SOFT MATERIALS AT THE CENTER FOR HIERARCHICAL MATERIALS DESIGN

Juan de Pablo, University of Chicago
October 31, 2016
• Weak interactions, order $k_B T$
• Always evolving, often far from equilibrium
• Often amorphous, difficult to “define”
• One compound can behave very differently
  - linear polyethylene
  - branched polyethylene
• Complicated theoretical descriptions, hard to solve
• Lack of data
• ...
CALPHAD Method – Metallic Alloys

\[ G = G_{id}^\phi + G_E^\phi \]

\[ G_{id}^\phi = R \cdot T \cdot \sum_{i=1}^{n} x_i \cdot \ln(x_i), \quad i = 1, \ldots, n \]

\[ G_E^\phi = \sum_{i,j=1 \atop i \neq j}^{n} x_i x_j \sum_{z=0}^{m} z L(x_i - x_j)^z + \sum_{i,j,k=1 \atop i \neq j \neq k}^{n} x_i x_j x_k L_{ijk} \quad z = 0, \ldots, m \]

“Modelling of phase diagrams and thermodynamic properties using Calphad method – Development of thermodynamic databases”
A Universal Platform

Multiblocks - DSA

CHiMaD

OPVs - Composites

Rheology

Charged polymers - coacervates
OPV Polymers and Liquid Crystallinity - Model

Intra-molecular Interactions: Worm-like chain model

\[
\frac{\mathcal{H}_b}{k_B T} = -\varepsilon \sum_{i=1}^{n} \sum_{s=1}^{N-2} \frac{[r_i(s+2) - r_i(s+1)] \cdot [r_i(s+1) - r_i(s)]}{b^2}
\]

\( b \) --- bond length

\( \varepsilon \) --- controls chain stiffness

Inter-molecular Interactions:
segment-segment incompatibility

\[
\frac{\mathcal{H}_{nb}}{k_B T} = \rho_o \int_V dr \chi_{\phi_A(r)}\phi_B(r) + \frac{\kappa}{2} [1 - \phi_A(r) - \phi_B(r)]^2
\]

orientational coupling

compressibility

CHIMaD
NanoMine

Catherine Brinson, NU
Wei Chen, NU

Polymer Design

Juan de Pablo, UChicago
Ian Foster, UChicago
Paul Nealey, UChicago
Heinrich Jaeger, UChicago

processing, structure and property parameters for polymer nanocomposite systems

generate characteristic properties for design of polymer blends and copolymers for engineering applications.
• Data curation: literature and lab, automation, smart query tools, visualization tools

Joint w/ Wei Chen, Linda Schadler
PPDB: Method (1)

- Automated knowledge extraction from text, equations, tables and figures.

Roselyne Tchoua (CI)
PPDB: Method (2)

• Leverage knowledge from crowd-sourced experts to aid classification and knowledge extraction.

MENG 22000

Roselyne Tchoua (CI), Debbie Audus (NIST), Jian Qin (IME), Mladen Rasic(IME)
PPDB: Method (3)

• Create a curated database for a range of polymer properties & present molecular engineers with approved relevant data for materials design. Port to other materials/properties.
Available Tools

- All applications on the site now run natively on mobile devices.
- Interactive Output from the database, obtain chi value, system details, method, and source of chi value.
- Interactive phase diagrams, free energy plots, data points, etc.

Input screen for generation of Lattice Cluster Theory phase diagram with semiflexibility.
DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS

to revolutionize nanomanufacturing. The interest and exponential growth in research activity and expenditure is driven by the semiconductor industry.

Intel, Mentor Graphics, Global Foundries, IMEC
Directed self-assembly of block copolymers on lithographically defined nanopatterned substrates

1. Interferometric Lithography
2. Patterned Imaging Layer
3. Deposit Block Copolymer Film
4. Self-assembled Domains

- X-PS cross-linking
- Pattern the PR
- O2 etching
- PR strip with solvent
- -OH brush grafting
- BCP annealing
- PMMA removal
Directed assembly of essential features for the fabrication of integrated circuits as defined by representatives from the microelectronics industry.

History

Methods

Attributes of DSA

Case Studies
DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS

USE-CASE GROUP

P. NEALEY, UCHICAGO

DESIGN GOALS

- Materials and processes for sub 10 nm lithography
- Scaling to 5 nm resolution

Relevant samples from industrial partners

Resonant Soft X-ray Scattering (RSoXS)

300mm Wafer

Coupon with back-etched membrane

Variable angle transmission measurement

Reconstruct $Q_x$-$Q_z$ map

- Enable widespread use of DSA nanotechnology.
- Need to establish proven manufacturing-relevant materials and processes to realize sub 10 nm resolution, and scaling to 5 nm.
- Standard metrology cannot be used to develop and validate predictive models or prototypical systems.
- Objective: develop fully 3D metrology tools of DSA structures based on RSoXS
- Experiments are performed on samples fabricated by industrial partners
- Results are quantitatively compared with those of molecular simulations
- Intimate coupling with advances in models, materials design, and processing.

Pattern characteristics

(W/L_0, $\gamma_{interfacial}$)

Polymer properties

(x, N, $\gamma$)

Input parameters:

SEM

2D Model

Fit to experiment

Couple to molecular simulation

$W/L_0 \approx 0.98$

$W/L_0 \approx 0.75$

$W/L_0 \approx 1$

$W/L_0 \approx 0.6$
**4X density multiplication**

**Target Morphology**

What are the
- optimal stripe width?
- pattern characteristics?

Miskin et al., PNAS, 2016
GISAXS and CDSAXS

GISAXS

CDSAXS

Sunday et al., *ACS Nano*, 2014
Traditional Interpretation

Candidate morphologies constructed from simple geometric shapes

- Treated as a geometric problem
- Average shape described as combinations of simple patterns

Sunday et al., *ACS Nano*, 2014
Scattering from Simulations

Thermodynamic and Boundary Conditions

Evolutionary Optimization to select Input Parameters

Morphology from Molecular Simulations

Calculate Fourier Transform of Shape with no interface

Convolute Interfacial Width: \( \sigma = f(\chi N) \)

Add the fluctuation of interface

Low \( \chi \) material: High Fluctuations

High \( \chi \) material: Low Fluctuations

Khaira et al., submitted, 2016

DOE Grand Challenges Rep.
Directed Self-Assembly on Chemical Patterns

Types of Chemical Patterns

Two Toned: xPS is totally preferential to PS

Three-Toned: Top of xPS is preferential to PS while side walls are PMMA preferential

• 3X density multiplication of block copolymer of periodicity 28 nm
Optimization Results

![Graph showing optimization results with iterations and objective function values.](image)
Optimization Results

- W/L0 ≈ 0.93
- Approximately 1.5 nm height difference between xPS and backfill brush.

Difference in $\chi_N$ between top of xPS and sidewalls suggests three-toned pattern.

**Three-Toned:** Top of xPS is preferential to PS while side walls are PMMA preferential.
Morphology for Different Stripe Widths

Guiding Stripe Width

W: 0.47L₀
W: 0.66L₀
W: 0.72L₀
W: 0.93L₀
W: 1.14L₀
CDSAXS, TEM & GISAXS

$W = 1.14L_o$
CHARGE DRIVEN ASSEMBLY OF SOFT MATTER

To develop new materials based on multi-valent ionic interactions. This direction is significant because it can yield new types of self-assembled structures. Knowledge of the as-yet unexplored phase behavior of polyelectrolyte complexes is scientifically significant and technologically relevant.

Solvay, Mars, Dupont --- Startup
Coarse-grained MD for Coacervate

- molecular dynamics
- bead-spring chain
- soft repulsion (TICG)
- soft Coulomb short range
- Ewald Sum long range
- constant dielectric permittivity
- salt beads
Self Assembly

- PAA & PDMAEMA 1:1 ratio, concentration 0.11M
- Length unit $R_{ee} = 10.2 \text{nm}$,
- 50 beads per chain,
- 71.6 polymer beads per $R_{ee}^3$
- Coulomb strength parameter
  
  Bjerrum length $\lambda_B = \frac{e^2}{\varepsilon_r k_B T} = 0.7 \text{nm} = 0.09 R_{ee}$
- Runs on GPU with HOOMD

Self Assembly Phase Diagram

Phase Diagram

Rheology

\[ G(t) = \langle \tau_{xy}(t')\tau_{xy}(t' + t) \rangle \]

Coarse-grained TICG for charged copolymers

PAGE-PEO diblocks/PAGE-PEO-PAGE triblocks

van der Kooij et al., J. Langmuir 48 (2012); Hunt et al., J. Adv. Mater. 43 (2011);
**Materials Driven by Charge Complexation**

**DESIGN GOALS**
- Control hydrogel bulk structure by varying lengths of molecular constituents and polymer loading
- Tune hydrogel sensitivity to salt and pH by varying block lengths
- Combination of salt, pH and macromolecular structure gives tissue-matching tunable moduli
- Extension to polypeptide materials with desired biocompatibility and biodegradability envisioned

- Electrostatically cross-linked hydrogels obtained from mixing aqueous solutions of $\text{A}^+\text{BA}^+$ and $\text{C}^-\text{BC}^-$ triblock copolymers.
- Polyelectrolyte complex (PEC) domains serve as tunable cross-links. Micelles are the artificial “atoms” in these self-assembled structures.
- The ratio of charged:neutral block size determines
  - Size of the PEC domains
  - Aggregation number
- Polymer loading dictates the PEC domain arrangements.
- Combining block size ratio and polymer loading variations allow for tunable mechanical properties
End-to-end distribution
• Directed assembly of multiblock copolymers
• Complex coacervation
• Liquid crystalline polymers - OPV materials
• Polymer nanocomposites

Towards a universal platform that enables data analysis, data base population, and rational materials design
**Education & Outreach**

- Industrial partnerships
  - Intel, Mentor Graphics, Global Foundries
  - Dupont, DOW Corning, Good Year
  - Solvay, Polyera, Mars
- SPIE DSA Course
- Museum of Science and Industry
- Chicago Collegiate Scholars Program
  - 120 students
  - Nationally recognized
  - 99.5% graduate 4 yr college
  - 75% graduate from highly selective colleges
Impact Adsorption and Dissipation

Sid Nagel, UChicago
Heinrich Jaeger, UChicago
Juan de Pablo, UChicago

- Aaron Forster (NIST)
- Chelsea Davis (NIST)
- Chris Soles (NIST)
- Michael Riley (NIST)

International Workshop on Impact Mitigation
August 8, 2016, U. Chicago
Dense suspensions ‘by design’ for effective impact energy dissipation

**Problem:** Want material that conforms to arbitrary and possibly evolving surfaces and can dissipate large amounts of impact energy

**Proposed solution:** Dense suspensions of hard particles in liquid

- liquid-like and highly conforming at low applied stress
- dynamically (and reversibly) transform to solid-like state at large applied stress

**Chicago discovery** (Nature 487, 2012): Impact-induced dynamic jamming fronts propagate into the suspension, generating a growing solid mass that takes up the impact momentum

**Next steps:** impact response by design
Dense suspensions ‘by design’ for effective impact energy dissipation

Key idea: tailor B/G ratio in solid-like state to optimize energy dissipation

Two-pronged approach:

Dense suspension coupled to cellular network with tuned B/G
- Control over wide range of responses

Dense suspension with added designer particles
- Optimized dynamic range of response

Network dynamics (Nagel)
Suspension dynamics (Jaeger)

Multiscale simulations (de Pablo)
Systematic Coarse-Graining

Boltzmann inversion

\[ U_{an,i+1} = U_{an,i} + f k_B T \ln \frac{p_{an,i} + v}{p_{an,target} + v} \]

\[ U_{nb,i+1}(r) = U_{nb,i}(r) + f k_B T \ln \frac{g_i(r) + v}{g_{target}(r) + v} \]

Relative entropy

\[ S_{rel} = \sum_{\nu} p_{AA}(\nu) \ln \left( \frac{p_{AA}(\nu)}{p_{CG}(M[\nu])} \right) + S_{map} \]

\[ S_{rel} = \beta (U_{CG} - U_{AA})_{AA} - \beta (A_{CG} - A_{AA}) + S_{map} \]

Faller et al., 2009, 2015
Carmichael & Shell, JPCB, 2012
Hinckley & de Pablo, JCTC, 2015
Rely on Effective Models

“Perfection is achieved, not when there is nothing more to add, but when there is nothing left to take away.”

Antoine de Saint-Exupery, *Vol de Nuit*, 1900-1944
POLYMER MATRIX COMPOSITES

to develop a “materials informatics initiative” including integrated databases, curation, visualization, and analysis tools to relate macroscale polymer composite behavior to chemical constituent and kinetic behavior, and linking these resources to further development of high-performance modeling and predictive tools

Owens Corning, Good Year
USE-CASE GROUP

POLYMER MATRIX COMPOSITES

DESIGN GOALS

- Short term: Cellulose-polymer nanocomposites with optimized interphase behavior for high modulus/diffusion resistance
- Short term: DBs/Models/tools to predict interphase properties and diffusion/modulus of the system
- Long term: develop databases, models and tools to enable prediction of hierarchical composite behavior based on constituent components and processing

The database system “NanoMine” was created for polymer nanocomposite material systems, including:

- Curated data from literature in an open source, searchable database, based on Materials Data Curator developed at NIST
- Statistical/machine learning-based methods and tools, eg for identifying the key microstructure descriptors
- Material property simulators for prediction of macroscopic properties using data from DB, predicted microstructures

Additional tools and resources being developed. Interphase data and predictions being added based on molecular modeling efforts and local characterization experiments in Use Case.
Mechanoresponsive Damage Sensing

Non-fluorescent

\[ \epsilon \]

\[ \Delta \]

Fluorescent

Nanoindenter ▼

Epoxy

0mN

50mN

0°, 1µm/s

0°, 50µm/s

0°, 100µm/s

180°, 1µm/s

180°, 50µm/s

180°, 100µm/s

Fluorescence Intensity (a.u.)

Scratch Distance (µm)

0°, 1µm/s

0°, 50µm/s

0°, 100µm/s

180°, 1µm/s

180°, 50µm/s

180°, 100µm/s

Constrained Geometries for Simulating External Force (COGEF)

Gilman, Phelan, Woodcock, Wang, Davis, Khare
bulk heterojunction organic solar cells (OSCs) represent an alternative solar energy harvesting system. New polymers and theoretical methods developed will deepen our understanding in structure/property relationship and push the performance of OSCs towards commercial applications.
ORGANIC BULK HETEROJUNCTION POLYMER SOLAR CELLS

DESIGN GOALS

1. Develop OPV solar cells with high efficiency, low cost and long term stability.
2. Establish structure/property relationship via synthesis, physical characterization, theoretical investigation and device engineering to guide further explorations of new and more efficient materials.

PTB7-Th:PID2:PCBM Ternary OPV System

- New polymers with varied band gaps were synthesized either as electron donor or acceptors.
- Ternary OPV solar cells were developed that exhibit high efficiency and large enhancement.
- New methods are being developed to modify the generic molecular dynamics force field method to fully describe the aromatic semiconducting polymers.
- Electronic properties of these polymers are modelled based on sophisticated quantum mechanical calculation.
- Collaborations with NIST scientists are ongoing via sample exchanges and teleconferences.

**Ternary OSC with PTB7-Th and Two acceptors**

Inverted device architecture: ITO/ZnO/PTB7-Th:TPBDT:PC$_{71}$BM/MoO$_3$/Ag

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF, (%)</th>
<th>PCE, (%)</th>
<th>Highest PCE, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th:PC$_{71}$BM (1:1.5)</td>
<td>0.77±0.01</td>
<td>18.1±0.1</td>
<td>67.9±0.7</td>
<td>9.5±0.1</td>
<td>9.8</td>
</tr>
<tr>
<td>PTB7-Th:TPBDT:PC$_{71}$BM (1:0.05:1.5)</td>
<td>0.77±0.01</td>
<td>18.7±0.2</td>
<td>67.2±0.2</td>
<td>9.8±0.1</td>
<td>10.2</td>
</tr>
<tr>
<td>PTB7-Th:TPBDT:PC$_{71}$BM (1:0.1:1.5)</td>
<td>0.76±0.01</td>
<td>19.4±0.2</td>
<td>68.3±0.8</td>
<td>10.1±0.1</td>
<td>10.3</td>
</tr>
<tr>
<td>PTB7-Th:TPBDT:PC$_{71}$BM (1:0.2:1.5)</td>
<td>0.77±0.01</td>
<td>19.6±0.4</td>
<td>67.7±0.2</td>
<td>10.1±0.2</td>
<td>10.5</td>
</tr>
</tbody>
</table>
Validation of coacervate density from self-assembly

Coacervate phase simulation

Adjust polymer and salt concentration to match chemical potentials and pressure

\[ P_{coac}(\varphi_{polymer}, \varphi_{salt}) = P_{water} \]
\[ \mu_{coac}^i(\varphi_{polymer}, \varphi_{salt}) = \mu_{water}^i \]

\( i \rightarrow \{\text{salt+/-, water}\} \)

Water phase simulation

Calculated with Widom insertion method

\[ \frac{(\mu - \mu_0)}{k_B T} = -\ln(\exp(-\Delta E_t)/k_B T)_{NVT} \]