Mesoscopic simulation for the prediction of macroscopic properties of nanostructured systems.

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The technology vision 2020

Vision 2020

New Chemical Science & Engineering Technology

Supply Chain Management

Information Systems

Manufacturing & Operations

Chemical Sciences

Enabling Technologies

Process Science & Engineering Technology

Chemical Measurement

Computational Technologies

Computational Molecular Science

Process Simulation & Modeling

Operations Simulation & Optimization

Large Scale Integration/Smart Systems

Computational Fluid Dynamics

Vision

Roadmap

Implementation

Industry Today

Goals

R&D Priorities

Partnerships

Industry 2020

Commercial Use

Workshops

Roadmaps

Collaborative R&D

Technology
The 4° Industrial revolution – Industry 4.0

Drivers
- Quality of life
- Engineering Sciences

Mobility

μElectronics

ICT

1st
- Steam engine
- 1782
- Power generation
- Mechanical automation

2nd
- Conveyor belt
- 1913
- Industrialization

3rd
- Computer, NC, PLC
- 1954
- Electronic Automation

4th
- Cyber Physical Systems
- 2015
- Smart Automation

Materials Genome Initiative

Strategic Plan
Nanoscale science and engineering

- Promise of unprecedented understanding and control over basic building blocks and properties of natural and man-made objects

- Recent survey: Nanotechnology Long-term Impacts and Research Directions: 2010 – 2020 **

- Theory, modeling and simulation (TMS)
  - Expected to play key role in nanoscale science and technology
    - Springer, September 30, 2010
      - Also available on the web at http://www.wtec.org/nano2/

* M. Roco, FY 2002 National Nanotechnology Investment Budget Request
** M.Roco, FY 2010 WTEC, Inc., 2010
New generation of products and productive processes (2000-2030)

- Timeline for beginning of industrial prototyping and nanotechnology commercialization

1st: Passive nanostructures (1st generation products)
Ex: coatings, nanoparticles, nanostructured metals, polymers, ceramics

2nd: Active nanostructures
Ex: 3D transistors, amplifiers, targeted drugs, actuators, adaptive structures

3rd: Nanosystems
Ex: guided assembling; 3D networking and new hierarchical architectures, robotics, evolutionary

4th: Molecular nanosystems
Ex: molecular devices ‘by design’, atomic design, emerging functions

Converging technologies
Ex: nano-bio-info from nanoscale, cognitive technologies; large complex systems from nanoscale

Based on NANO2, Fig. 6 [3]
Twelve global trends to 2020

- Theory, modeling & simulation: x1000 faster, essential design
- “Direct” measurements – x6000 brighter, accelerate R&D & use
- A shift from “passive” to “active” nanostructures/nanosystems
- Nanosystems, some self powered, self repairing, dynamic
- Penetration of nanotechnology in industry - toward mass use; catalysts, electronics; innovation– platforms, consortia
- Nano-EHS – more predictive, integrated with nanobio & env.
- Personalized nanomedicine - from monitoring to treatment
- Photonics, electronics, magnetics – new capabilities, integrated
- Energy photosynthesis, storage use – solar economic by 2015
- Enabling and integrating with new areas – bio, info, cognition
- Earlier preparing nanotechnology workers – system integration
- Governance of nano for societal benefit - institutionalization

Source: MC Roco, April 10 2014
Nanostructures design

Efficient nano structures are obtained from rational design

AND NOT

With a Trial & Error approach
The Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt, Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems".
Materials Genome Initiative (MGI)

- Developing a materials innovation infrastructure, through advances in and integration of:
  - Computational tools
  - Experimental tools
  - Digital data and informatics

- Achieving National goals in energy, security, and human welfare with advanced materials

- Equipping the next generation materials workforce
TMS: role of GPUs

Molecular complexity
N. of time steps * n. atom simulated in one day

Simple atom simulation
For a simple monoatomic fluid is the n. of atoms that can be simulated for 10ns in one day
Accelerator packages:
GPU, KOKKOS, OPT, USER-CUDA, USER-INTEL, USER-OMP

GPU cluster =
Dual 8-core Sandy Bridge Xeons with 2 Kepler GPUs
Multiscale Molecular Modeling
Multiscale Molecular Modeling


ACS Nano, 2012, 6(8): 7243-53


Soft Matter, 2013, 9, 2936-2946


College on Multiscale Computational Modeling of Materials for Energy Applications - ICTP
Modelling and experiments

Acronyms (and corresponding methods) indicated in the figure:
TM&S methods (in rectangles)
AIMD: ab initio molecular dynamics; CMD: classical molecular dynamics; MC: Monte Carlo

Experimental techniques (in ovals)
INS: inelastic neutron scattering; QENS: quasi-elastic neutron scattering; NSES: neutron spin echo spectroscopy; NMR: nuclear magnetic resonance; XR: X-ray reflectivity; SHG: second harmonic generation; SFG: sum frequency generation; CTR: crystal truncation rod (an X-ray method); XSW: X-ray standing wave; NR: neutron reflectivity
Outline of talk

- Introduction
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- Mapping procedure
  - From atomistic simulation to mesoscale
  - From mesoscale to micro FEM

- Applications
  - Functionalized nanoparticles in nanostructured polymer matrices
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    - On nanoparticles
    - Multivalent self assembly building blocks in nanoparticles

- Conclusions
From atoms … to beads

Molecular Dynamics

Dissipative Particle Dynamics

\[ f_i = \sum_{\substack{i \neq j}} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \]

\[ F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\hat{r}_{ij} & (r_{ij} < 1) \\ 0 & (r_{ij} \geq 1) \end{cases} \]

\[ F_{ij}^D = -\gamma \omega^D r_{ij}(\hat{r}_{ij} \cdot \mathbf{v}_{ij})\hat{r}_{ij} \]

\[ F_{ij}^R = \sigma \omega^R r_{ij} \theta_{ij} \hat{r}_{ij} \]

Conservative
fluid / system dependent

Dissipative
frictional force, represents viscous resistance within the fluid - accounts for energy loss

Random
stochastic part, makes up for lost degrees of freedom eliminated after the coarse-graining

- Polymeric materials are modeled by connecting **beads** by harmonic **springs**

\[ f_i = \sum_j C r_{ij} \]
From Forrest and Sutter, 1995

- Soft potentials were obtained by averaging the molecular field over the rapidly fluctuating motions of atoms during short time intervals.
- This approach leads to an effective potential similar to one used in DPD.
Parameters for mesoscale models

- bead size and Gaussian chain architecture
  - From characteristic ratio \( C_\infty \) in terms of Kuhn length
- bead mobilities \( M \),
  - From bead self diffusion coefficients - MD
- effective Flory-Huggins interactions
  - Method 1: polymer blends, copolymers, spherical nanofillers
    - Differences in non bonded energies between bulk and isolated chain
  - Method 2: nanofillers of any size and shape
    - From energy distribution in MD considering **density distribution** around nanofiller
bead size, chain architecture

- MD NPT runs on homo polymers
  - Monomer length
  - $C_\infty$ calculation and Kuhn length
  - Chain architecture

\[
\begin{align*}
\langle r^2 \rangle_0 &= C_\infty n^2 = NL^2 \\
r_{\text{max}} &= NL
\end{align*}
\]

MD NPT runs on homo polymers
- Monomer length
- $C_\infty$ calculation and Kuhn length
- Chain architecture

Estimation of DPD parameters from atomistic simulations

\[ F_{\text{tot}} = n F_i + n F_j + \gamma n E_{ij} \]

Single, binary, ternary

Binding energies are rescaled considering the

Density profiles from MD

From beads to micro FEM

Dissipative Particle Dynamics

Soft potentials calculations

\[ F_i = f(a_{ii}, a_{ij}, \ldots, r_c) \]

Characteristic dimension of mesoscopic system

Micro - FEM Simulation

FEM Analysis:
Macroscopic properties

From beads ... to micro: fixed grid

- Geometry: map cubes to Palmyra tetrahedrons
- Laplace equation is solved for electric conductance, diffusion and permeability
  \[ \text{div } \sigma(r) \text{ grad } \varphi = 0 \]
- Local deformation allow the calculation of mechanical properties

\[
\frac{\partial}{\partial x} \left[ \frac{E}{1+v} \left( \epsilon_{ik} + \frac{v}{1-2v} \epsilon_{ll} \delta_{ik} \right) \right]
\]

microFEM modelling: variable grid

- Platelets orientation
  - Alignment is defined and assigned to each platelet
- Pure component properties definition
  - Properties of the stacks is based on mesoscale simulations
  - Pure component properties from MD or experimental data

Simulation protocol for core-shell nanoparticles

Atomistic interface

mesoscale interface

Density profile of the interface (DPD)

Mechanical properties of the interface (Mesosprop)

Palmyra filler

Volumetric average of properties

Mechanical properties of the pure filler

Palmyra simulation
MoDeNa project: Modeling of morphology
Development of micro and Nano Structures

http://www.modenaproject.eu/
MoDeNa: Multiscale modeling Framework

http://www.modenaproject.eu/
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• Conclusions
Self assembly of nanoparticles in block copolymers

• Organic polymer and inorganic particles mixing (PPNs)
  – PPNs fabrication process via self-assembly
  – By dispersion of particles in diblock copolymers
• Predicted microstructure morphology depends on
  – nature of the system
    • chemistry and architecture of the blocks
    • volume fraction of the nanoparticles
    • strength and type of interactions
  – process conditions
    • temperature
    • shear
• SCOPE: model the system morphology
• Experimental evidence by Chiu et al.
  – poly styrene-2 vinyl pyridine
• Applications:
  – Opto electronic industry

Lamellae: A (or B) covering

- segregation in the center of the corresponding domain;
- perfect agreement with experimental evidences.

Lamellae: A and B covering (A₆B₆)

- nanoparticles at the interfaces between the A-B blocks
  - Agreement with experiments
PS grafting only: loading: $\phi_p = 0.2$

- For $PS4Au8$ system, large regions of nanoparticles (red) – exp. evidence
- Same tendency to migrate to the interface as the PS grafting density decreases
  - Line legend:
    - (green), $PS$;
    - (blue), $PVP$;
    - (red), $Au$.

Selective placement of magnetic nanoparticles in diblock copolymer films

• Goal:
  – NPs selectively placed into the PMMA domains?
  – Max concentration for preserving lamellar morphology?
  – Verify Mesoscale model (DPD)
• Materials & methods
  – diblock copolymer PS-\(b\)-PMMA
  – compatibilized magnetic (\(\text{Fe}_3\text{O}_4\)) nanoparticles
  – 1, 2, and 5% wt
  – Solvent vapor annealing

Selective placement of magnetic nanoparticles in diblock copolymer films

- Diblock copolymer PS-\textit{b}-PMMA lamellar structure with solvent vapor annealing
Selective placement of magnetic nanoparticles in diblock copolymer films

- Placement of (Fe$_3$O$_4$) nanoparticles
  - Satisfactory and selective dispersion
  - into the PMMA lamellar-region
  - up to a concentration of 5 wt% 
  - cluster formation with dimensions of few NP units

- DPD model is verified and reliable
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Grafted silica nanoparticles in polymers

- Particles embedded in a polymer matrix and grafted with polymer chains.
  - Matrix: polydispersity, molecular weight
  - Particles: size, chemical nature, surface treatment
  - Grafting agents: chemical nature, grafting density, molecular weight, polydispersity

- Grafted nanoparticles and semi crystalline polymers
  - Core: amorphous SiO\(_2\) 5-10 nm diameter
  - Linker: Si based component
  - Grafted polymer chains: polystyrene 2k – 20k
  - Polymer: amorphous polystyrene 100k
A general view of the project

- Polystyrene – silica grafted nanoparticles: different scales:

  - Single nP MC
  - MD & Cg MD
  - DPD 1:1
  - DPD 1:n
  - DPD 1:many

Parameters from: COSMO-RS or MD

Increasing time and length
Comparison with experiments – CG level II

0.5% wt and 0.31 chains/nm²  0.5% wt and 0.82 chains/nm²

5.0% wt and 0.31 chains/nm²  5.0% wt and 0.82 chains/nm²

Grafting density
Aggregation vs. dispersion: effect of grafted chain length

- Increasing grafted chain length favors uniform distribution of nP in the matrix

Chain length

- 2.5k Da and 0.51 chains/nm²
- 21.3 k Da and 0.31 chains/nm²
- 103.7 k Da and 0.53 chains/nm²

Fixed grafted density and PS matrix 100k
### Summary of the mechanical properties

<table>
<thead>
<tr>
<th>% NP</th>
<th>$E_C$ (GPa)</th>
<th>$E_C/E_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grafting density 0.5 chains/nm$^2$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.59 (2.60±0.1)</td>
<td>1.03</td>
</tr>
<tr>
<td>5</td>
<td>2.94 (2.81±0.2)</td>
<td>1.17</td>
</tr>
<tr>
<td>10</td>
<td>3.45</td>
<td>1.37</td>
</tr>
<tr>
<td><strong>Grafting density 0.7 chains/nm$^2$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.62</td>
<td>1.04</td>
</tr>
<tr>
<td>5</td>
<td>3.07</td>
<td>1.22</td>
</tr>
<tr>
<td>10</td>
<td>3.55</td>
<td>1.41</td>
</tr>
<tr>
<td><strong>Grafting density 1 chains/nm$^2$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.62 (2.75±0.2)</td>
<td>1.04</td>
</tr>
<tr>
<td>5</td>
<td>3.34 (2.87±0.1)</td>
<td>1.33</td>
</tr>
</tbody>
</table>
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Systems for biomedical applications: 1 – 1000 nm

- **100 nm**
- **50 nm**
- **25 nm**
- **10-15 nm**

**Dendrimers**

Hyperbranched polymers (5-25 nm)

**Polymer-drug**

Polymer-protein (5-50 nm)

**Block copolymer micelles**

(10-200 nm)

**Nanocapsules**

(20-1000 nm)

**Nanoparticles**

(2-100 nM)

**Liposomes**

(80-200 nm)

**Self-assembling systems**

(5-25 nm)
Self assembly of nanostructures on gold nanoparticle cores

**Table 1:** Gold nanoparticles coated with mixtures of thiolates of 1 and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_{\text{SAM}}^{[a]} )</th>
<th>Core diameter [nm]([b])</th>
<th>MPC composition([c])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2.2 ± 0.4</td>
<td>( \text{Au}<em>{400}(\text{S-C8-TEG})</em>{54}(\text{S-F8-PEG})_{54} )</td>
</tr>
<tr>
<td>2([d])</td>
<td>1</td>
<td>1.6 ± 0.2</td>
<td>( \text{Au}<em>{150}(\text{S-C8-TEG})</em>{33}(\text{S-F8-PEG})_{33} )</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>2.5 ± 0.4</td>
<td>( \text{Au}<em>{540}(\text{S-C8-TEG})</em>{108}(\text{S-F8-PEG})_{43} )</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1.9 ± 0.2</td>
<td>( \text{Au}<em>{230}(\text{S-C8-TEG})</em>{66}(\text{S-F8-PEG})_{16} )</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>1.9 ± 0.3</td>
<td>( \text{Au}<em>{240}(\text{S-C8-TEG})</em>{68}(\text{S-F8-PEG})_{3} )</td>
</tr>
</tbody>
</table>

Color legend:
- solvent=turquoise
- TEG/PEG=green
- C8=grey
- F8=purple
- gold=brown

1
Stripes
Stripe thickness ~ 0.65-0.7 nm

F8 ~ 1.2+ 3.1 nm
C8 ~ 1.3+ 1.9 nm

Self assembly of nanostructures on gold nanoparticules

2: effect of core size

3: effect of grafted composition

2: effect of core size

Janus nanoparticle

Stripe-like pattern

Domains

Color legend:
- solvent=turquoise
- TEG/PEG=green
- C8=grey
- F8=purple
- gold=brown
Multifunctional Nano vectors - Theranostics

- Development of **Nano vectors** for bioactive components:
  - drug targeting
  - controlled release
- Optimal bioactive concentration remains constant for long time
  - High specify
  - Controlled release
  - Reporting

Gene therapy: nucleic acids delivery

A. The dendrimer AD and

B. representation of its adaptive self-assembly upon interaction with siRNA for siRNA delivery.

Gene therapy: nucleic acids delivery

- Nano vectors should:
  - Prevent degradations
  - Enhance cellular uptake
  - Improve bio distribution and pharmaco kinetics

Design and optimization of the nanovector structure

Binding capacity and protection

Anticancer drug-loaded spherical nanovectors

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In summary …

• Multiscale molecular modeling protocol
  – Mapping atomistic to mesoscale
  – Mapping mesoscale morphology to microFEM

• Useful for the design of nanostructured systems
  – Interpretation of experiments
  – Virtual ‘nanoscope’
  – Design of active nano materials and nano systems

• From classical nanotechnology to nanomedicine
  – Classical industries (automotive, opto-electronic, polymer…)
  – Pharmaceutical industry
  – Nano medicine
  – Bio based economy

• General design approach for nanostructured materials & systems
Nano-Bio Technology has a bright future

- Nano-bio technology will have in 21 century the same importance that oil, polymers and semi conductors had in the 20 century

- Convergence of …. 
  - Society needs and new technologies 
  - Experiment and TMS 
  - Complex systems and computer power

- What is needed? 
  - Basic competences in physics, chemistry and biology 
  - Nano Characterization and nano fabrication tools 
  - HPC and computational algorithms 
  - Strong integration and scientific relationships among hospitals, medical research centers, universities and industries 
  - High quality highly integrates university system
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