incorporate observed phenomena and DFT/MD simulations for CNT/Ni interface using rule-based approach.
- More exhaustive parameter study has to be performed.
- Identify rate limiting steps and physical scales.
  - Knowledge can be used to develop more rigorous multi-scale approaches.

Summary & Conclusions

- Binding C adatom on various Ni surfaces and Ni Cluster facets.
  - Small clusters yield the same results as larger clusters and extended surfaces.
  - Ni(100) facet is favored over the Ni(110) and Ni(111) surfaces.
- Calculation of input parameters for continuum calculations.
  - Calculate strain energy due to curvature and relate to pentagons.
  - Determine energy of dangling bonds and relate to edge free energy.
- Why are Fe, Co, and Ni are good catalysts and Cu and Au are not?
  - BE of Cu and Au to Fullerene flake are ~ 1 eV less than Ni, Co, and Fe.
  - Comparison of BE of a carbon and a metal atom in a hexagon to the BE in separated pentagons indicates that, for the catalytic metals, <u>the hexagon is stable</u> against break-up into two pentagons.
- Growth of Baby Tubes on Ni(111) Surface:
  - Energetics indicate that growth is reaction limited.
  - Concerted motion may be important for incorporation of C into nanotubes.