Characterization and Design of Nanomaterials Through Multiscale Modeling & Simulation

Tahir ÇAĞIN
Laboratory for Computational Engineering of Nanomaterials and Devices
http://che.tamu.edu/orgs/groups/Cagin/

Artie McFerrin Department of Chemical Engineering
Texas A&M University
E-mail: cagin@che.tamu.edu
Summary

• Rational Design and Characterization via Modeling and Simulation

• Multiscale Modeling Hierarchy and Materials Simulation

• Examples of Applications in Functional Materials
  – Multiscale modeling PMMA Thin Films
  – Hydrogen storage and Delivery (MOFs)
  – Thermo-electrics
  – Piezo-electrics and Ferro-electrics
  – Amplified Fluorescence Quenching Polymers for IED sensing
  – Structure, Assembly and Transport in Cyclic Peptide nanotubes (CPNT)
  – Stress Corrosion Cracking in Fe based alloys
  – Nuclear Fuel materials
  – Damage Cascade Simulations
  – Magnetic Shape Memory Alloys
Design/Characterization Through Modeling Paradigm

Model Formulation, Implementation and Simulation

Analysis for Design and Characterization

MATHEMATICS

Theory

Physics & Chemistry & Biology
Multiscale Simulation and Modeling Hierarchy

- Quantum Mechanics
- Molecular Dynamics
- Coarse Graining
- Micro Mechanics
- Engineering Process

Time
- Months
- Hour
- Second
- $10^{-15} \text{s}$
- $10^{-12} \text{s}$
- $10^{-9} \text{s}$
- $10^{-6} \text{s}$

Distance
- $10^{-10} \text{m}$
- $10^{-9} \text{m}$
- $10^{-6} \text{m}$
- $10^{-2} \text{m}$
Develop a methodology for the numerical simulation of large models of polymeric thin films so that realistic estimation of mechanical and thermal properties can be obtained.

Diffusive equations, like the Fourier eq. for conduction heat transfer, do not account for the effect of energy carriers (i.e. phonons) in thermal properties. Molecular Dynamic simulations can be implemented to solve this problem.

However, the computer resources needed to simulate a film of the necessary length and time scale (few tens of nanometers, microseconds) are prohibitive.
Coarse Grain Molecular Dynamics

- Groups of atoms represented by a single bead
- Used for complex molecules in biosciences (proteins, DNA)
- Used in simulations of entangled polymer melts
<table>
<thead>
<tr>
<th>Model</th>
<th>Atoms/Beads</th>
<th>Run time (hrs)</th>
<th>1 ns, local comp. (4-loc)</th>
<th>Atoms/Beads</th>
<th>Run time (hrs)</th>
<th>100 ns, Hydra (16-loc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomistic</td>
<td>2256</td>
<td>25.58</td>
<td></td>
<td>18002</td>
<td>~ 1000</td>
<td></td>
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<tr>
<td>6 Beads</td>
<td>900</td>
<td>4.85</td>
<td></td>
<td>7200</td>
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<tr>
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<td></td>
<td>4800</td>
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<tr>
<td>4 Beads b</td>
<td>600</td>
<td>2.45</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Beads a</td>
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<td>1.28</td>
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<td>3600</td>
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<td></td>
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<tr>
<td>3 Beads b</td>
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<td>1.90</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>2 Beads</td>
<td>300</td>
<td>0.85</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A system of 18k atoms of PMMA is a 5x5x5 nm box.

Few tens of nanometers and microseconds are now attainable

A 20x5x5 nm box of 3-bead model running for 1 μs on Hydra (64-loc) will take ~ 14 days.
Metal Organic Framework (MOF) for High Capacity Hydrogen Storage and Delivery
M. Mani Biswas, T. Cagin

- Crystalline material
  - Metal oxide clusters at vertexes,
  - Connected by organic linkers.
- Porous, large surface area (2500 - 5000 m²/gm)
- Low density (0.59 gm/cc)

- Crystals can be designed
  - Geometry, pore size can be varied (3.8 - 30 Å)
  - Linker molecule of different chemistry can be chosen

- Selective storage of guest molecule inside free volume
  - Hydrogen gas storage, gas separation
  - Drug delivery vehicle
- Designable property
  - Catalysis, molecular detection

Research Plan

- Study Mechanical & Transport Properties
- Study Hydrogen sorption
- Other Materials
- CNT Network

System Integration

Theoretical Investigation using Classical MD simulations and Quantum Level calculation - properties of Metal Organic Frameworks (MOF) for efficient hydrogen storage and delivery

Study Hydrogen generation from renewable sources - Biological

Build a device for hydrogen delivery to fuel cell
Loading at 100 MPa (298k)

Unloading at 300 MPa (298k)

Depressurize at 100 MPa

M. Mani-Biswas, T. Cagin, “Shape memory effect in MOFs”, to be submitted.
Ferroelectrics & Piezoelectrics

Domain Wall: Interface of polarization domains

Determine piezoelectric response and macroscopic polarization

Fatigue switchable polarization

Used in many applications
- RAM
- Actuators
- Transducers
- Sensors

http://www.materials.leeds.ac.uk/luec/ActMats/Domain2.jpg

Zhang, Cagin, Goddard, PNAS 103, 14695 (2006); Cagin et al, CMES 24, 215 (2008); Majdoub, Sharma, Cagin, PRB 78, 12407 (2008); PRB 77, 125424 (2008)
J. Haskins, A. Kinaci, T. Cagin in progress.
Simulations excel in investigating nanostructures and the origin of bulk properties.

Domain Walls

PZT nanotubes for memory devices

Nonlinearly strained cantilever polarization enhancement
Temperature behavior of PZT calculated by polarizable force fields.
Hysteresis behavior of PT and PZT.

Triangle field of 1 GHz with maximum strength of 0.27 V/Å.

The simulations shows characteristic ferroelectric hysteresis behavior.
Problem: Inter-dependence of $\sigma$, $\kappa$ and $S$ through carrier concentration.

$ZT = \frac{S^2 \sigma}{\kappa} T$

Increasing $ZT$ is difficult - conflicting Properties

C. Sevik, T. Cagin, in progress
A. Kinaci, C. Sevik, T. Cagin, in progress

Current Bulk Thermoelectric Materials

- $\text{Zn}_2\text{Sb}_3$
- $\text{Yb}_{0.19}\text{Co}_{4}\text{Sb}_{12}$
- $\text{CeFe}_{4}\text{Co}_{x}\text{Sb}_{12}$
- $\text{Bi}_2\text{Te}_3$
- $\text{CsBi}_{4}\text{Te}_6$
- $\text{PbTe}$
- $\text{Si}_{1-x}\text{Ge}_x$
- $\text{AbPb}_{m}\text{Sb}_{2+m}$

$ZT$ : Figure of Merit

Temperature (K)

$10^{17} \quad 10^{18} \quad 10^{19} \quad 10^{20} \quad 10^{21}$

Carrier Concentration

$K_e$ $K_L$

$ZT_{\text{max}}$
Transport Properties From \textit{Ab initio} Theory
New trends in thermoelectrics: Complex oxides and structural miniaturization (superlattices, nanowire, quantumdots ...)

**Manipulating properties of SrTiO$_3$**

- External stress
- Chemical alloying
- Controlled defects
- Structuring in atomic scale etc...

Effect of simple shear on conduction properties of SrTiO$_3$
Structure and Chemistry at interface of Si-nc & silica

Strain Profile in Si Nanocrystals

- Core of the NC is unstrained.
- Volumetric strain and hydrostatic strain (calculated with Pryor’s method) shows similar behavior as expected.
- Bond lengths and strain shows opposite behavior.
TNT-AFP complexation

10^{-15} g detection limits (Fido™, Nomadics Inc.)

Compared to canines

Quenching
Time Dependent DFT study of IED Sensing Mechanisms
Stability and Optimization

<table>
<thead>
<tr>
<th>Name</th>
<th>Exp.</th>
<th>Sim.</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>9.5 A</td>
<td>9.6 A</td>
</tr>
<tr>
<td>b</td>
<td>15.1 A</td>
<td>15.3 A</td>
</tr>
<tr>
<td>c</td>
<td>15.1 A</td>
<td>15.1 A</td>
</tr>
</tbody>
</table>

Crystalline nanotubes

8-Peptide System

12-Peptide System
Transport Properties

Diffusion of water in Peptide Nanotubes is faster compared with equivalent diameters of CNTS.

Self Diffusion Coefficient

\[
\left\langle (x(t + \Delta t) - x(t))^2 \right\rangle = 6 \times D \times t
\]

*Einstein’s Relationship*

**DETAILS**
From the analysis of curves of mean square displacement along axial direction.

<table>
<thead>
<tr>
<th>System</th>
<th>Diameter (Å)</th>
<th>Diff. coeff. (calc) cm²/s (1×10⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk water</td>
<td>—</td>
<td>2.17</td>
</tr>
<tr>
<td>12-peptide</td>
<td>14</td>
<td>1.23</td>
</tr>
<tr>
<td>(15,15) CNT</td>
<td>15</td>
<td>0.41</td>
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<tr>
<td>8-peptide</td>
<td>8.8</td>
<td>0.41</td>
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<tr>
<td>(9,9) CNT</td>
<td>8.6</td>
<td>0.25</td>
</tr>
<tr>
<td>(8,8) CNT</td>
<td>7.2</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Mechanical Properties

SIDE CHAIN- SIDE CHAIN
INTERTUBULAR HYDROPHOBIC
INTERACTIONS

HYDROGEN BONDING
INTERACTION ALONG THE
NANOTUBES

Stress-Strain

\[ \Delta E = \frac{V_0}{2} \sum C_{IJ} \eta_I \eta_J + \frac{V_0}{6} \sum C_{IJK} \eta_I \eta_J \eta_K \]

Anisotropic Isothermal Elastic Constants

<table>
<thead>
<tr>
<th>C_{ij}</th>
<th>value (GPa)</th>
<th>C_{ij}</th>
<th>value (GPa)</th>
</tr>
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<td>C11</td>
<td>8.09</td>
<td>C66</td>
<td>0.77</td>
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<tr>
<td>C22</td>
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<td>C33</td>
<td>19.65</td>
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<td>9.56</td>
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<tr>
<td>C44</td>
<td>1.23</td>
<td>C14</td>
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<tr>
<td>C55</td>
<td>1.23</td>
<td>C23</td>
<td>9.59</td>
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</table>

Stress-Corrosion Cracking (SCC) in Fe

- Concerns vast range of application
- Combined influence of stress & corrosive environment
- SCC is proved to be connected to GB
  - introduction of impurity element
  - giving no sign of warnings

\[ E_bN_I = E_{tot}^{GB}(N_{Fe}, N_I) - N_I E_I - E_{tot}^{GB}(N_{Fe}^0) - \frac{N_{Fe} - N_{Fe}^0}{N_{Fe}^0} E_{tot}^{bulk}(N_{Fe}^0) \]

- Carbon ties strongly
- GB0 & GB±/-2 are favorite sites: geometry other than chemistry

\[ \Sigma 3 \ (111) \ grain \ boundary \ - \ 96 \ Fe \ atoms \]
**Behavior of Sulfur segregation**

Fig. Average binding energy of Sulfur as function of layer occupation

Tab. Behavior of GB cell under S attachment

<table>
<thead>
<tr>
<th>layer</th>
<th># of occ.</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>d, Å</th>
<th>- Eb/S, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean cell</td>
<td>0</td>
<td>6.92</td>
<td>7.99</td>
<td>20.29</td>
<td>3.15</td>
<td>-</td>
</tr>
<tr>
<td>GB0</td>
<td>1</td>
<td>6.92</td>
<td>8.00</td>
<td>20.47</td>
<td>3.51</td>
<td>-5.14</td>
</tr>
<tr>
<td>GB0</td>
<td>2</td>
<td>6.92</td>
<td>8.03</td>
<td>20.60</td>
<td>3.61</td>
<td>-5.22</td>
</tr>
<tr>
<td>GB0</td>
<td>3</td>
<td>6.96</td>
<td>8.00</td>
<td>20.75</td>
<td>3.68</td>
<td>-5.11</td>
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<tr>
<td>GB0 &amp; GB2</td>
<td>4</td>
<td>6.96</td>
<td>8.02</td>
<td>20.84</td>
<td>4.27</td>
<td>-5.06</td>
</tr>
<tr>
<td>GB0 &amp; GB2 &amp; GB2</td>
<td>8</td>
<td>6.89</td>
<td>7.96</td>
<td>22.12</td>
<td>5.36</td>
<td>-4.86</td>
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<tr>
<td>GB0 &amp; GB2 &amp; GB2 &amp; GB-2</td>
<td>12</td>
<td>6.94</td>
<td>8.02</td>
<td>22.12</td>
<td>4.95</td>
<td>-4.46</td>
</tr>
</tbody>
</table>

- **Average binding energy, eV/atom**
- **# of S occupation in one layer**
- **Substitution to GB2**
- **Interstitial to GB0**
- **Substitution to GB4**

**Expansion in z-dimension, Å**

- **z-expansion due to GB separation**
- **S atoms expose repulsive forces**
- **Interactions around GB broken**
Behavior of GB cell under P, N, C and B attachment

<table>
<thead>
<tr>
<th>Elements</th>
<th># of occ.</th>
<th>Δ*a, Å</th>
<th>Δ*b, Å</th>
<th>Δ*c, Å</th>
<th>Δ*d, Å</th>
<th>-Eb/S, eV</th>
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<td>0.00</td>
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<td>0.34</td>
<td>-6.78</td>
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<tr>
<td></td>
<td>2</td>
<td>0.00</td>
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<td>-7.46</td>
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<tr>
<td></td>
<td>4</td>
<td>0.01</td>
<td>0.02</td>
<td>0.60</td>
<td>1.15</td>
<td>-7.41</td>
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<tr>
<td></td>
<td>8</td>
<td>-0.04</td>
<td>-0.06</td>
<td>0.80</td>
<td>1.14</td>
<td>-6.22</td>
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<tr>
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<td>0.10</td>
<td>-0.14</td>
<td>1.13</td>
<td>1.25</td>
<td>-5.91</td>
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<tr>
<td>N</td>
<td>1</td>
<td>0.03</td>
<td>-0.01</td>
<td>-0.02</td>
<td>0.29</td>
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<td>-8.95</td>
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<tr>
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<td>0.04</td>
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<tr>
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<td>-0.05</td>
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<tr>
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<td>-0.23</td>
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<td>-0.01</td>
<td>0.08</td>
<td>0.25</td>
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</tr>
<tr>
<td></td>
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<td>-0.02</td>
<td>0.18</td>
<td>0.27</td>
<td>-7.96</td>
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<tr>
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<td>-0.04</td>
<td>0.40</td>
<td>0.81</td>
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<td></td>
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<td>0.20</td>
<td>0.61</td>
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<td>-0.18</td>
<td>0.50</td>
<td>0.52</td>
<td>-6.39</td>
</tr>
</tbody>
</table>

Fig. Comparative separation of Fe Σ3 (111) GB under the attack of different impurity atoms (S, P, N, C, B)
Fig. Behavior of Fe Σ3 (111) GB due to the precipitation of C, B, P and N

- The same binding tendency to a specific locations at GB
- Little interactions from impurity particles on the same layer
- S & P causes the separation of GB, which may initiate cracks
- B & C have little effects on GB mechanical properties
- N weakens the GB structure through formations of cavities and voids
• **First Principles DFT+U studies on (Ce,Th) O2 alloys**
  
  – Structure, Mechanics, Dynamics, Alloying of CeO2 and ThO2

Calculated lattice parameters, mechanical properties for CexTh1−xO16.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>a0</th>
<th>B0</th>
<th>C11</th>
<th>C12</th>
<th>C44</th>
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<tr>
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<td>131</td>
<td>95</td>
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<td>Ce4Th4O16</td>
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<td>5.383</td>
<td>208</td>
<td>376</td>
<td>124</td>
<td>76</td>
<td></td>
</tr>
</tbody>
</table>
High speed particle impact on atomic scale

- Radiation damage, degradation and embitterment (nuclear material shields, space gadgets etc.)
- Ion implantation, deposition (semiconductor device production)
- Surface modification (surface hardening, corrosion resistance etc.)

Thermal spike and following thermalization in Cu-Ni superlattice

Simulation of microstructure evolution under irradiation in Cu-Ni superlattice

DBTT = ductile to brittle transformation temperature
Magnetic Shape Memory Alloys

-Ni$_2$MnIn

- **Heusler alloy** structure
  - L21 in austenite phase
- Ferromagnetic due to separation of magnetic moments residing on Y atoms
- Ni$_2$MnGa most extensively studied, with reported recoverable strains $\approx$10% in the martensite phase

http://www.riken.jp/lab-www/nanomag/research/heusler_e.html
Magnetostructural Coupling in Ni$_2$MnIn

We apply volume-conserving strains to determine the magneto-mechanical response:

- tetragonal shear

\[ \varepsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \frac{-\delta^2 - 2\delta}{(\delta + 1)^2} \end{bmatrix} \]

- pure shear

\[ \varepsilon = \begin{bmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \frac{\delta^2}{1 - \delta^2} \end{bmatrix} \]
Polyimide-nanotube composites for electro-active materials


- (β – CN)APB/ODPA Polyimide
- Piezoelectric polyimide
- Exceptional thermal, mechanical, and dielectric properties
- Amorphous in nature
- Potential use in high temperature application
Acknowledgements

Financial Support: NSF, DARPA, ONR, ARO, DOE, & AFRL

NSF (ITR-ASE: stress corrosion)
NSF (IGERT): nanofluidics, SMA, CPNTs
NSF: fire retardant PNC’s
DARPA (PROM: FE and TE materials)
ONR (Energetic Materials)
ONR (H-Pd under extreme conditions)
ARO (Energetic Materials)
AFRL (Thermo electrics)
AFRL (IED Sensing)
DOE (Nuclear Fuels)
DOE (Multiscale Modeling)
CONACyT (Domain walls in FE devices)
CONACyT (Dielectric Gate Stacks)
TAMU (Transport in bio-nano systems)
PIIF (H-storage systems)
TUBITAK (Si-nanocrystals)
TUBITAK (MSMA’s)
PMMA thin film electronics

ARMAN, HASKINS
CHAKRABARTY, KINACI, SEVIK
PHAM, SHIV, OJEDA, CAGIN
KAMANI, LIZAROZU
BISWAS, CARVAJAL, WILLIAMS, NJOREGE

TAMU Super Computing Facility

Summer 08