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Multiscale Model-Based Process Systems Engineering

Progress and Challenges

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Outline

- An overview of multiscale modeling
- Drivers of nanomaterials research/New frontiers
- Control in self-assembly
- Design of materials for energy and sustainability
- Outlook

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- **An overview of multiscale modeling**
- Drivers of nanomaterials research/New frontiers
- Control in self-assembly
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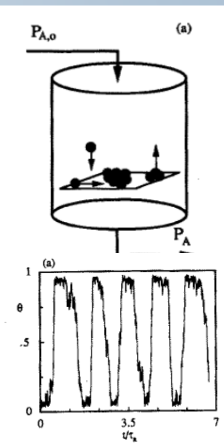
Some Esoteric Problems in Nonlinear Dynamics

- The first demonstration of hybrid multiscale modeling
  - ❖ Spatial KMC coupled with ODEs

The effects of phase transitions, surface diffusion, and defects on surface catalyzed reactions: Fluctuations and oscillations

D. G. Vlachos, L. D. Schmidt,[a] and R. Aris

8306 J. Chem. Phys. 93 (11), 1 December 1990 0021-9606/90/238306-08$03.00



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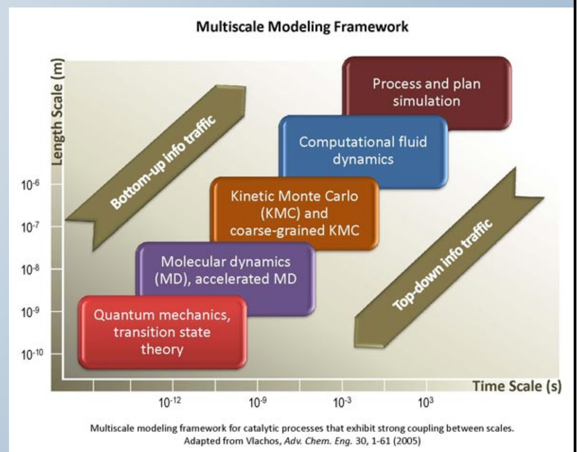
Multiscale Modeling

- Mathematical & computational methods developed
  - Bottom up modeling
    - **Process engineering**



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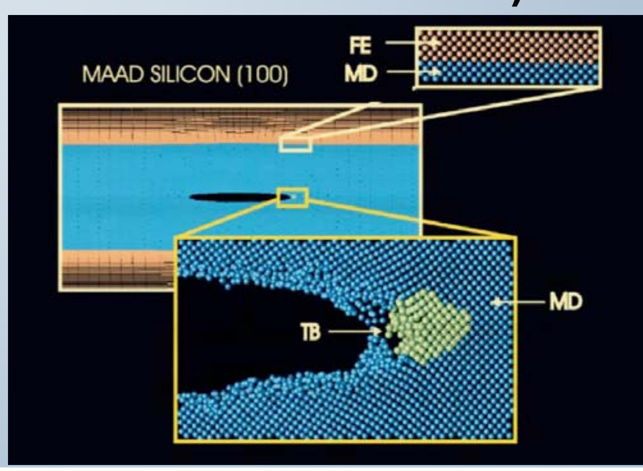
Materials Mechanics (Dislocation, Crack Initiation)



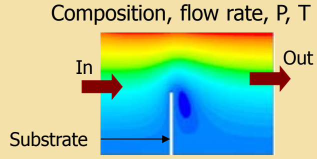
See also quasi-continuum method: Tadmor et al. (1996), Philips (1998)

Broughton et al., PRB 1999

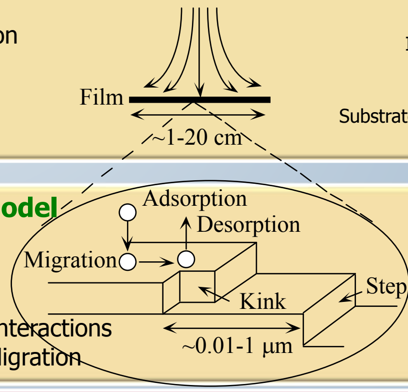
Fluid – Surface Coupling

Gas-phase continuum model/Finite difference

Continuum heat & mass transfer, fluid mechanics equations for a stagnation flow geometry



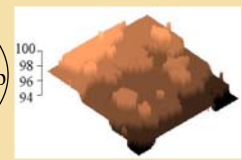
Dynamic coupling through fluxes



Surface atomistic model

KMC simulation

Solid-on-solid lattice
First-nearest neighbors interactions
Adsorption-Desorption-Migration

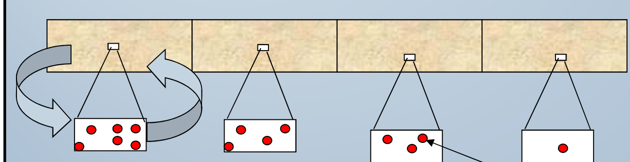


See also subsequent work on control of thin film roughness by Christofides and Cu electrodeposition by Braatz

Vlachos, *Appl. Phys. Lett.* 74, 2797 (1999)

Bridging the Gap of Length and Time Scales

- The **tooth-gap** (Kevrekidis) and **heterogeneous multiscale method** (E) were introduced
  - Different models are used at different grids
  - Pass dynamically info between grids
  - **Speedup due to length and time scale disparity**
    - **Simulate small lengths for short periods with the micro solver**



Gear et al., *Phys. Letters A* **316**, 190 (2003); **E** et al., *Phys. Rev. B* **67**, 092101 (2003)

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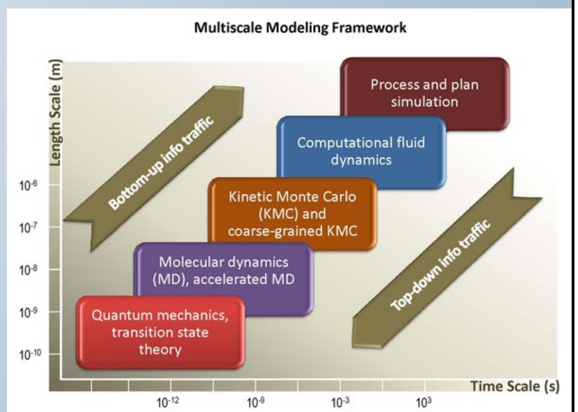
Multiscale Modeling

- Mathematical & computational methods developed
  - Bottom up modeling
    - Process engineering
  - Coarse-graining



Multiscale modeling framework for catalytic processes that exhibit strong coupling between scales. Adapted from Vlachos, *Adv. Chem. Eng.* 30, 1-61 (2005)

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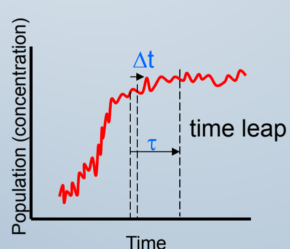
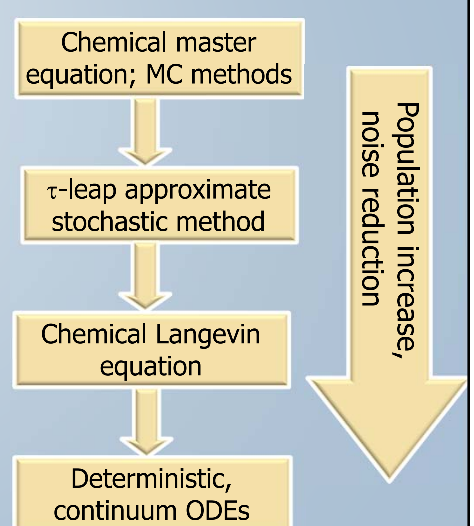
Temporally Coarse-Grained KMC

- Monte Carlo (MC) methods (Gillespie, 1975; 1976)
- A hierarchy of models exists for well-mixed systems





Review: Chatterjee and Vlachos, *J. Comp.-Aided Mater. Des.* **14**, 253 (2007)

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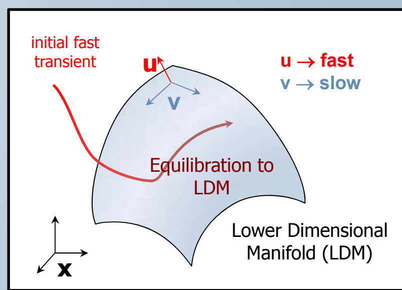
Temporally Coarse-Grained KMC

- Monte Carlo (MC) methods (Gillespie, 1975; 1976)
- A hierarchy of models exists for well-mixed systems
- Stochastic low dimensional manifold (SLDM): overcome stiffness[1]
  - CSP assisted partitioning[2]
  - Convergence to LDM[2]



[1] Gillespie, Petzold, E, Kaznessis, Vlachos, etc.

[2] Samant and Vlachos, *J. Chem. Phys.* **123**, 144114 (2005)

Review: Chatterjee and Vlachos, *J. Comp.-Aided Mater. Des.* **14**, 253 (2007)

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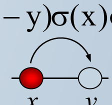
A Hierarchy of Coarse Grained KMC Simulations

Microscopic Stochastic Process

Hamiltonian: $H(\sigma) = -\frac{1}{2}\sum_{x\in M}\sum_{y\neq x} J(x-y)\sigma(x)\sigma(y) + \sum_{x\in M} h\sigma(x)$

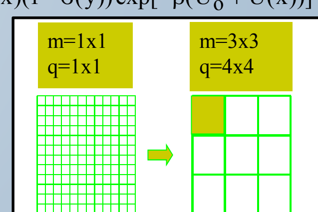
Microscopic processes/transition probabilities, e.g., surface diffusion



$\nu(x\to y,\sigma) = \nu_o\sigma(x)(1-\sigma(y))\exp[-\beta(U_o + U(x))]$

Mesoscopic Stochastic Process

$\eta_k = \sum_{y\in D_k}\sigma(y)$ q=number of points in a coarse cell



$\bar{U}_i = \sum_{k\in M_c}\bar{J}_{ik}\eta_k + \bar{J}_{00}(\eta_i - 1) - h$

$\bar{H}(\eta) = -\sum_{k\in M_c}\bar{U}_k\eta_k = -\frac{1}{2}\sum_{i\in M_c}\sum_{k\in M_c, k\neq i}\bar{J}_{ik}\eta_k\eta_i - \frac{\bar{J}_{00}}{2}\sum_{i\in M_c}\eta_i(\eta_i - 1) + \sum_{k\in M_c} h\eta_k$

$\bar{\nu}(k\to i,\eta) = \nu_o\eta_k(q-\eta_i)\exp[-\beta(U_o + \bar{U}_k)]$

J. Comp. Phys. **186**, 250 (2003)

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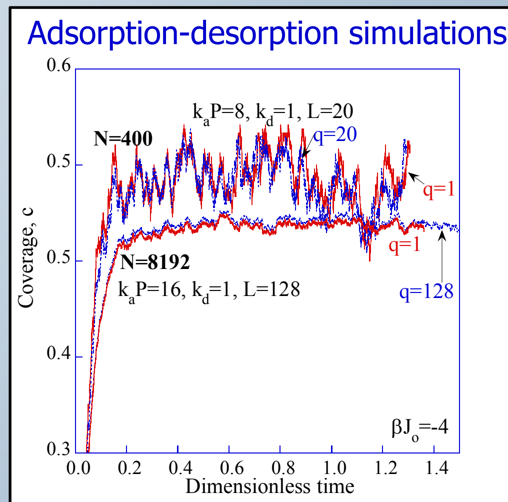
The Only CG Method with Correct Noise

- The noise is correctly simulated by coarse-grained KMC simulations at the same length scale
- The Gibbs states and the Large Deviation Principles of the coarse-grained and the microscopic processes are asymptotically (long potential) identical



Katsoulakis et al., *PNAS* **100,** 782 (2003)

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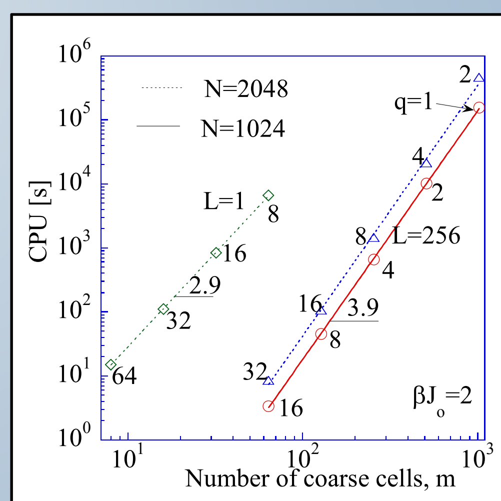
Profound CPU Savings Enable Simulation of Realistic Scales

- **CPU~1/$q^{2\text{-}4}$**
  - 4-5 sites per dimension in 3D, leads to 10^8 reduction of CPU!
  - **Overcome hydrodynamic slowdown (diffusion): q^2**
  - More savings can result by employing local update search algorithms for coarse potentials
- **Simulation of large length scales is feasible**



Katsoulakis and Vlachos, *J. Chem. Phys.* **119**, 9412 (2003)

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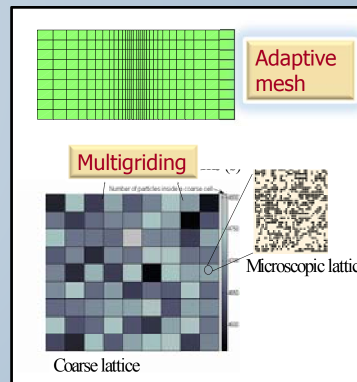
Overview of Spatial Acceleration Methods

- Spatial adaptivity[1]
  - A posteriori error estimates guide mesh refinement and generation of phase diagrams
- High accuracy
  - Higher order closures[2]
  - Multigrid/Relaxation criteria[2]
  - Rigorous cluster expansions/Theory[3,4]
- Multicomponent systems[5,6]
- Time scale acceleration



[1] Chatterjee et al., *JCP* **121**, 11420 (2004); *PRE* **71**, 0267021 (2005); Katsoulakis, Plechac, et al., J. Non Newtonian Fluid Mech. (2007)
[2] Chatterjee and Vlachos, JCP **124**, 0641101 (2006)
[3] Katsoulakis, Plechac, et al., *ESAIM, Math Model. Num. Anal.* **41**, 627-660 (2007)
[4] Katsoulakis, Plechac, Sopasakis, SIAM Num. Anal. (2006)
[5] Chatterjee and Vlachos, JCP **127**, 034705 (2007)
[6] Collins, Chatterjee and Vlachos, JCP, **129**, No. 184101 (2008)

Review: Chatterjee and Vlachos, *J. Comp.-Aided Mater. Des.* **14**, 253 (2007)

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Continuum Mesoscopic Equations

- Mesoscopic equation (for diffusion)

$$\partial c_t = -\nabla \cdot \left(-\mu[c]\nabla\left(\delta\varphi[c]/\delta c\right)\right)$$

$$\frac{\partial c}{\partial t} = \nabla.\left\{De^{-\beta J*c}\left[\nabla c - \beta c(1-c)\nabla J*c\right]\right\}$$

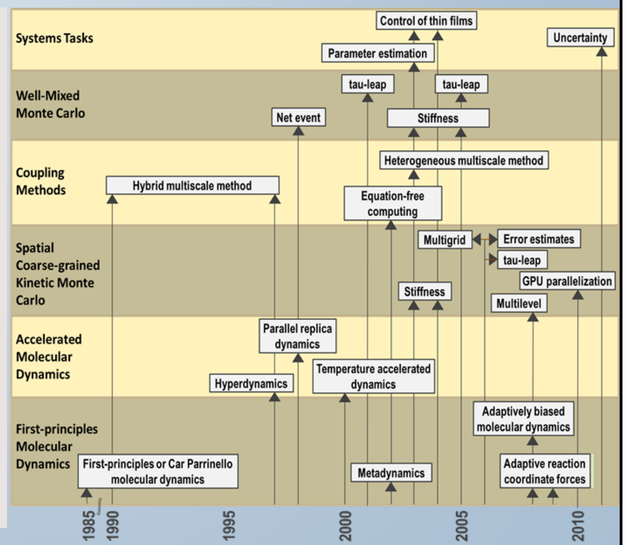
$$J*c = \iint J(|r-r'|)c(r')dr'$$

- Mesoscopic equations include essential physics
  - Intermolecular forces, microscopic mechanisms
  - Are exact when interactions are long ranged
- Amenable to systems tasks
- Spectral methods for efficient, parallelizable calculations

PRL **85**, 3898 (2000); *PRL* **84**, 1511-1514 (2000); *Chem. Eng. Sci.* **58**, 895 (2003)

The 30,000 Miles Airview

- Significant progress made on method development and testing
- Focus has been on **prototype problems**
- Field is maturing
- **Much less work has been done at the systems' level**



Vlachos, *AIChE J.* **58(5)**, 1314 (2012)

Outline

- An overview of multiscale modeling
- **Drivers of nanomaterials research/New frontiers**
- Control in self-assembly
- Design of materials for energy and sustainability
- Outlook

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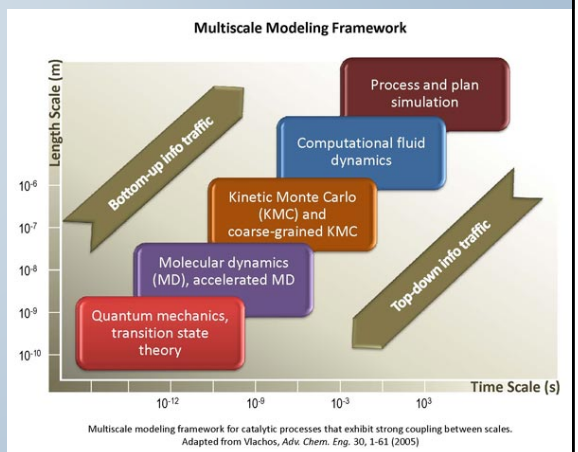
Multiscale Modeling

- Mathematical & computational methods developed
  - Bottom up modeling
    - **Process engineering**
  - Coarse-graining
  - **Top down modeling**
    - **Product engineering**



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APOLLO 13: Houston We Have a Problem

- Multiscale modeling methods from prototype systems do not apply/extend well to real problems
- Real problems are hard!

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Realistic Nanomaterials Process Modeling: New Frontiers

- Product design and control at the nanoscopic scale
- Emergent behavior and/or emergent properties
- Combinatorial complexity
- Validation, verification, and uncertainty
- Computer architectures

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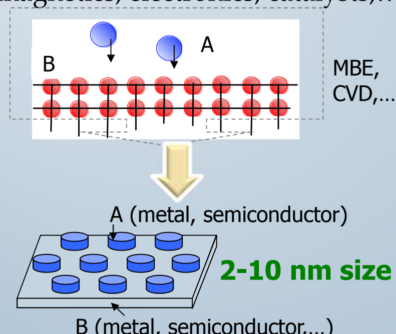
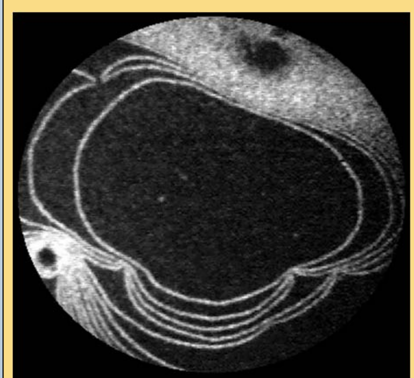
Self-Assembly in Heteroepitaxy

- Self-organization is a bottom up strategy for materials synthesis
  - Low cost; broad applications (optical, magnetics, electronics, catalysts,…)



LEEM images, 1 x 1 mm^2, 10^7 Pb atoms



Pb/Cu(111): *Nature* **412**, 875 (2001)

- Non-uniform shape, size, spacing obtained

- How does one 'control' stuctures and thereby enable scaling up?

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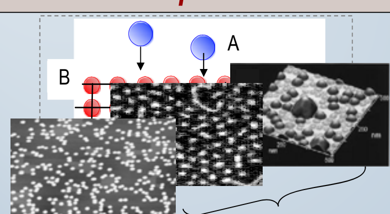
Bottom-up Fabrication is Attractive

Bottom-up fabrication



- Stable minimum free energy structures
- **Small feature size**
- Use of existing deposition technologies
- **Scalable, economically viable**
- **Disordered structures**

Top-down fabrication

Electron-beam (EB) Lithography

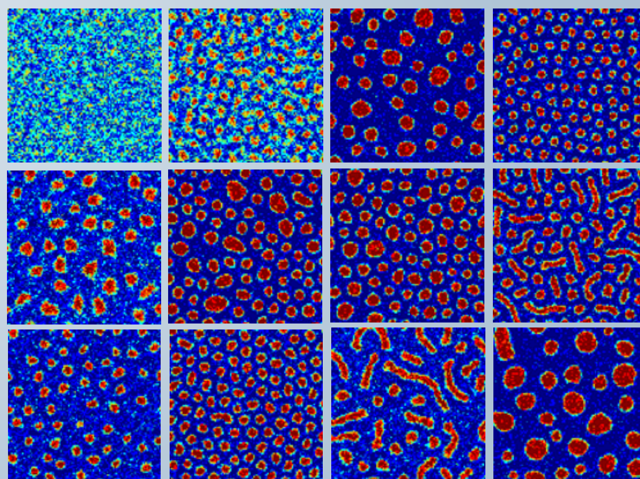
Focused ion Beam (FIB) Lithography

Atomic force Microscopy (AFM)

- Strain defects often formed
- EB, FIB: **Feature size > 45 nm**
- Need for new deposition technologies
- AFM: **Not scalable**, not economically viable

Emergent Behavior

- Collective behavior not predicted from atom-atom interactions
- Patterns very sensitive to operating conditions



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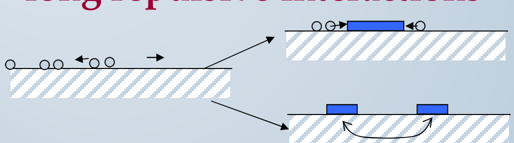
Role of Interactions in Self-Assembly

- Patterns form by the interplay of short attractive and **long repulsive interactions**

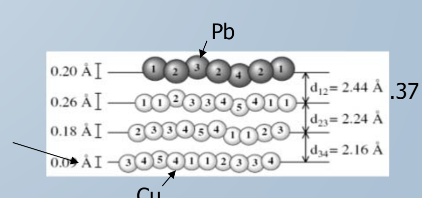


Elastic repulsion > 20 lattice constants long

$$J(r) = j_0\left(e^{-(r/r_a)^2} - \chi e^{-(r/r_r)^2}\right)$$

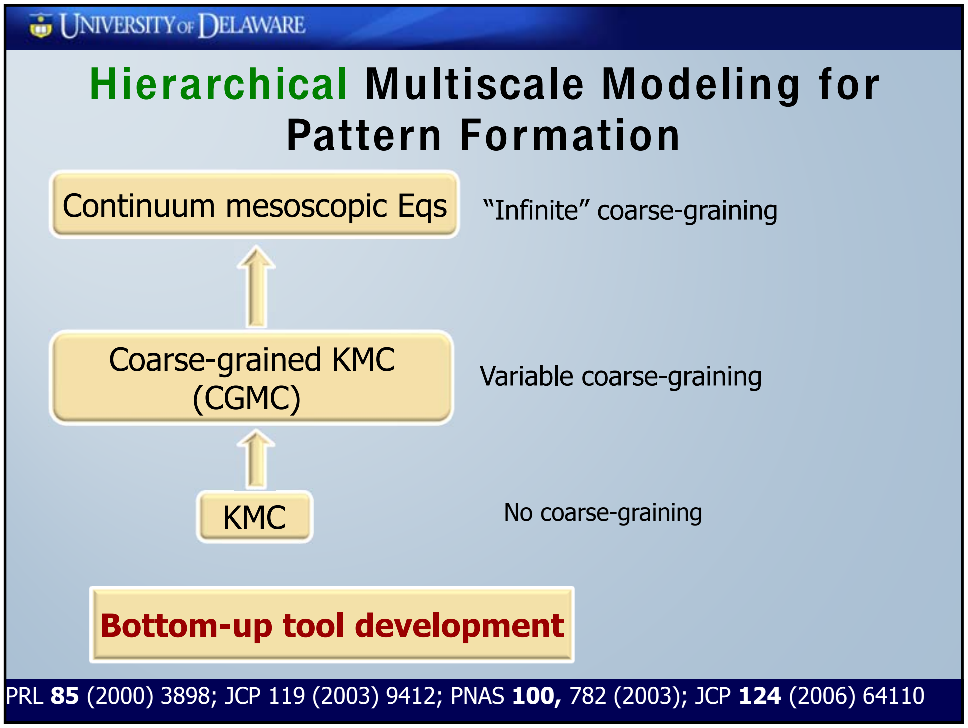
$$\chi \approx \frac{Ea^3}{1-\nu^2}\left(\frac{\Delta a}{a}\right)^2$$

- Repulsive interactions
  - Lattice-mismatch
  - Electronic effects



J. Phys. Condensed Matter 13 (2001) 1793

- **Computational cost prohibitive for atomistic KMC**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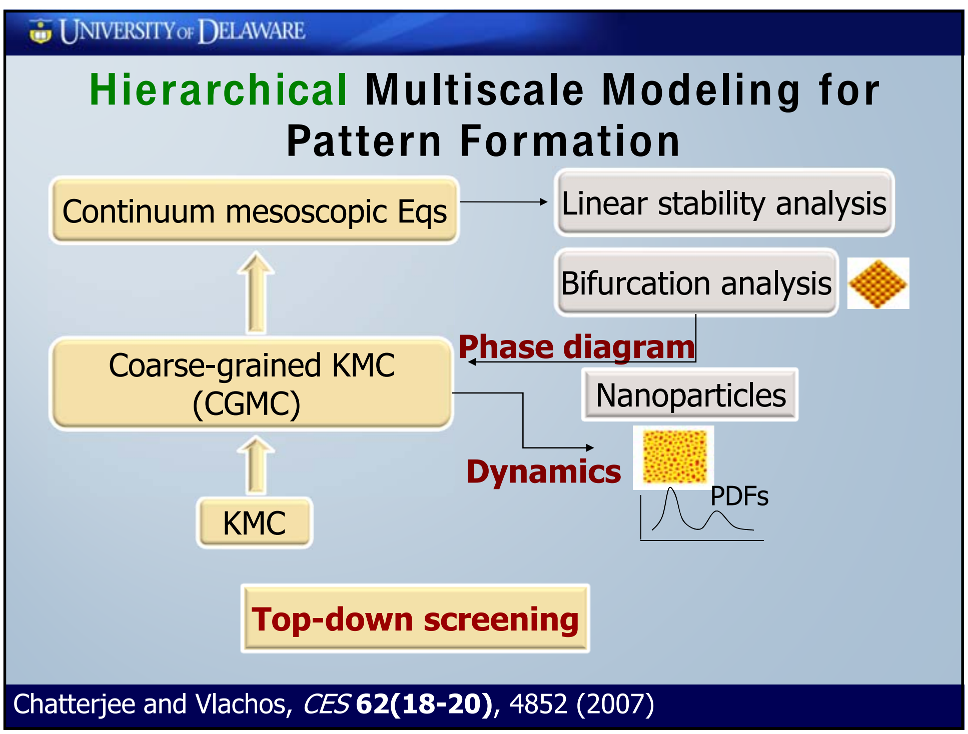
Hierarchical Multiscale Modeling for Pattern Formation
Continuum mesoscopic Eqs
"Infinite" coarse-graining
Coarse-grained KMC (CGMC)
Variable coarse-graining
KMC
No coarse-graining
Bottom-up tool development
PRL 85 (2000) 3898; JCP 119 (2003) 9412; PNAS 100, 782 (2003); JCP 124 (2006) 64110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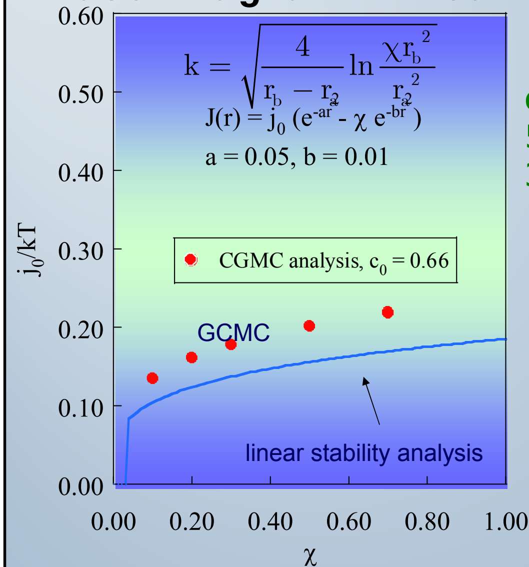
Hierarchical Multiscale Modeling for Pattern Formation
Continuum mesoscopic Eqs
Linear stability analysis
Bifurcation analysis
Phase diagram
Coarse-grained KMC (CGMC)
Nanoparticles
Dynamics
PDFs
KMC
Top-down screening
Chatterjee and Vlachos, CES 62(18-20), 4852 (2007)

Phase Diagram: Linear Stability vs. GCMC



q	CPU	CPU reduction
5x5	11 hr	0.4×10^6 times
3x3	3-4 d	7×10^3 times

$\lambda = 12 - 22\,\mathrm{nm}$

$N = 300 \times 300$ lattice sites

$a = 1\,\mathrm{nm} \Rightarrow 0.3\,\mu\mathrm{m} \times 0.3\,\mu\mathrm{m}$

Chatterjee and Vlachos, *CES* **62(18-20)**, 4852 (2007)

Patterns' Shape: Nonlinear Analysis

Different shapes form under certain conditions

$$\alpha + \Theta\nu + \Xi > 0$$

$$\alpha = -2w(1-2c_0) - 3w - 3w^2\beta(1-2c_0)$$

$$\Theta = 4w_1(1-2c_0) - 4c_0(1-c_0)(w + w_1 - ww_1)$$

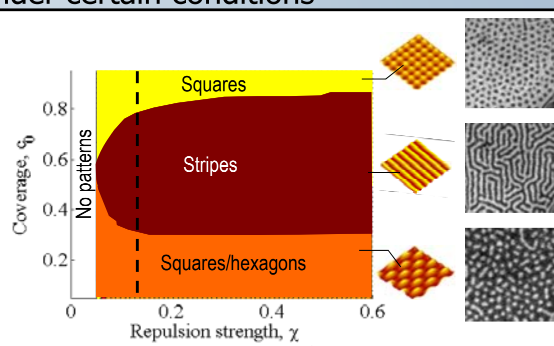
$$\nu = -\beta^2 k^2 w^2 c_0(1-c_0) - \beta k^2 w(1-4c_0+2c_0^2)$$

$$\Xi = 8\beta^2 w_2 w(1-2c_0)^2$$

$$w = \iint J(\xi,\eta) e^{ik_x\xi} d\xi d\eta$$

$$w_1 = \iint J(\xi,\eta) e^{2ik_x\xi} d\xi d\eta$$

$$w_2 = \iint J(\xi,\eta) e^{i(k_x\xi + k_y\eta)} d\xi d\eta$$



Exp: J. Phys. Condensed Matter 14 (2002) 4227

- Patterns are in qualitative agreement with experimental data
- Key differences are: (1) labyrinths, (2) order-disorder

Chatterjee and Vlachos, *CES* **62(18-20)**, 4852 (2007)

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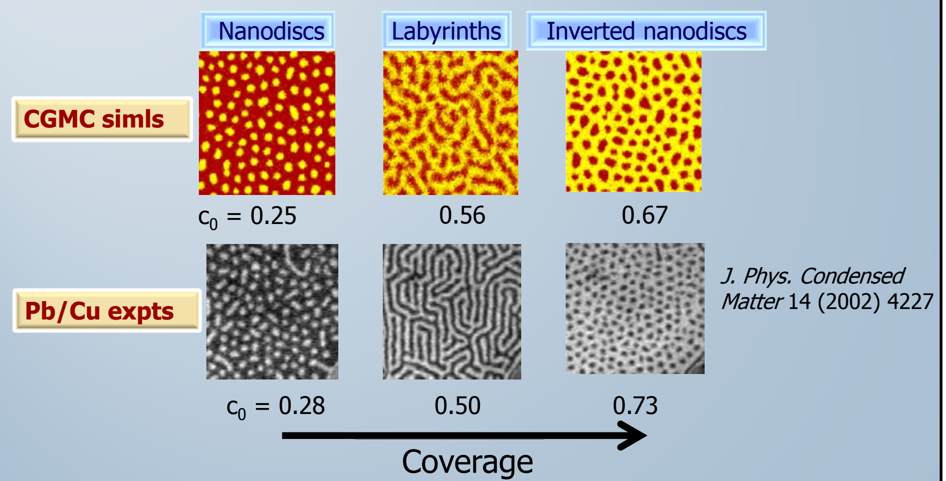
CGMC Simulations Mimic Experiments



Chatterjee and Vlachos, *CES* **62(18-20)**, 4852 (2007)

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Open Questions

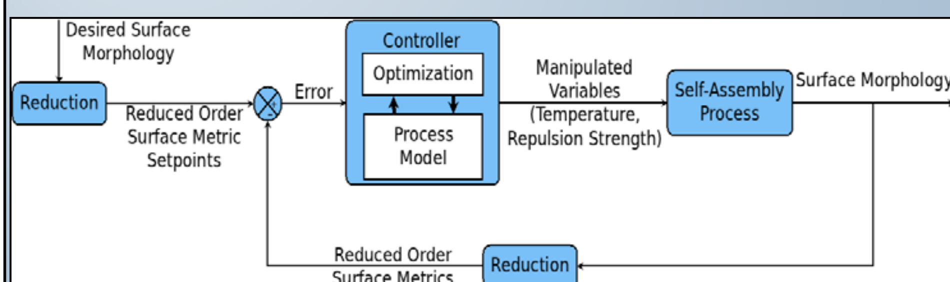
- Hierarchy of length and time scales
  - Process model-based control impossible
- Emergent behavior
  - Sluggish dynamics, sensitivity to conditions
- Extremely high dimension (distributed parameter systems)
- Intrinsic stochastic fluctuations
- Poor controllability
  - Control nanoscale features over several orders of magnitude
  - A mere handful of manipulated variables at the macroscale
- Poor observability
  - Measurements of features are unavailable online

Systems Tasks Needed

- Overall control strategy
- Gradient estimation
- Sensitivity analysis
- Efficient and robust optimization algorithms (agent based)
- Quantitative metrics to compare with experiments

Overarching Approach

- Determine the degree of controllability
- Implement a control strategy
- Account for statistical information in experiments and models (pdfs)



[1] J. McGill et al., B.A. Ogunnaike, D.G. Vlachos J. Comput. Phys. (2012)
[2] J. McGill, B.A. Ogunnaike, D.G. Vlachos, In Preparation

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Finite Differencing Gradient Estimation

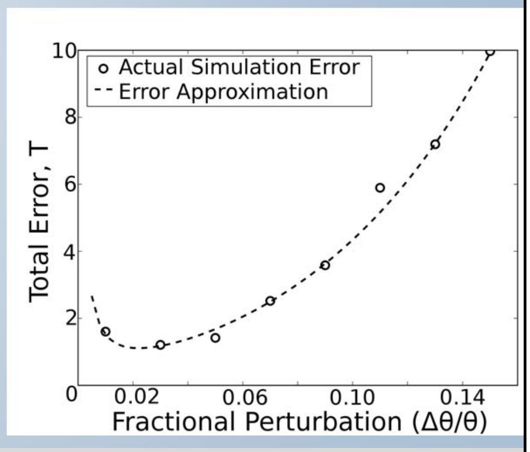
- Easy to implement
- FD gradient estimate

$$E(G)=\frac{E(f(\theta+\Delta\theta))-E(f(\theta-\Delta\theta))}{2\Delta\theta}+O(\Delta\theta^2)$$

$$\mathrm{var}(G)=\frac{1}{(2\Delta\theta)^2}\left[\mathrm{var}\left(f|_{\theta+\Delta\theta}\right)+\mathrm{var}\left(f|_{\theta-\Delta\theta}\right)\right]$$

- Total error:

$$T=\left(\frac{\mathrm{var}(G)}{n}\right)^{1/2}+O(\Delta\theta^2)$$



- **There is an optimal choice for Δθ**
- CPU: Linear scaling with number of parameters
- Variance reduction methods: CNR and CRP

McGill et al., *J. Comput. Phys.* **231**, 7170(2012)

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Likelihood Ratio Gradient Estimation

- A weighted average similar to importance sampling

$$\frac{\partial E(f)}{\partial\theta_j}=E\left(f\,\frac{\partial \ln p_v}{\partial\theta_j}\right)$$

$$\frac{\partial \ln p_v}{\partial\theta_j}=\sum_{i=1}^{n}\left[\frac{I(\mu_i,j)}{\theta_j}-\tau_i h_j(S_i)\right]$$

$$I(\mu_i,j)=\begin{cases}1 & \text{if } \mu_i=j\\ 0 & \text{if } \mu_i\neq j\end{cases}$$

- **Calculate the entire gradient vector from *one* simulation**
- Trivial code modification (record reaction fired and time)

$I(\mu_i,j)$	: indicator function
μ_i	: reaction fired at i^{th} event
τ_i	: time step of i^{th} event
S_i	: state at i^{th} event
$h_j(\cdot)$	: related to propensity of j^{th} reaction
p_v	: joint pdf for random variables

McGill et al., *J. Comput. Phys.* **231**, 7170(2012)

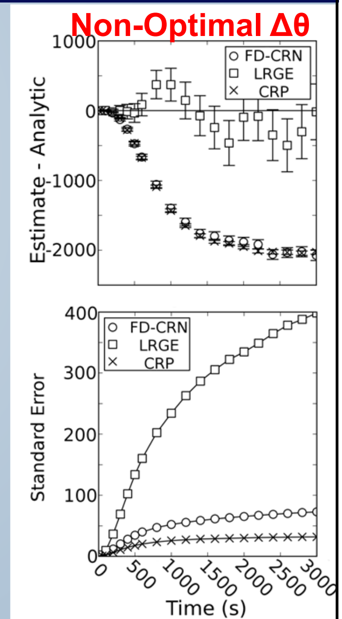
LRGE vs. FD Estimation Methods

- Likelihood ratio method is unbiased compared to FD methods
- LRGE is a better estimator despite having a large variance
- LRGE requires fewer simulation evaluations

LRGE: Likelihood ratio gradient estimation[1]

FD-CRN: **FD** with common random numbers

CRP: Common reaction path method[2], low variance **FD**



[1] J.A. McGill et al., J. Comput. Phys. (2012)
[2] M. Rathinam et al., J. Chem. Phys. (2010)

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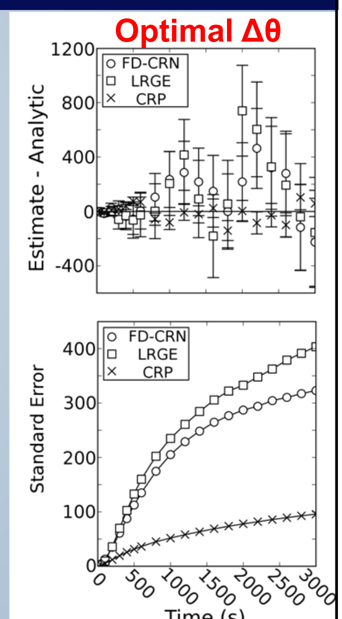
- LRGE requires fewer simulation evaluations

LRGE: Likelihood ratio gradient estimation[1]

FD-CRN: **FD** with common random numbers

CRP: Common reaction path method[2], low variance **FD**



[1] J.A. McGill et al., J. Comput. Phys. (2012)
[2] M. Rathinam et al., J. Chem. Phys. (2010)

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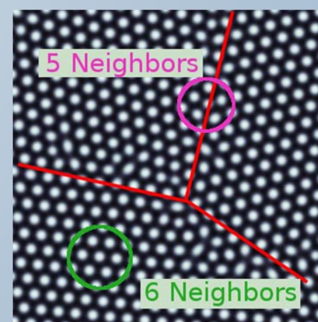
Define Metrics

- Difficult to use images as process outputs for control
  - Translations and rotations: *morphologically equivalent* but *different images*
- Morphological information arises from **image analysis**
- Define **metrics** that are *invariant to basic transforms* on the image

Metrics (9)
- ✓ Hexagonal order parameter
- ✓ Distance between islands
- ✓ Characteristic length
  - ✓ From spectral analysis of surface[1]
- ✓ Number of defects
- ✓ Minkowski measures[2]
  - ✓ Area fraction
  - ✓ Perimeter of nanodots
  - ✓ Euler characteristic (connectivity)



Abukhdeir and Vlachos, J. Comp. Phys. (2011); [2] Legland et al., Image Anal Sterol (2007)

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Eliminate Correlated Metrics

- Many surface metrics (9) exist but are **not** necessarily **independent**
- **Cannot use metrics directly** as process outputs
  - Correlations cause *instability* in controller

Contour plots of metrics vs. manipulated variables

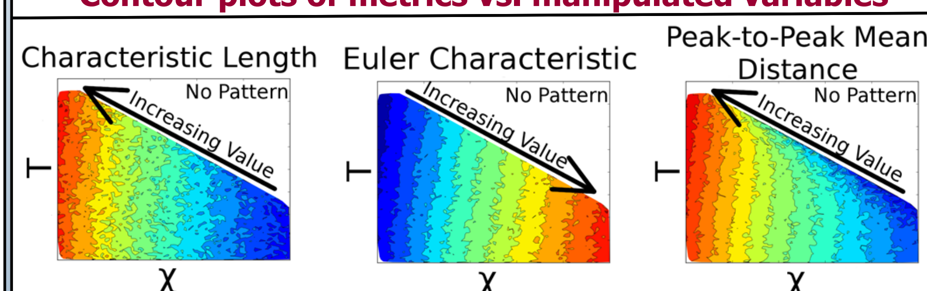

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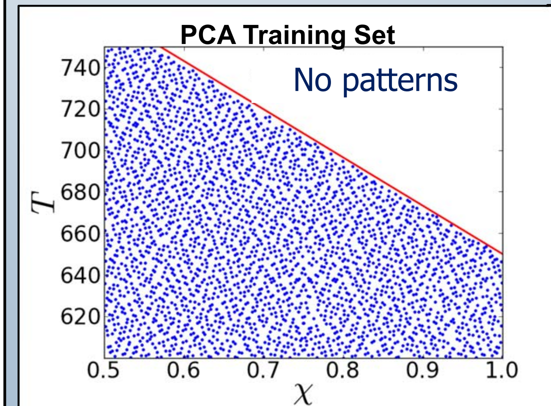
Image Reduction via PCA

- Use Principal Component Analysis (PCA) to **find an orthogonal basis** for surface metrics



Methodology

- Surfaces were simulated for long time starting from a random initial configuration
- Final morphology reduced to metrics
- Procedure repeated for many T- χ pairs

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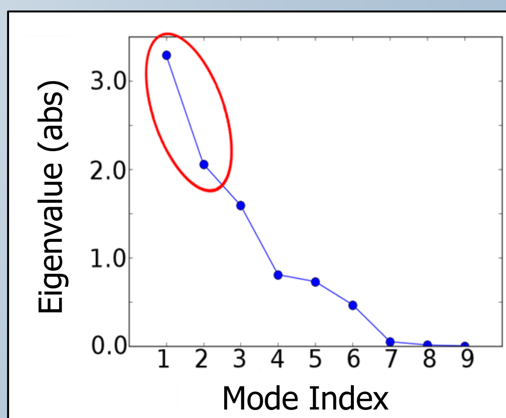
Image Reduction via PCA

- Find an orthogonal basis for surface metrics
- Use PCA modes as process outputs
  - Orthogonality implies *some controllability*
  - Unaccounted modes treated as a disturbance
- First two modes dominate



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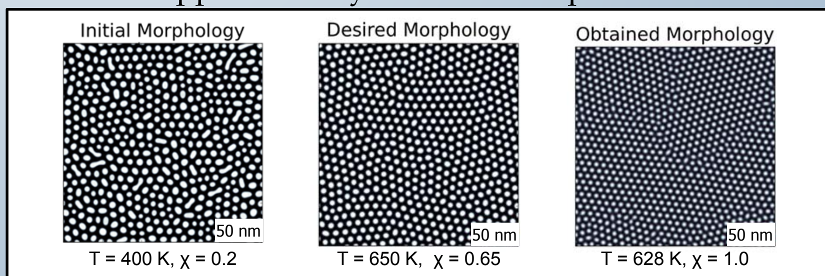
PCA Modes in a Simple PI Controller

- **PCA modes** can be used as **process observables**
- Are they *good* observables?
  - Proof of concept with a simple PI controller
  - Assumed approximately first order response



- **Control is possible** (error reduced by order of magnitude)
  - Refinement of controller should yield better results

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Open Questions

- Hierarchy of length and time scales
  - Process model-based control impossible
- Emergent behavior
  - Sluggish dynamics, sensitivity to conditions
- Extremely high dimension (distributed parameter systems)
- Intrinsic stochastic fluctuations
- Poor controllability
  - Control nanoscale features over several orders of magnitude
  - A mere handful of manipulated variables at the macroscale
- Poor observability
  - Measurements of features are unavailable online

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Outline

- An overview of multiscale modeling
- Drivers of nanomaterials research/New frontiers
- Control in self-assembly
- **Design of catalytic materials for energy and sustainability**
- Outlook

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Predicting Novel Catalytic Materials

- First principles methods (DFT) promise to deliver strategies for rational catalyst design
- Current studies limited to cases when:
  - Thermodynamics (heat of adsorption) dominates[1,2]
  - Linear interpolation is employed[3]

$N_2+3H_2=2NH_3$

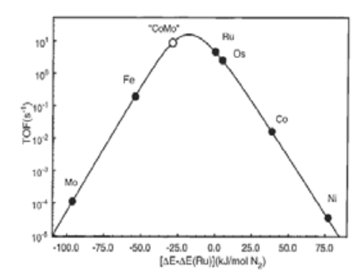
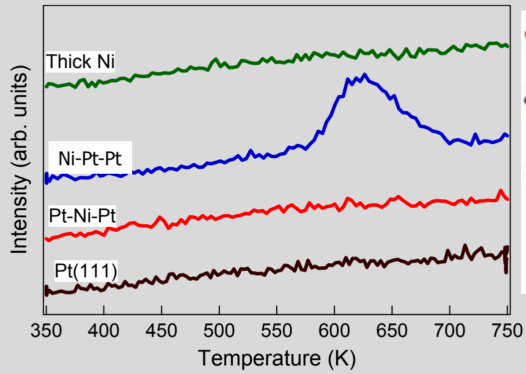
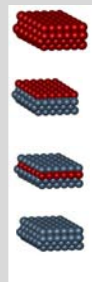


Figure 1. Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen. The synthesis conditions are 400 °C, 50 bar, gas composition H_2:N_2 = 3:1 containing 5% NH_3.

[1] Strasser et al., *J. Phys. Chem. B* **107**(40), 11013 (2003)
[2] Greeley and Mavrikakis, *Nat. Materials* **3**(11), 810 (2004)
[3] Jacobsen et al., *J. Am. Chem. Soc.* **123**, 8404 (2001)

Molecular Architecture Plays a Pivotal Role in Emergent Materials





3.0 Langmuir NH_3 at 350K at UHV

- Ammonia decomposes on Ni-Pt: $2NH_3=N_2+3H_2$
- No decomposition on other surfaces
- Ni-Pt is the most active catalyst

Hansgen, Chen, and Vlachos, *Nature Chem.* **2**, 484-489 (2010)

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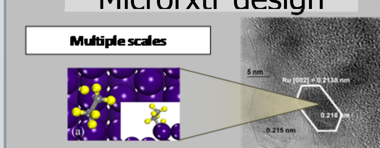
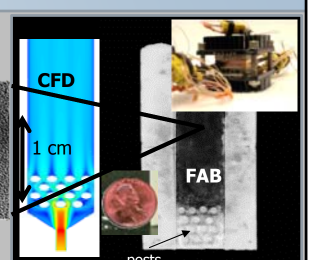
Complexity in Catalytic Modeling

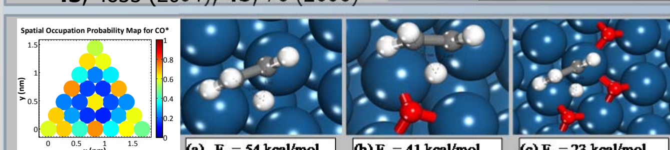
- Multiscale problem/catalyst heterogeneity
- Large mechanisms
- Complex feedstocks

Microrxtr design

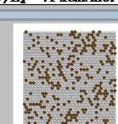




Norton, *Ind. Eng. Chem. Res.* **43**, 4833 (2004); **45**, 76 (2006)

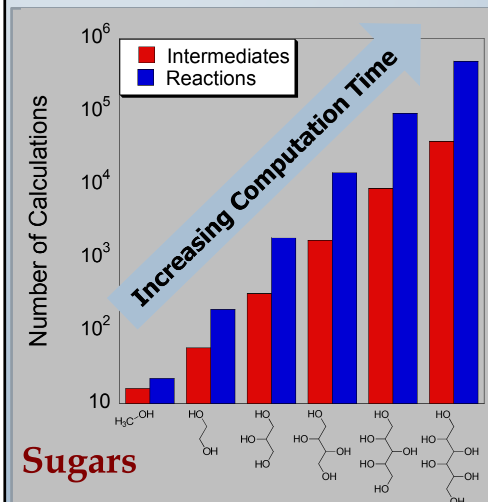


Wang et al., *J. Chem. Phys.* **133**, 224503 (2010)



Review: Salciccioli et al., *Chem. Eng. Sci.* **66**, 4319 (2011)

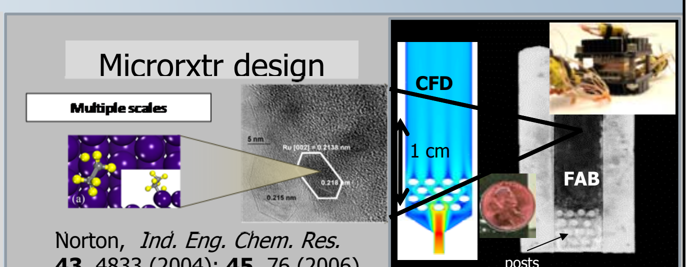
Modeling Reactions of Large Molecules is Challenging



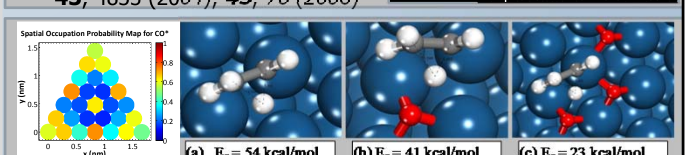
- Combinatorial explosion in number of calculations
- Semi-empirical methods can potentially identify relevant species and reactions instantaneously
- **There is little understanding of the errors associated with these techniques**

Complexity in Catalytic Modeling

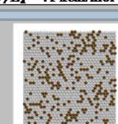
- Multiscale problem/catalyst heterogeneity
- Large mechanisms
- Complex feedstocks
- Adsorbate heterogeneity
- Combinatorial problem due to coverage effects
- Catalyst dynamics



Norton, *Ind. Eng. Chem. Res.* **43**, 4833 (2004); **45**, 76 (2006)



Wang et al., *J. Chem. Phys.* **133**, 224503 (2010)



Review: Salciccioli et al., *Chem. Eng. Sci.* **66**, 4319 (2011)

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Overarching Concept: Hierarchical Multiscale Modeling

- Start with a sufficiently simple but physically relevant model at each scale
- Link all models
- Perform a sensitivity analysis
- Identify important scale and parameter(s)
- Use higher level theory for this scale and parameter(s)
- Iterate

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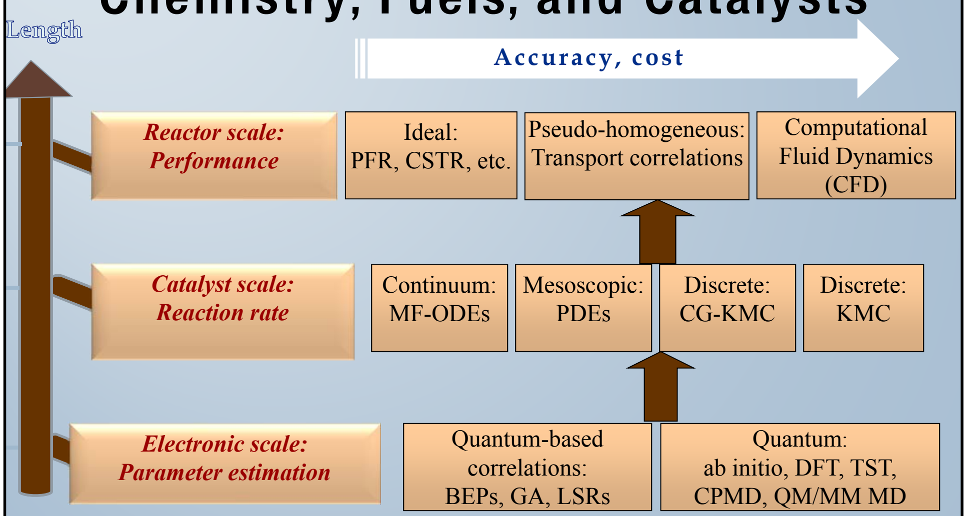
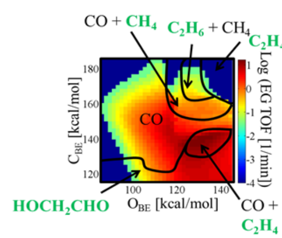
Hierarchy Enables Rapid Screening of Chemistry, Fuels, and Catalysts



Toward High Throughput Computing: Metal and Metal-like Catalysis

Linear Scaling Relations (LSRs) → Group Additivity (GA) → Brønsted Evans Polanyi (BEP) → Microkinetic Model (MKM)

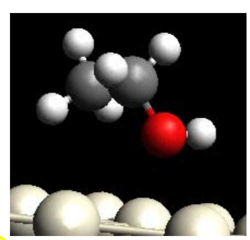
- Thermochemistry via group additivity & LSRs
- Reaction barriers and pre-exps via BEPs and TS
- Perform MKM
  - DFT-based or semi-empirical based: Screen and refine via DFT
- Assess model predictions via experiments



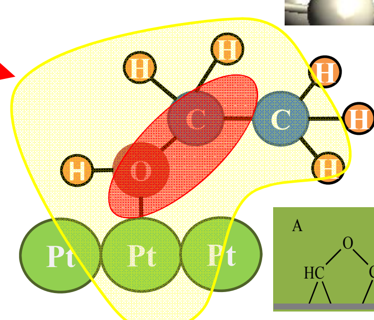
Salciccioli, Y. Chen, and Vlachos, *J. Phys. Chem. C* **114**, 20155 (2010); Salciccioli et al., *J. Phys. Chem. C* **116**, 1873 (2012)

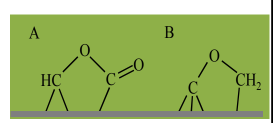
Group Additivity for Adsorbed Species

- Binding for oxygenates traced to (CHyOx) groups
- Use alcohols and dehydrogenated intermediates of alcohols, esters, ethers, acids to develop groups
- Include contributions for $\Delta H_{f,298}$, S(T) and $C_p(T)$



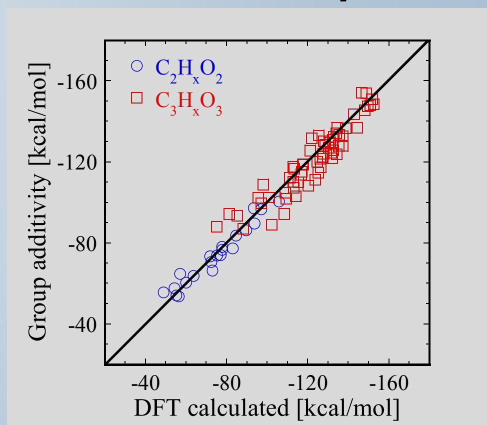
Group	$\Delta H_{f,298}$ Value [kcal/mol]
[C(C,H$_2$)-O(M,H)]	-50.2
[C(C,H,M)-O(H)]	-46.8
[C(C,M$_2$)-O(H)]	-39.3
[C(C,H$_2$)-O(M)]	-26.1
[C(C,H,M)-O(M)]	-26.5
[C(C,M,M)-O(M)]	-33.4
[C(C,M)=O]	-33.4
[C(C$_2$,H)-O(M,H)]	-51.1
[C(C$_2$,M)-O(H)]	-42.9
[C(C$_2$,H)-O(M)]	-25.1
[C(C$_2$,M)-O(M)]	-23.0





Group Additivity for Adsorbed Species

- 2^{nd}-order effects included:
  - 4-member ring strain
  - Weak interactions
  - Hydrogen bonding
- Calculations of $\Delta H_{f,298}$ of $C_2H_xO_2$ and $C_3H_xO_3$ species show good quantitative agreement

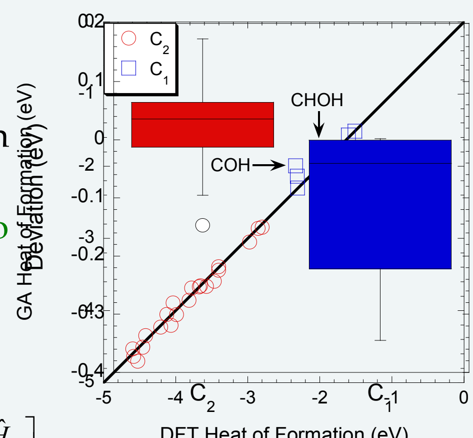


This method can be used for initial screening of larger hydrocarbons and different oxygenates (alcohols, polyols, esters, ethers, acids) found in bio-oil

Salciccioli et al., *J. Phys. Chem. C* **114**, 20155 (2010); *J. Phys. Chem. C* **116**, 1873 (2012)

Estimated Heats of Formation May Show Systematic Deviations

- Regressed groups show errors which are normally distributed with zero mean
- Unregressed C_1 oxygenate group values have nonzero mean



Species Type	Mean	Std. Dev.	No. Points
C_2	0.02	0.08	21
C_1	-0.11	0.13	7

Error: $\varepsilon_{H_f} = H_f - \hat{H}_f$

Mean: $E[\varepsilon_{H_f}] = E[H_f] - E[\hat{H}_f]$

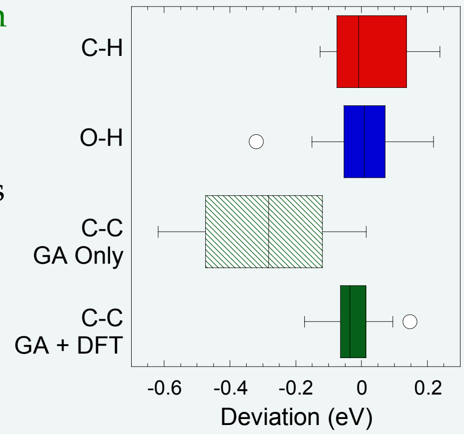
Variance: $Var[\varepsilon_{H_f}] = Var[H_f] + Var[\hat{H}_f] - 2Cov[H_f, \hat{H}_f]$

Sutton and Vlachos, *J. Cat.*, Submitted

Estimated Heats of Reaction Inherit Systematic Errors in Parent Species

- Bias in heats of formation propagates to heats of dissociation reactions forming C_1 species
- DFT values for C_1 species eliminate this bias

Reaction	Mean	Std. Dev.	No. Points
C-H	0.01	0.10	24
O-H	0.01	0.13	18
C-C GA Only	-0.28	0.20	21
C-C GA + DFT	-0.02	0.08	21



Sutton and Vlachos, *J. Cat.,* Submitted

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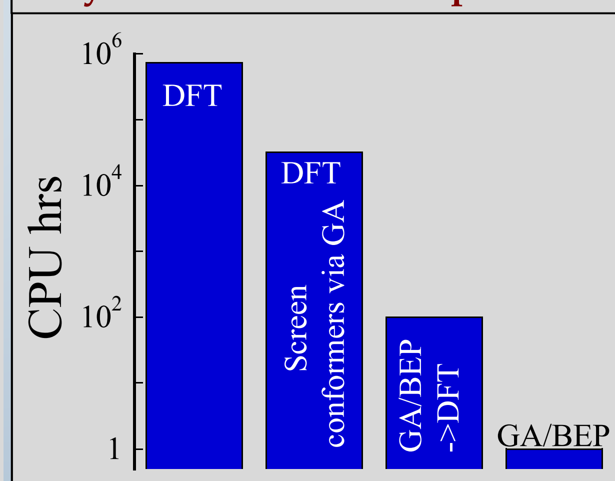
Computational Savings from Hierarchy

- Profound computational savings
- (**Important**) information content remains the same

Glycerol thermal decomposition



Chen et al., *J. Phys. Chem.* **115(38)**, 18707 (2011)

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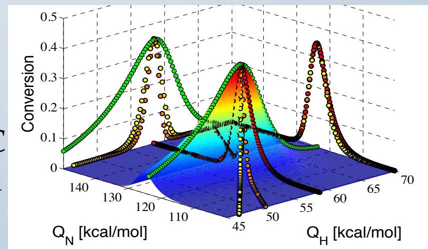
High Throughput Multiscale Model-based Catalyst Design

350 °C
1 atm



NH_3 decomposition

$$NH_3 + * \Leftrightarrow NH_3*$$
$$NH_3* + * \Leftrightarrow NH_2* + H*$$
$$NH_2* + * \Leftrightarrow NH* + H*$$
$$NH* + * \Leftrightarrow N* + H*$$
$$2N* \Leftrightarrow N_2 + 2*$$
$$2H* \Leftrightarrow H_2 + 2*$$

- Search is done on atomic descriptors while running the full chemistry and reactor models
- Optimal catalyst properties are identified

Prasad et al., *Chem. Eng. Sci.* **65**, 240 (2010)

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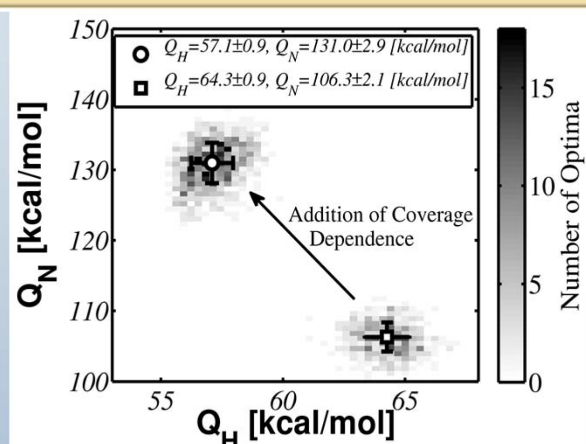
Parametric and Model-Hierarchy Uncertainty

Effect of adsorbate-adsorbate interactions



Ulissi et al., *J. Catal.* **281**, 339 (2011)

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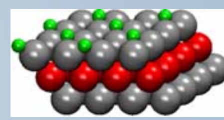
Identifying Bimetallic Catalysts

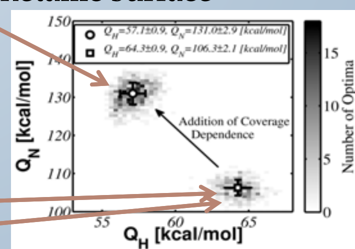
Metals	BE_N (kcal/mol)
PtTiPt	56.5
PtVPt	59.5
PtCrPt	72.6
PtMnPt	84.9
PtFePt	83.9
PtCoPt	87.0
PtNiPt	89.8
NiPtPt	**137.5**
CoPtPt	*159.9*
FePtPt	169.9
MnPtPt	162.2
CrPtPt	166.5
VPtPt	184.1
TiPtPt	191.5
Pt	102.1
Ni	113.8

Surface



Subsurface

- Optimum heat of chemisorption of N of ~130 kcal/mol
- NiPtPt is a good prospective bimetallic surface



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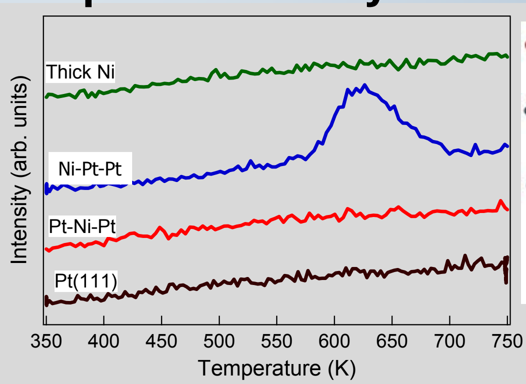
Emergent Behavior Verified Experimentally for the First Time



3.0 Langmuir NH_3 at 350K at UHV

- Ammonia decomposes on Ni-Pt: $2NH_3=N_2+3H_2$
- No decomposition on other surfaces
- **Ni-Pt is the most active known catalyst**

Hansgen, Chen, and Vlachos, *Nature Chem.* **2**, 484-489 (2010)

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Open Questions

- Uncertainty quantification
  - What data and at which scale to inject data?*
  - Beyond continuum models: e.g., Stochasticity
- Molecular structure and composition of catalyst
  - Optimize catalyst loading to explore bifunctionality
  - Extend to multicomponent catalysts
  - Account for crystal structure beyond core-shell
- Consider catalyst stability and catalyst dynamics
- Construct and search databases
  - Structure, composition, chemistry, reactor operating conditions

* Prasad et al., *Ind. Eng. Chem. Res.* **47**, 6555 (2008); ***48,*** 5255 (2009)

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Outline

- An overview of multiscale modeling
- Drivers of nanomaterials research/New frontiers
- Control in self-assembly
- Design of catalytic materials for energy and sustainability
- **Outlook**

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Conclusions/Outlook

- Multiscale modeling of prototype models is mature
- Inverse engineering (optimization and control) at the nanoscale is challenging and offers opportunities
- Many interesting problems are either complex or emergent and their modeling is plagued by combinatorial complexity
- Hierarchical multiscale modeling is an approach coping with these issues
- Error quantification , code verification and validation, and uncertainty propagation are essential
- Parallelization holds promise for substantial speedup

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- Students/Postdocs
  - Materials design: Abhijit Chatterjee; Jake McGill; Nasser Abukhdeir
  - Energy/Catalysis: Danielle Hansgen; Ying Chen; Mike Salciccioli; Vinay Prasad
- Collaborators
  - Markos Katsoulakis (UMass) and Petr Plechac (UD); Mathematical underpinnings
  - Michela Taufer (UD); GPUs
  - Tunde Ogunnaike (UD); Control
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