

Multiscale Modeling and its Application to Catalyst Design and Portable Power Generation

Dion Vlachos

Department of Chemical Engineering and Center for
Catalytic Science and Technology

University of Delaware

Newark, DE 19716

www.che.udel.edu/vlachos, vlachos@udel.edu

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- Application of multiscale modeling to
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - Experiment design

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- Application of multiscale modeling to
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - Experiment design

Down-scaling for future energy needs

- Distributed energy
 - On-board H_2 production
 - Electric reliability
 - Local solutions, e.g., farms based on biomass



Smart Car

Courtesy: Ballard Power Systems



- Portable energy (electronics)

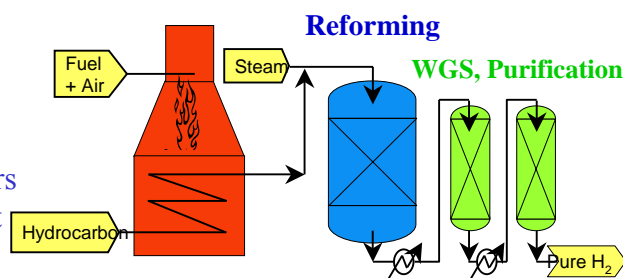


Outline

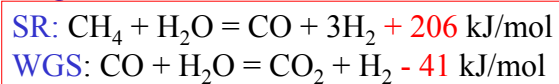
- Decentralized, future energy production
- **Miniaturization differs from scaling up**
- Multiscale modeling
- Application of multiscale modeling to
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - Experiment design

Large scale H₂ production is industrially mature

- Steady state operation
- Reforming:
 - endothermic, heat transfer controlled
 - Fixed bed catalytic reactors with Ni catalyst for syngas



- **Large scale flames supply the heat**
 - **Half of NG is burned to CO₂ and H₂O**
- Complex downstream processing WGS and PROX or membrane separation/PSA
- Slow ($\tau \sim 1s$); bulky



Steam reforming is a bulky process



Schested, *Cat. Today* 111 (2006) 103

First example of on-board reforming

- GM unveiled the world's first gasoline fuel processor for fuel cell propulsion at the annual automotive management conference in Traverse City, Mich.
- The Gen III processor, packaged in a Chevrolet S-10 pickup, reforms 'clean' gasoline onboard, extracting a stream of hydrogen to send to the fuel cell stack.

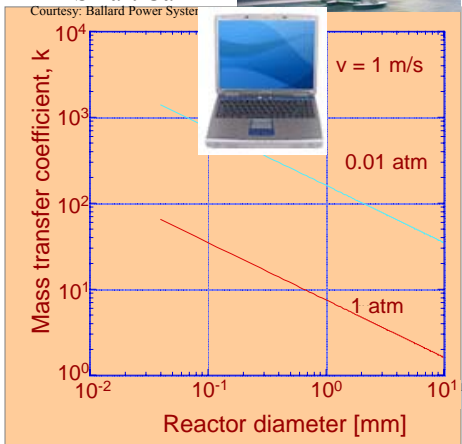


Microsystems for transportation and portable applications

- Advantages
 - Process intensification
 - High heat and mass transfer coefficients
 - Multifunctionality
 - Compactness
 - Inherently safe
- Scale out is feasible for portable (small scale) devices



Smart Car



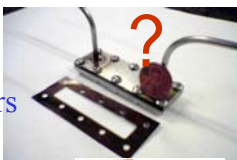

Microscales impose challenges and offer opportunities¹

- Laminar flows - mixing?
 - Small systems - enough catalyst?
 - Reactors shake - no moveable parts
 - Need small pressure drops
 - Transient operation very common
 - Fast startup and shutdown require active catalyst and fast heat transfer
 - Catalyst deactivation can become a major issue
 - Fast chemistry
 - Different systems' engineering²
- Monolithic type reactors

Dynamics

New chemistry and catalysts

Flowsheets/Optimization

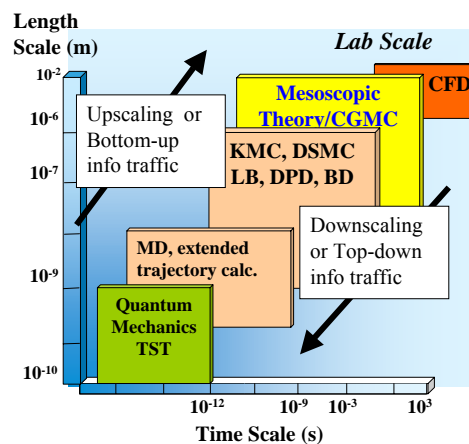
¹ Norton *et al.*, "Downsizing chemical processes for portable hydrogen production", in *Microreactor Techn. Process Intensification*, ACS Symp. Series 914, 179 (2005)

² Mitsos *et al.*, *IECR* 43, 74 (2004)

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- **Multiscale modeling**
- Application of multiscale modeling to
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - Experiment design

The multiscale simulation paradigm: A bottom-up ladder

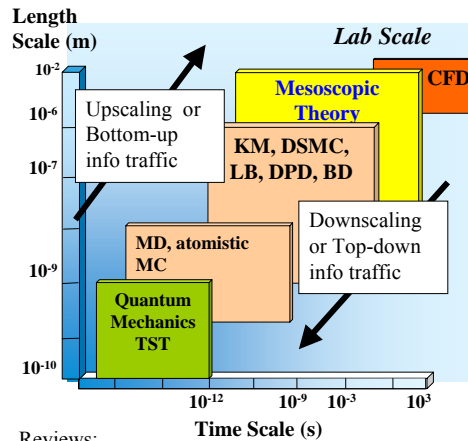


- Previous work
 - focused usually on a single scale and one way of information passing
 - developed structure-properties relations (molecular descriptors) without attention to processing

Reviews:

Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);
Chatterjee et al., *Chem. Eng. Sci.*, *ISCRE Issue* (2004);
Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

The Multiscale Simulation Paradigm: Predict macroscopic performance from first principles



Reviews:

Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);

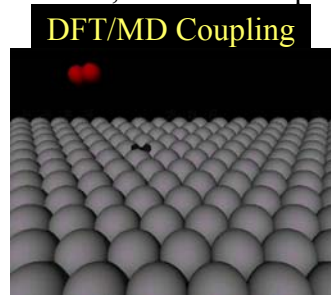
Chatterjee et al., *Chem. Eng. Sci.* **59**, 5559 (2004);

Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

* For noise control in hybrid siml, see work by groups of Braatz, Christofides, Vlachos

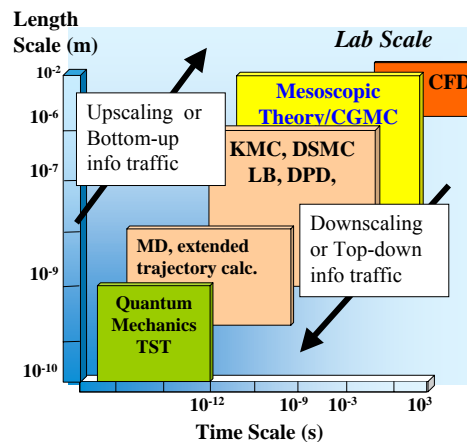
Challenges

- Phenomena and models are strongly coupled
- Develop bridges between models of various scales to enable accurate, robust, efficient, seamless coupling*



Ludwig and Vlachos, *Mol. Simul.* (2004)

The multiscale simulation paradigm: A bottom-up ladder



Reviews:

Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);

Chatterjee et al., *Chem. Eng. Sci.*, *ISCRE Issue* (2004);

Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

- Direct multiscale simulation (hybrid, coarse graining) is possible for systems of moderate complexity

- It is plagued by computational cost for complex systems, such as chemical reactors

- Are all scales and phenomena important?

Hierarchical, multiscale model development

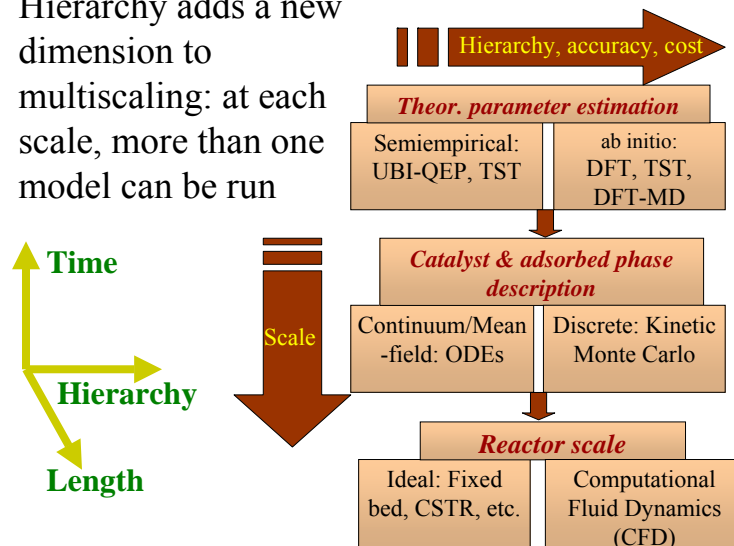
- Lower Level Theory
- Microkinetic model chemistry parameters
 - Semi-empirical techniques (BOC), TST
- Catalyst model
 - Mean field approximation
- Fluid flow/Transport
 - Simple reactor models (PFR, CSTR, transp. correlations)

Hierarchical, multiscale model development

- Last theoretical level:
Engineering models are needed for reactor optimization and control and for model-based catalyst design
- Feature identification toolbox enables hierarchical model development and reduction

Hierarchy enables rapid screening of chemistry, fuels, and catalysts

- Hierarchy adds a new dimension to multiscaling: at each scale, more than one model can be run



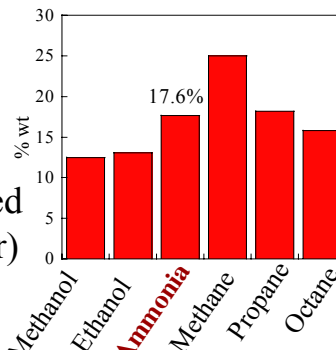
Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- **Application of multiscale modeling to**
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - Experiment design

NH₃ cracking for H₂ production

- **Good hydrogen carrier**

- High energy density
- Stored as a liquid (at 25 °C, 8 atm)
- One of the most widely produced chemicals (>100 metric tones/yr)
 - Haber-Bosch Process
 - Infrastructure is already set up



- **Catalytic decomposition of pure NH₃ on Ru^{1,2}**



– Slightly endothermic

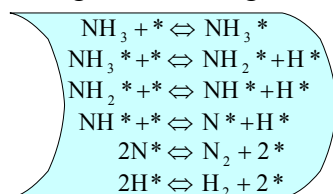
¹ Deshmukh et al., Ind. Eng. Chem. Res. (2004)

² Ganley et al., AIChE J. (2004)

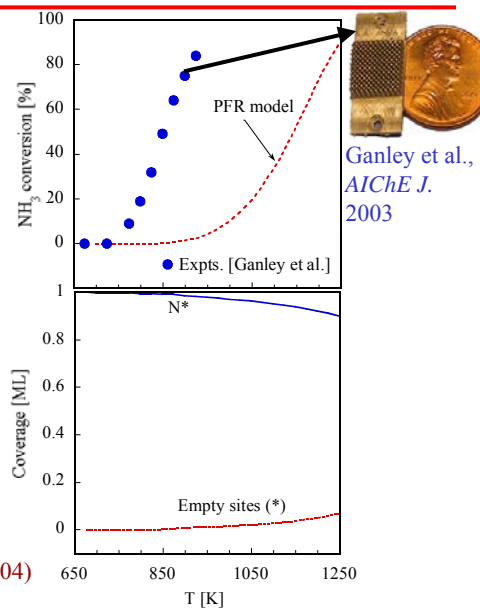
– Minimal downstream processing

NH₃ decomposition on Ru: 2NH₃ = N₂ + 3H₂

- NH₃ as a storage medium
- ‘Pure’ H₂ – No CO_x
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages

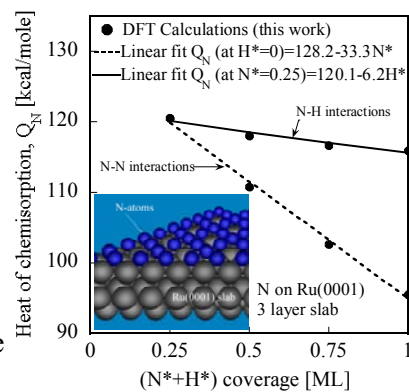


Mhadeshwar et al., *Cat. Letters* **96**, 13-22 (2004)



DFT is used to estimate lateral interactions

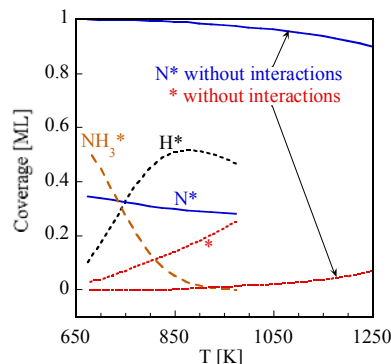
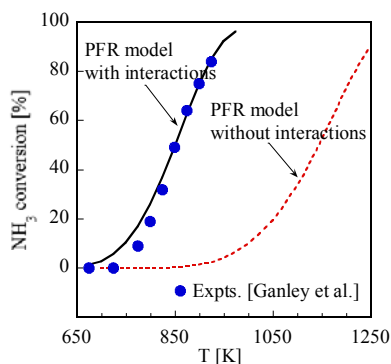
- DACAPO (solid-state electronic structure package by Hammer and coworkers*)
- 3-Layer slab of Ru(0001)
- 2×2 unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)



Deshmukh et al., *Int. J. Multiscale Comp. Eng.* 2, 221-238 (2004)

* Hammer et al., DACAPO version 2.7 (CAMP, Technical University, Denmark)

DFT-retrained microkinetic model describes the experimental data well

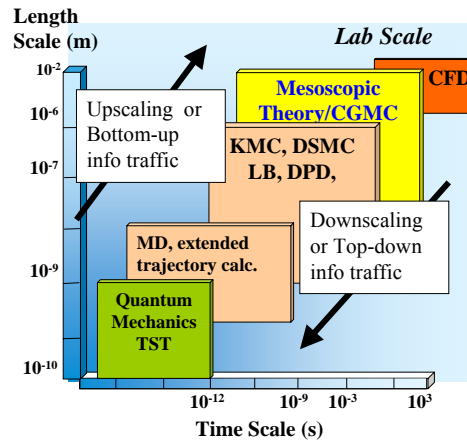


- H-H and N-H interactions are small
- N-N interactions completely change the chemistry
- **Extensive validation against UHV and high P data has been done**

Exps: Ganley et al., *AIChE J.* (2004)

Deshmukh et al., *Int. J. Multiscale Comp. Eng.* 2, 221-238 (2004)

The multiscale simulation paradigm: A bottom-up ladder



• Typical objective

- Mechanistic understanding
 - Reconcile large differences in published data
 - Process optimization:
- Process engineering**

Reviews:

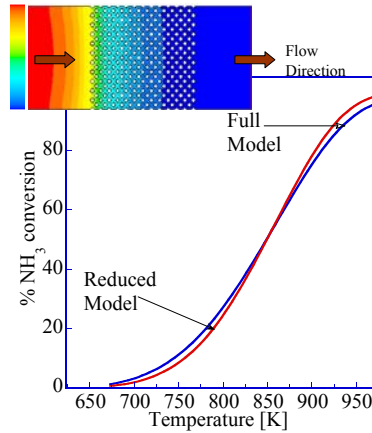
Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);
 Chatterjee et al., *Chem. Eng. Sci.*, *ISCRE Issue* (2004);
 Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- **Application of multiscale modeling to**
 - Development of detailed reaction mechanisms
 - **Microreactor design**
 - Process optimization
 - Catalyst design
 - Experiment design

Computer-aided chemistry reduction

- Sensitivity and Principal Component Analyses
 - No *a priori* assumptions
 - Identification of important reactions and species
- Small parameter asymptotics on species balances and site conservation
 - Simple algebra to derive a rate expression



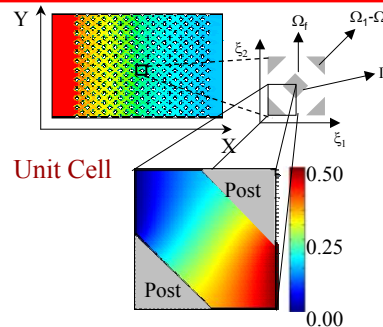
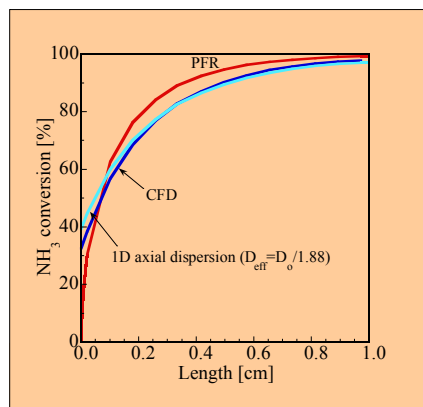
Mhadeshwar *et al.*, *Cat. Letters* **96**, 13 (2004)

$$\text{Reduced Model} \quad \sigma_{N_2} = k_4 \theta_{N_2}^2 - k_3 P_{N_2} \theta_*^2 \quad \theta_* = \frac{1}{1 + \frac{k_{11} P_{NH_3}}{k_{12}} + \sqrt{\frac{k_1}{k_2}} P_{H_2} + \sqrt{\frac{k_3}{k_4}} P_{N_2} + \sqrt{\frac{k_2}{k_1}} \frac{k_7 k_9 k_{11}}{2k_4 k_{10} k_{12}} P_{NH_3} P_{H_2}^{-0.5}}$$

μ Reactor is close to axial dispersion model D_{eff} vs. Geometric characteristics

- The method of homogenization is used that is based on separation of length scales

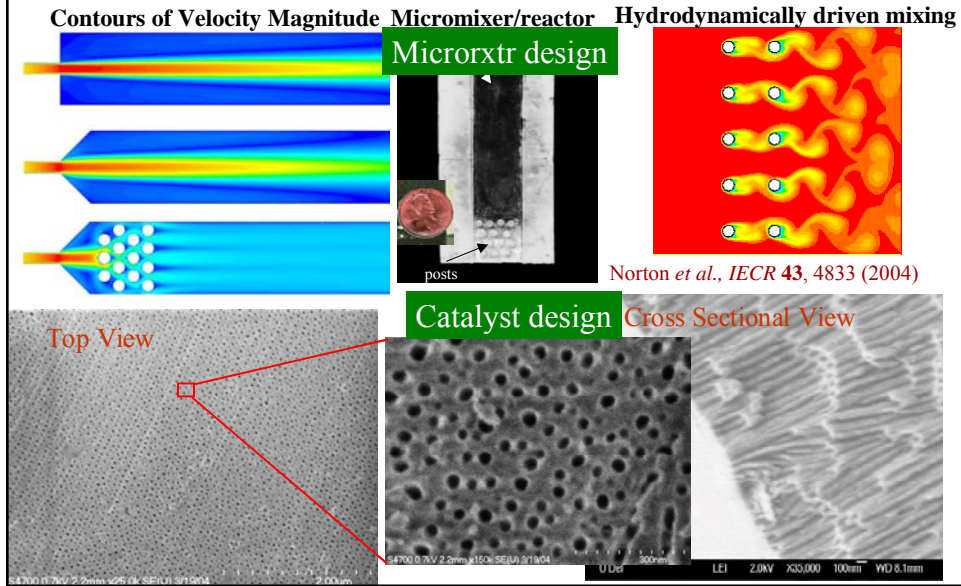
$$\varepsilon = \frac{\ell}{L} \ll 1$$



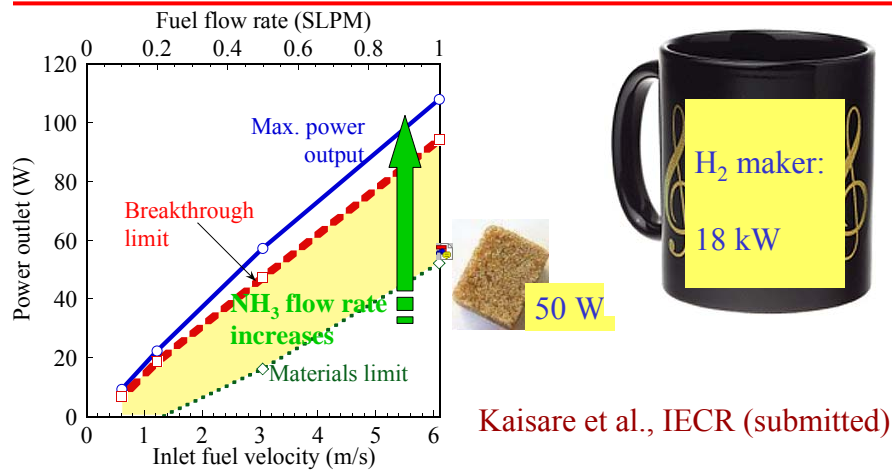
Multiscale simulation allows us to explore cheaply the effect of post shape, size, and density on microreactor performance by solving simple unit cell problems

Deshmukh *et al.*, *Int. J. Multiscale Comp. Eng.* **2**, 221-238 (2004)

Design and fab of microchemical systems via multiscale modeling



Attainable regions in multifunctional microdevices

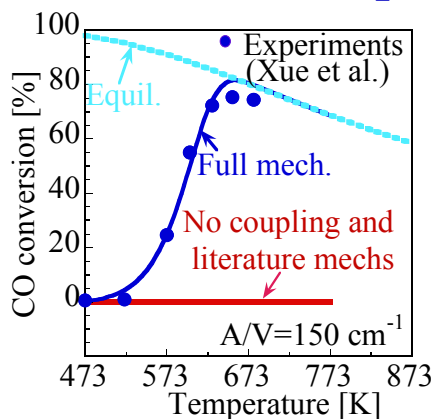


- Multifunctional devices provide **millisecond operation**
- Adjustment of flow rates can provide **variable power**
- Scaling out can supply transportation power levels

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- **Application of multiscale modeling to**
 - Development of detailed reaction mechanisms
 - Microreactor design
 - **Process optimization**
 - Catalyst design
 - Experiment design

Water-gas shift reaction on Pt:

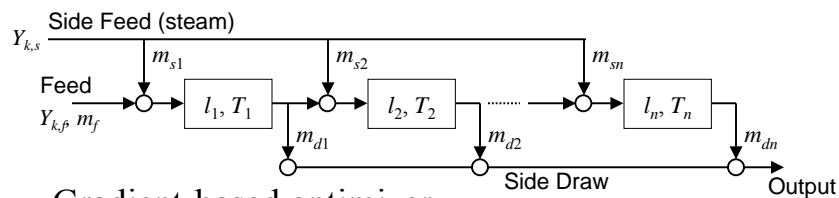


Thermodynamics¹ is important **but** not sufficient:
kinetics ‘corrects’ the WGS speed

¹Mhadeshwar et al., *J. Phys. Chem. B* (2003)

Reactor Superstructure Optimization

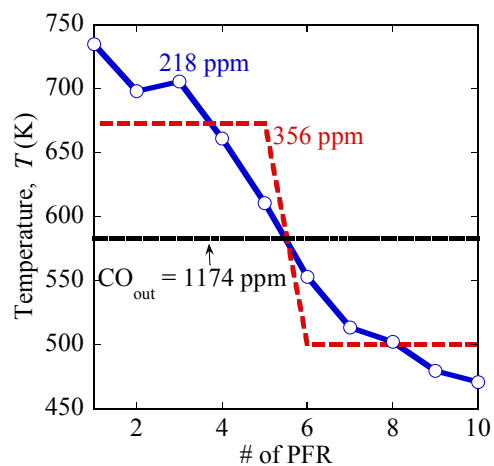
- Modeled as n PFRs in series
- Side feed and side draw from each reactor
- Each PFR: same length and different temperature



- Gradient-based optimizer

Process optimization: Optimum temperature profile in the WGS reaction

- Total length: $\sum_i l_i = 2 \text{ cm}$
- Inlet: 40 sccm feed (dry basis), with 18% CO
- Steam: $\sum_i m_{s,i} \leq 40 \text{ sccm}$
- Temperature constraints: $373 \text{ K} \leq T_i \leq 873 \text{ K}$
- All cases:
 - No split feed or side draw
 - All steam utilized
 - T constraints were inactive

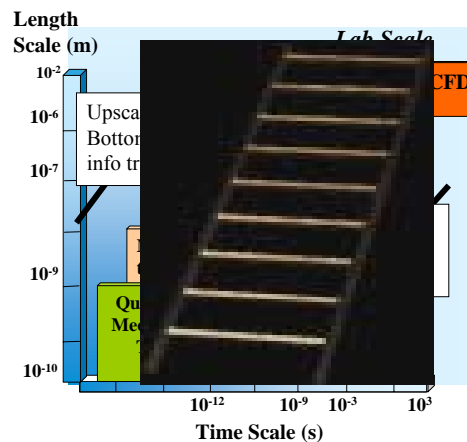


Vlachos et al., *Compt. Chem. Eng.* (2006)

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- **Application of multiscale modeling to**
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - **Catalyst design**
 - Experiment design

The multiscale simulation paradigm: A bottom up and top-down ladder



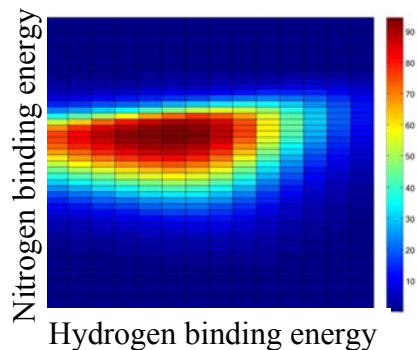
Reviews:

Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);
Chatterjee et al., *Chem. Eng. Sci.*, *ISCRE Issue* (2004);
Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

- **Typical objective**
 - Mechanistic understanding
 - Reconcile large differences in published data
 - Process optimization:
Process engineering
- **Opportunity**
 - Given a macroscopic behavior, design materials and/or control nanoscale
 - **Product engineering**

An example of catalyst optimization: NH₃ decomposition

Ammonia conversion (%) at 380 °C



- Search is done on **atomic descriptors** while running the full chemistry model
- **Libraries of computational information** are created via DFT
- Models are built
- Potential catalyst candidates are identified

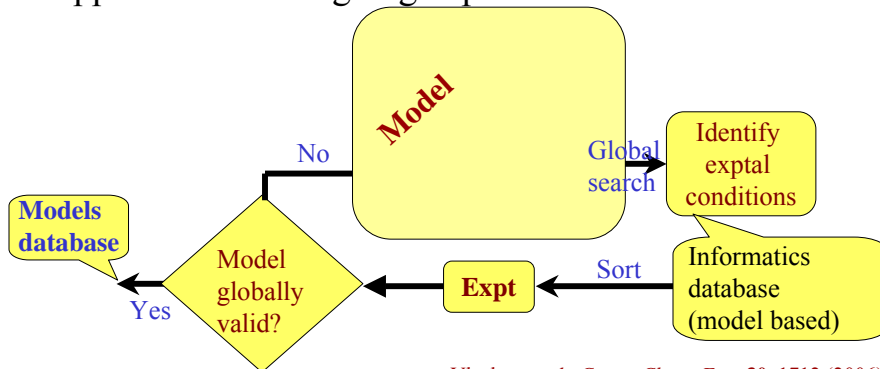
Ulissi et al.

Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- **Application of multiscale modeling to**
 - Development of detailed reaction mechanisms
 - Microreactor design
 - Process optimization
 - Catalyst design
 - **Experiment design**

Maximizing information content of a model

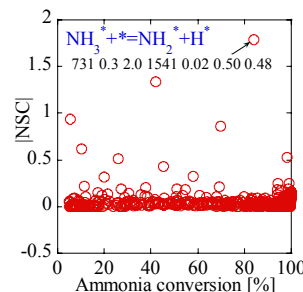
- Parameters are uncertain
- Often refined using statistically based experiments
- We need to bridge first-principles modeling with systems approaches in designing experiments



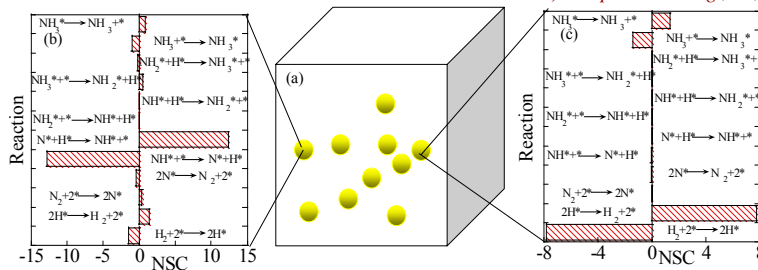
Vlachos *et al.*, *Comp. Chem. Eng.* **30**, 1712 (2006)

Model-based design of experiments: Ensuring global accuracy of models

- Global Monte Carlo search in **exptl parameter space** (τ , P, T, compos., A/V)
- Local sensitivity analysis
 - Only **a few model parameters are important** and can be **extracted, but change** in manipulated parameter space
- Sort by max NSC, RDS, MARI, ...

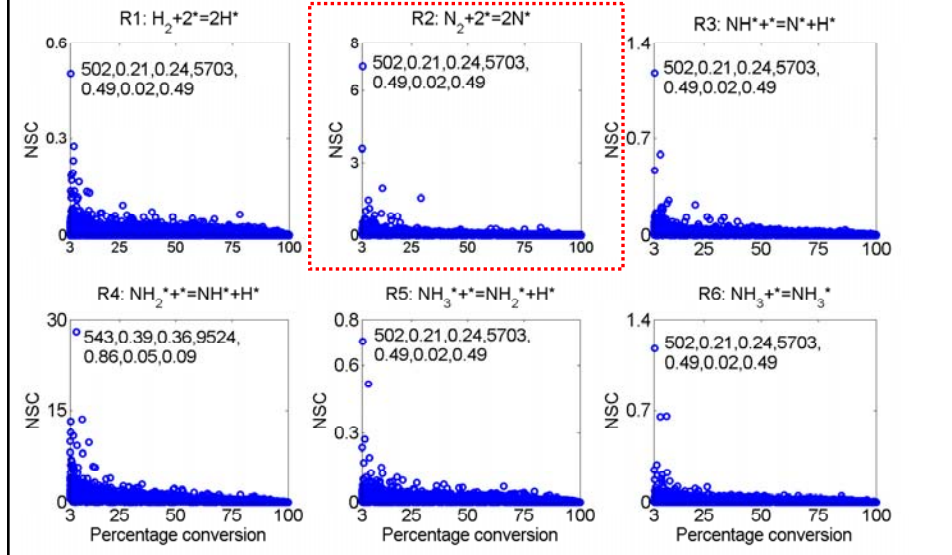


Vlachos *et al.*, *Comp. Chem. Eng.*, **30**, 1712 (2006)

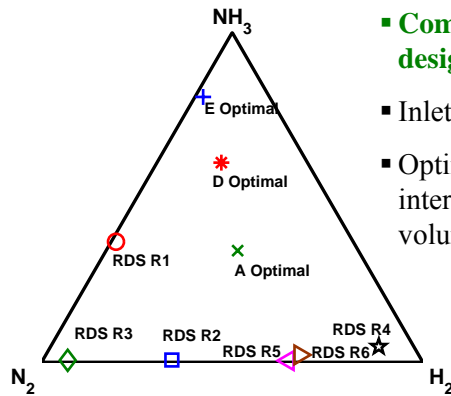


Normalized parameter sensitivity vs. conversion (CSTR)

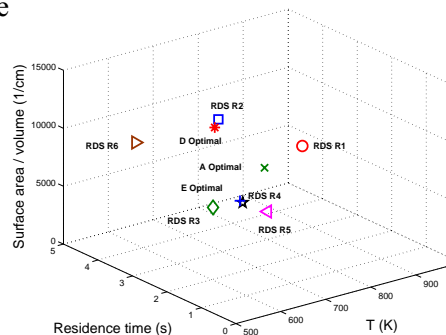
$\text{NH}_2^* + * = \text{NH}^* + \text{H}^*$ is the most sensitive reaction



Optimal statistical and physics-aided designs

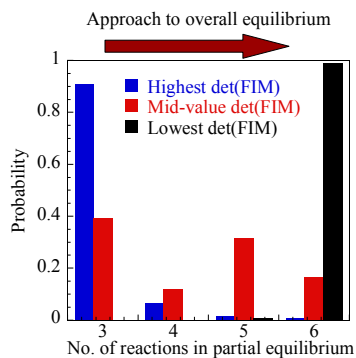


- Compared D, A, E and physics-aided designs
- Inlet composition space – no clear pattern
- Optimum at relatively low temperature, intermediate cat. surface area/reactor volume



Prasad and Vlachos, *Ind. Eng. Chem. Res.* (submitted)

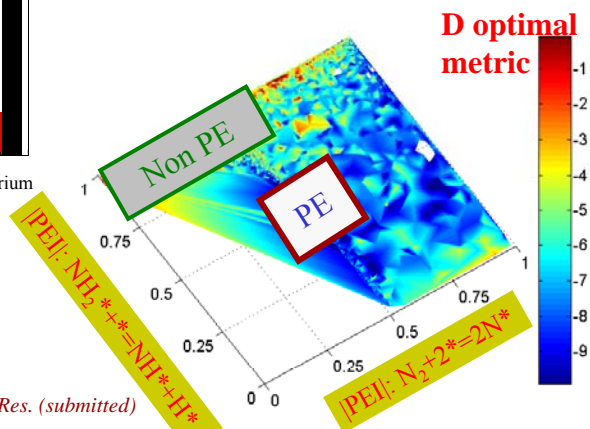
Kinetic relevance – D Optimality and partial equilibrium (PE)



High values of the det. of the Fisher info matrix correlate with fewer reactions in PE and farther from equil.

Partial equil. index:
 $PEI = r_f / (r_f + r_b)$

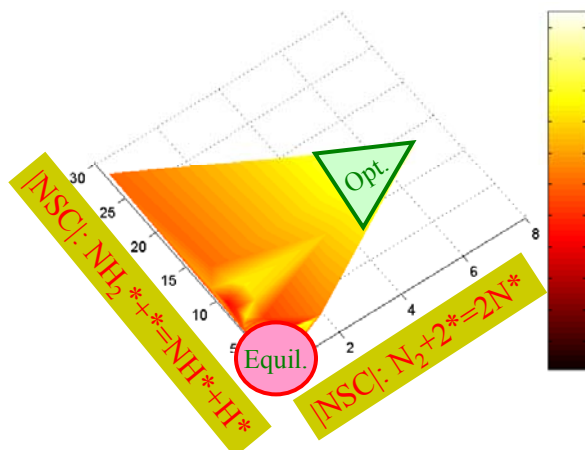
Prasad and Vlachos, *Ind. Eng. Chem. Res.* (submitted)



Kinetic relevance –

D Optimality and sensitivity coefficients

D optimal metric



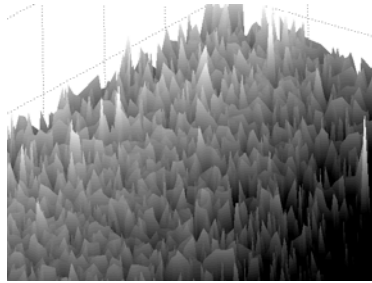
High values of the Fisher information matrix correlate with larger normalized sensitivity coefficients of the sensitive reactions

Prasad and Vlachos, *Ind. Eng. Chem. Res.* (submitted)

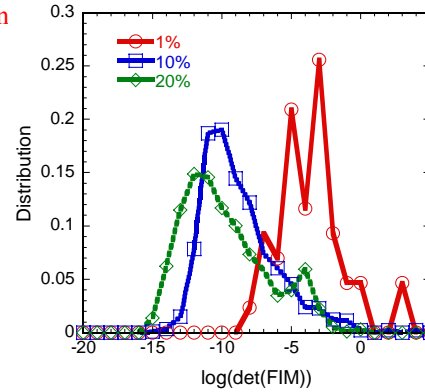
Is a Single Optimal Point Good Enough?

- The D optimal response surface is highly nonlinear
- You must be very close to the optimal point to ensure optimality
- Experimental constraints may make this unachievable

Representative cross-section of D optimal response surface

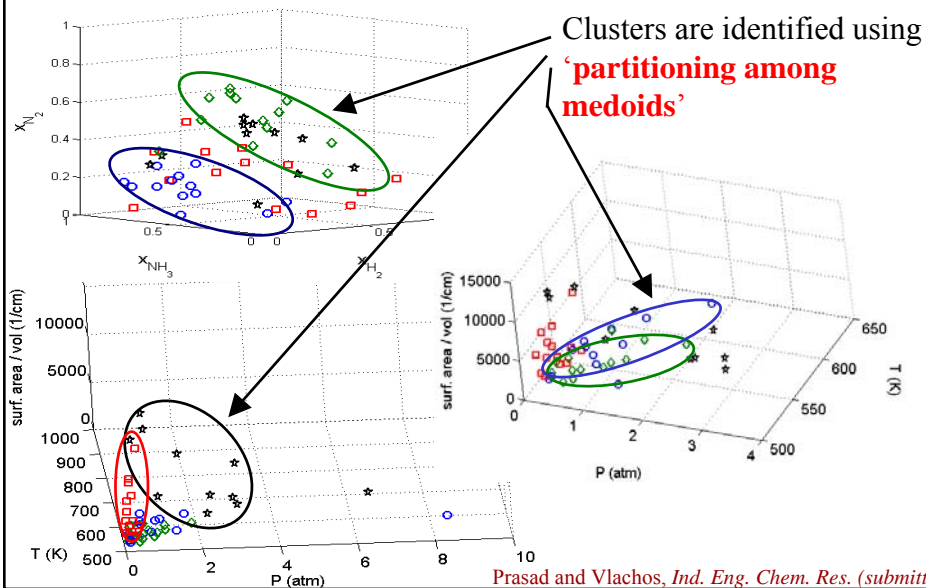


D optimal metric vs. distance from optimal point



Prasad and Vlachos, *Ind. Eng. Chem. Res.* (submitted)

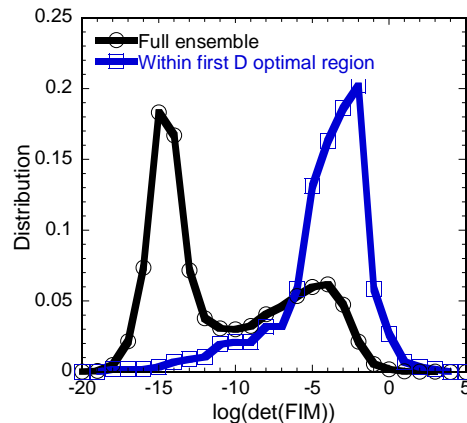
Identifying regions (clusters) of D-optimal data using informatics tools



Prasad and Vlachos, *Ind. Eng. Chem. Res.* (submitted)

Assessment of Informatics Approach

Distribution of D optimal metric within optimal region and in entire parameter space

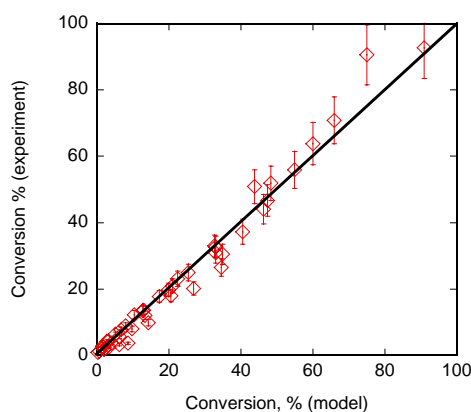


Sample anywhere within clusters (experimental flexibility)

Substantial improvement over single optimal points

Prasad and Vlachos

Proof of concept via experiments



- 44 new experiments conducted in optimal region
- Varied
 - Temperature
 - Catalyst amount
 - Inlet composition
- Good agreement of model prediction and data

Karim, Prasad, and Vlachos (in preparation)

Summary and future directions

- Future energy generation will happen at much smaller scales
- Downscaling is different even at the <1 mm scale
 - ✓ Dynamics of microsystems, systems integration, optimization, and control
- **Hierarchical multiscale modeling**
- Application of multiscale modeling to
 - Microreactor and process design
 - ✓ Model reduction is essential
 - Experiment design
 - ✓ Informatics tools could be valuable to replace ‘the optimum’ point with an ensemble of suitably chosen experiments
 - Catalyst design
 - ✓ Reverse engineering of processes and products

Acknowledgements

- Funding: ARO, ARL, PRF, DOE, NSF, Rohm Haas, ConocoPhillips
- Students and postdocs
 - Dan Norton (GE; μ burner modeling, fab, and exps)
 - Soumitra Deshmukh (Velocys; NH_3 microreactors; system integration)
 - Ashish Mhadeshwar (GE; Multiscale chemistry)
 - Justin Federici (UD; Microreactor exps)
 - Marina Lebedeva (PennState; Model reduction)
 - Ben Feist (Air Liquide; HTE with Jochen Lauterbach)
 - Niket Kaisare (IIT Madras; Dynamics; Size optimization)
 - Vinay Prasad (visiting Prof. from IIT Bombay; DOEs)
 - Zack Ulissi (UD; Catalyst optimization)
 - Ayman Karim (UD; NH_3 experiments)