Simulation-based Nanomaterials Design and Nanomanufacturing

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Objective: To investigate the feasibility of modeling and simulating nano structures based on a proposed periodic surface model from atomic to meso scales and to expand the horizon of available shapes for design engineers.

$$\psi(r) = \sum_{l=1}^{lM} \sum_{m=1}^{M} \mu_{lm} \cos \left(2\pi \kappa_{l}(p_{m} \cdot r)\right)$$

### Model construction

1a) Sodalite cages. Vertices are Si (Al). Edges represent Si-O-Si (Si-O-Al) bonds.

1b) intersection of P surface and 2 Grid surfaces

1c) P surface and its modulation with a Grid surface

### Reverse engineering and visualization

2a) Reconstructed loci surface from a Faujasite crystal (Each tetradecahedron encloses a Fe, each hexagonal prism encloses an Al, and each vertex of the polygons represents a Si)

2b) Reconstructed loci surface from a synthetic Zeolite crystal (Each tetrahedron encloses a Si, each vertex of the tetrahedral is a O, and each green sphere is a Na)

### Mathematical models of Bravais Lattice
**Computer-Aided Nano-Design**

**Periodic Surface (PS) Model**

\[
\psi(r) = \sum_{l=1}^{L} \sum_{m=1}^{M} \mu_{lm} \cos \left( 2\pi \kappa_l \left( p_m^T \cdot r \right) \right) = 0
\]

<table>
<thead>
<tr>
<th>P</th>
<th>D</th>
<th>G</th>
<th>1-WP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamellar</td>
<td>Rod</td>
<td>Spherical Micelle</td>
<td>Mesh</td>
</tr>
<tr>
<td>Grid</td>
<td>Membrane</td>
<td>Faujasite</td>
<td>Zeolite-s</td>
</tr>
</tbody>
</table>

\[
2\cos(x)\cos(y) + 2\cos(y)\cos(z) + 2\cos(x)\cos(z) - \cos(2x) - \cos(2y) - \cos(2z) = 0
\]

\[
9 + 4\cos(x) + 4\cos(y) + 4\cos(z) = 0
\]

\[
\cos(x) + \cos(y) + \cos(z) = 0
\]

\[
\cos(z) = 0
\]

\[
\cos(x)\cos(y)\cos(z) = 0
\]
Computer-Aided Nano-Design
Complex and porous structures by PS models

- Feature-based crystal construction
  - Mask operation
  - Union operation
  - Insertion operation

- Fractal structures
Phase-Change Materials Design

- A phase transition is a geometric and topological transformation process of materials from one phase to another, each of which has a unique and homogeneous physical property.
- Important to design various phase-change materials (e.g., for information storage and energy storage)
- The most critical step is to estimate the saddle points along the minimal energy path on high-dimensional potential energy surfaces
Geometry Guided Saddle Point Search

- Provide initial guess of transition path: FeTi+H
  - Guess 1: by linear surface interpolation
  - Guess 2: by potential-driven surface interpolation
Search Results by the Nudged Elastic Band Method

Activation Energy:
Experimental result = 0.2912 eV per atom
The default *coordinate linear interpolation* failed to find saddle point
*Surface linear interpolation* = 0.26285 eV per atom
*Potential-driven surface interpolation* = 1.1543 eV per atom
Concurrent Saddle Point Search

- Search both local minimums and saddle point at the same time
- Search multiple transition paths with only one initial pathway guess to provide a global view of energy landscape
Computer-Aided Nano-Manufacturing
Controlled Kinetic Monte Carlo (cKMC)

- cKMC is developed as a generalization of KMC to simulate both top-down and bottom-up processes in nanomanufacturing
  - KMC cannot simulate top-down processes
- cKMC defines two types of events
  - Self-assembly events – occur spontaneously (as in classical KMC)
  - Controlled events – occur at certain locations or at particular times deterministically to model particle re-arrangement as the direct result of external energy (force, light, field, etc.)
cKMC: Scanning Probe Lithography

<table>
<thead>
<tr>
<th>Number of sites involved</th>
<th>Reaction/transition event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R1: ( \text{controlled} \rightarrow \text{activated controlled} ) (controlled)</td>
</tr>
<tr>
<td>2</td>
<td>R2: ( \text{activated controlled} + \text{vacancy} \rightarrow \text{vacancy} + \text{activated controlled} ) (controlled)</td>
</tr>
<tr>
<td></td>
<td>R3: ( \text{vaporized workpiece} + \text{vacancy} \rightarrow \text{vacancy} + \text{vaporized workpiece} )</td>
</tr>
<tr>
<td></td>
<td>R4: ( \text{workpiece} + \text{vacancy} \rightarrow \text{vacancy} + \text{workpiece} )</td>
</tr>
<tr>
<td></td>
<td>R5: ( \text{vaporized workpiece} + \text{absorbent} \rightarrow \text{vacancy} + \text{absorbent} )</td>
</tr>
<tr>
<td></td>
<td>R6: ( \text{activated controlled} + \text{absorbent} \rightarrow \text{vacancy} + \text{absorbent} )</td>
</tr>
<tr>
<td>3</td>
<td>R7: ( \text{workpiece} + \text{workpiece} + \text{vacancy} \rightarrow \text{vacancy} + \text{workpiece} + \text{workpiece} )</td>
</tr>
<tr>
<td></td>
<td>R8: ( \text{vaporized workpiece} + \text{workpiece} \rightarrow \text{workpiece} + \text{workpiece} + \text{workpiece} )</td>
</tr>
<tr>
<td>4</td>
<td>R9: ( \text{activated controlled} + \text{workpiece} + \text{vacancy} \rightarrow \text{vacancy} + \text{workpiece} + \text{vacancy} + \text{vaporized workpiece} )</td>
</tr>
<tr>
<td></td>
<td>R10: ( \text{activated controlled} + \text{workpiece} + \text{workpiece} \rightarrow \text{workpiece} + \text{workpiece} + \text{workpiece} + \text{workpiece} )</td>
</tr>
</tbody>
</table>
cKMC: nanomanufacturing processes

Physical vapor deposition (PVD)

Ionized PVD

Nano-imprint lithography
Uncertainty in Modeling & Simulation

- **Aleatory Uncertainty:**
  - inherent random dispersion in the system. Also known as:
    - variability
    - random error
    - irreducible uncertainty

- **Epistemic Uncertainty:**
  - due to lack of perfect knowledge about the system. Also known as:
    - incertitude
    - systematic error
    - reducible uncertainty
    - model-form uncertainty
Generalized Hidden Markov Model for Cross-Scale Model Validation

\[
\frac{da}{dN} = m(\gamma_p)^\alpha a
\]

Similar to the Bayesian approach in model validation [Babuška et al. 2008, Oden et al. 2010]
Imprecise probabilistic distributions for uncertainty: 
*damage function* ($v$) from irradiation - the probability that a stable Frenkel pair is generated at certain level of *transfer or recoil energy* ($T$)

MD simulation observation (with uncertainty)
- bounds based on *std. dev.* of binomial distributions
- 16 simulation runs for each energy-radiation angle combination
# Reliable Atomistic Simulation

## Reliable kinetic Monte Carlo

- Simulate kMC with imprecise rates
- An efficient alternative to sensitivity analysis

### Event type | Species and reactions | Rate constant
--- | --- | ---
R1: water dissociation | $\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+$ | 10$^1$
R2: carbonic acid dissociation | $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ | 10$^1$
R3: acetic acid dissociation | $\text{AcH} \leftrightarrow \text{Ac}^- + \text{H}^+$ | 10$^1$
R4: reduced thionine first dissociation | $\text{MH}_3^+ \leftrightarrow \text{MH}_2 + \text{H}^+$ | 10$^1$
R5: reduced thionine second dissociation | $\text{MH}_4^{2+} \leftrightarrow \text{MH}_3^+ + \text{H}^+$ | 10$^1$
R6: acetate with oxidized mediator | $\text{Ac}^- + \text{MH}_4^+ + \text{NH}_4^+ + \text{H}_2\text{O} \rightarrow X\text{Ac} + \text{MH}_3^+ + \text{HCO}_3^- + \text{H}^+$ | 10$^1$
R7: oxidation double protonated mediator | $\text{MH}_4^{2+} \rightarrow \text{MH}^+ + 3\text{H}^+ + 2\text{e}^-$ | 10$^1$
R8: oxidation single protonated mediator | $\text{MH}_3^+ \rightarrow \text{MH}^+ + 2\text{H}^+ + 2\text{e}^-$ | 10$^1$
R9: oxidation neutral mediator | $\text{MH}_2 \rightarrow \text{MH}^+ + \text{H}^+ + 2\text{e}^-$ | 10$^1$
R10: proton diffusion through PEM | $\text{H}^+ \rightarrow \text{H}_+$ | 10$^{-2}$
R11: electron transport from anode to cathode | $\text{e}^- \rightarrow \text{e}_-$ | 10$^{-2}$
R12: reduction of oxygen with current generated | $2\text{H}_2\text{O}_- + 1/2\text{O}_2^- + 2\text{e}_- \rightarrow \text{H}_2\text{O}_- + \text{H}_2\text{O}^- \rightarrow 4\text{OH}^-$ | 10$^5$
R13: reduction of oxygen with current generated | $\text{O}_2^- + 4\text{e}_- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$ | 10$^3$

(a) H$_2$O in anode chamber

(b) H+ in cathode chamber
Thanks!

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