Soft Material Use Cases

OUTLINE

- **Use Cases**
  - Directed self-assembly of block polymers
  - Self-assembly of biomaterials
  - All-polymer organic solar cells
  - Polymer matrix composites
- **Tools**
  - GISAXS, SAXS, …
  - Theoretically informed coarse-grained approach
  - Evolutionary materials design
- **Data**

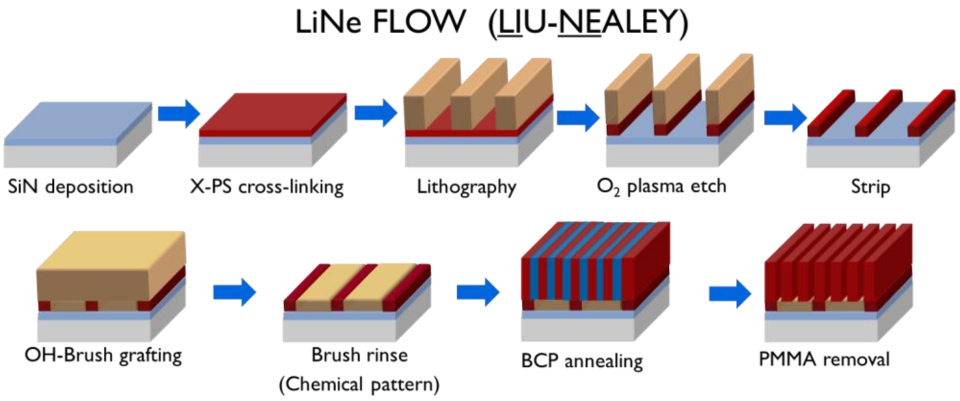
Directed Self-Assembly of Block Polymers

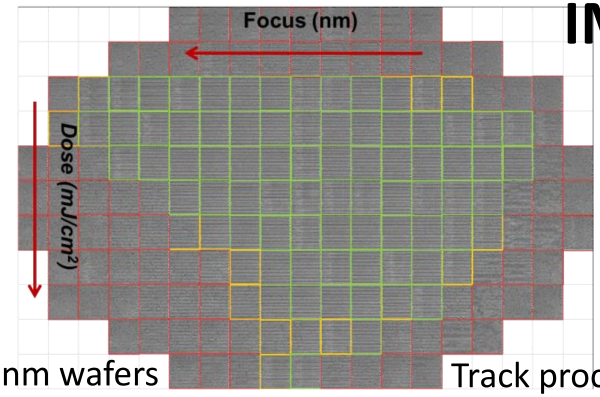
P. Nealey (UC), J.J. de Pablo (UC), H. Jaeger (UC), M. Olvera de la Cruz (NU), S. Sibener (UC), L. Yu (UC)

MOTIVATION

Lithography

- **Workhorse of semiconductor industry**
- **Important fraction of cost of electronic devices**
- **Need for new materials and processes for next-generation lithography**
- **Sub-10 nm patterning**
- **Need for metrology**
- **Need for design tools**

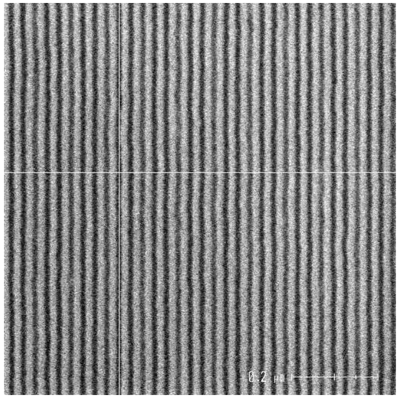




IMEC

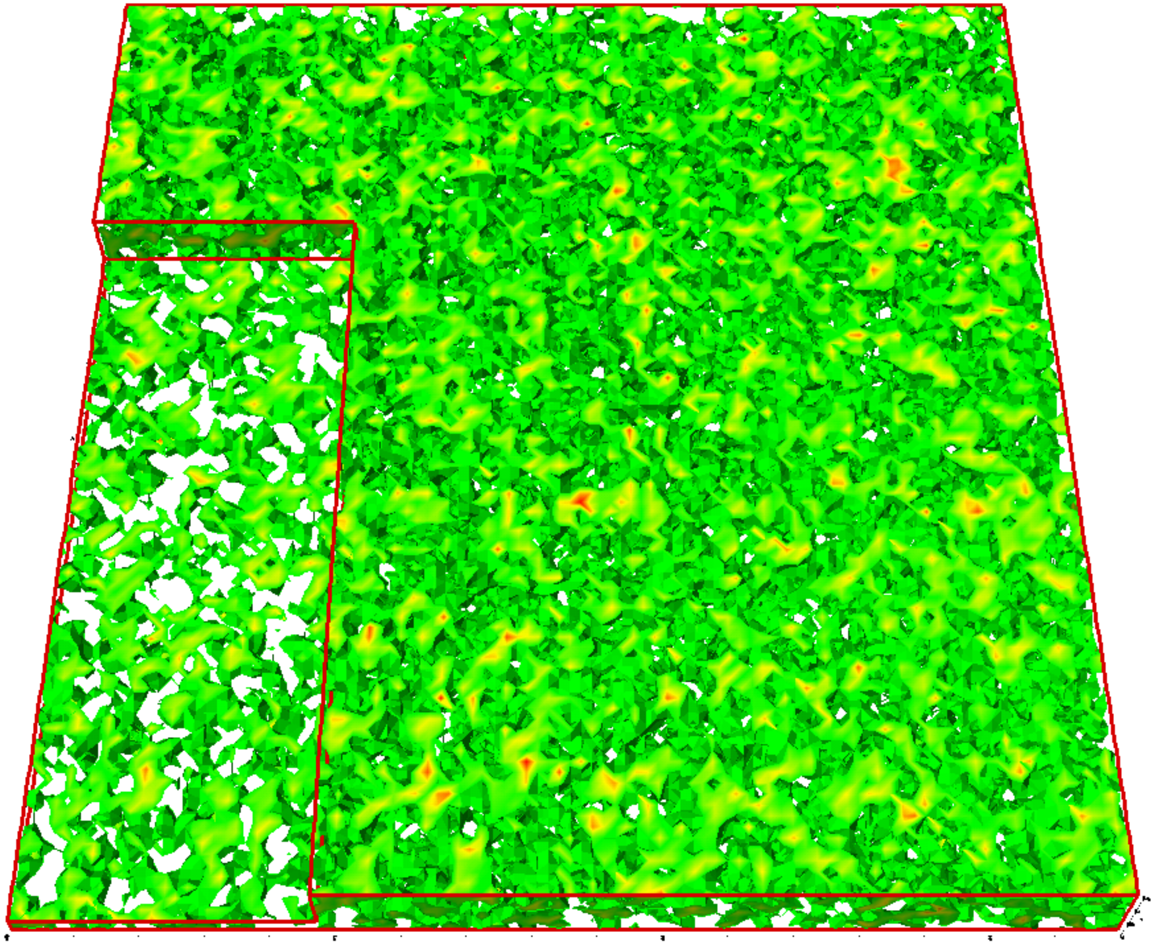
300 nm wafers

Track processing

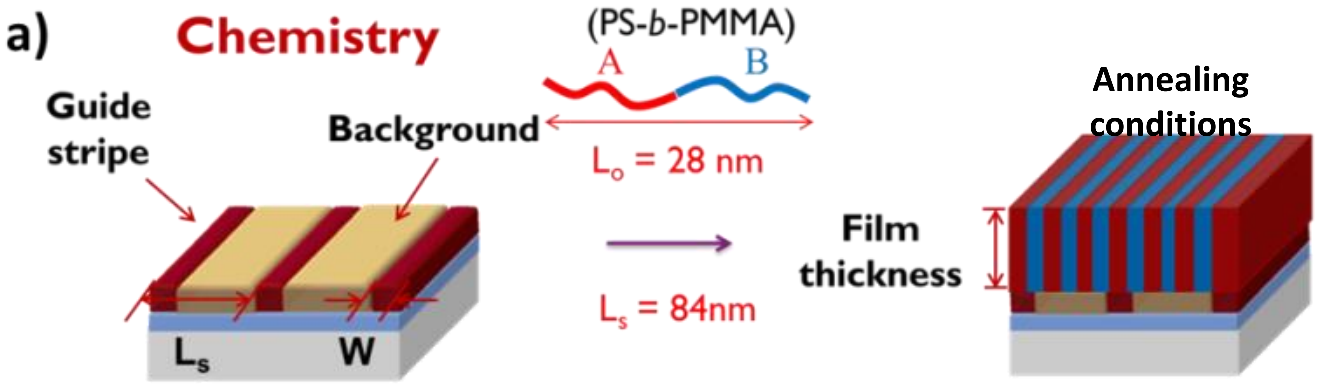


Initial Goals: Robust, pilot-line validated directed self-assembly for sub 10 nm lithography

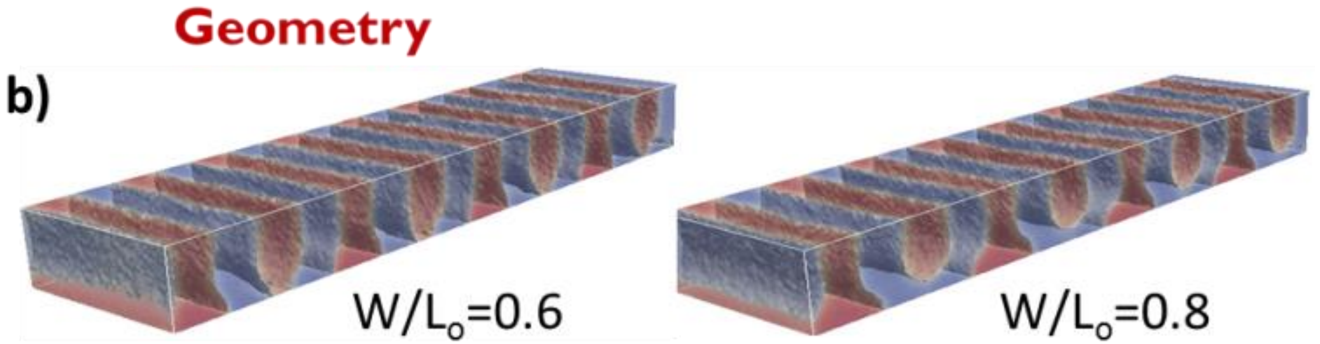
- Search for new polymers and processing techniques
- Design materials and processes
- Validate by comparison to experiment
- Develop metrology tools and advanced simulation tools for non-equilibrium assembly



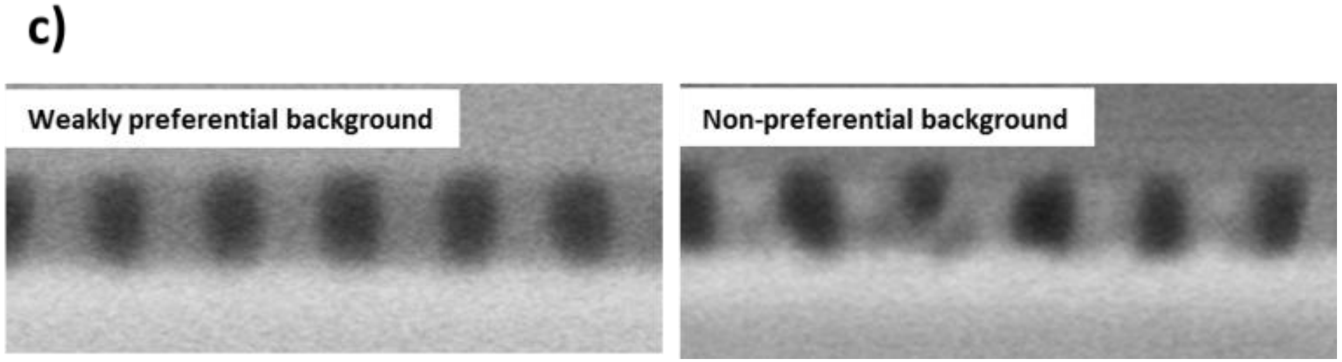
Detailed 3D Metrology is Required to Evaluate DSA Processes



Key parameters of DSA process



3D structure induced by non-ideal guide stripe width



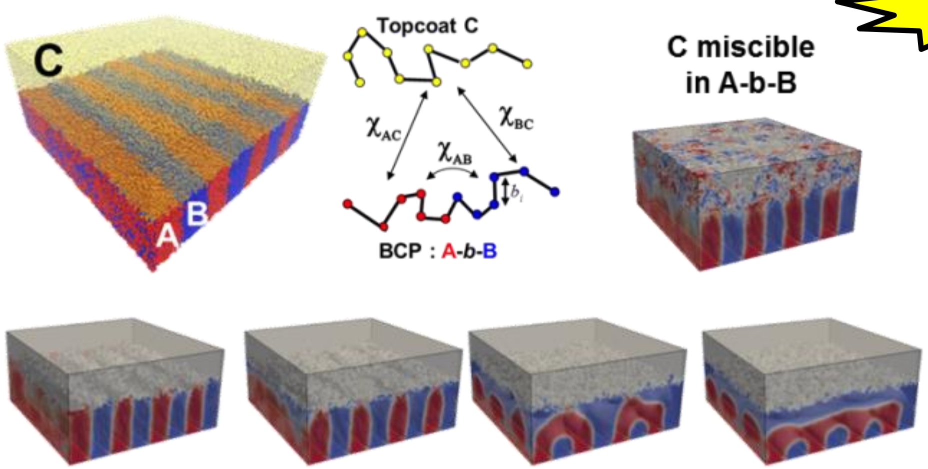
3D structure induced by incorrect chemistry in background regions

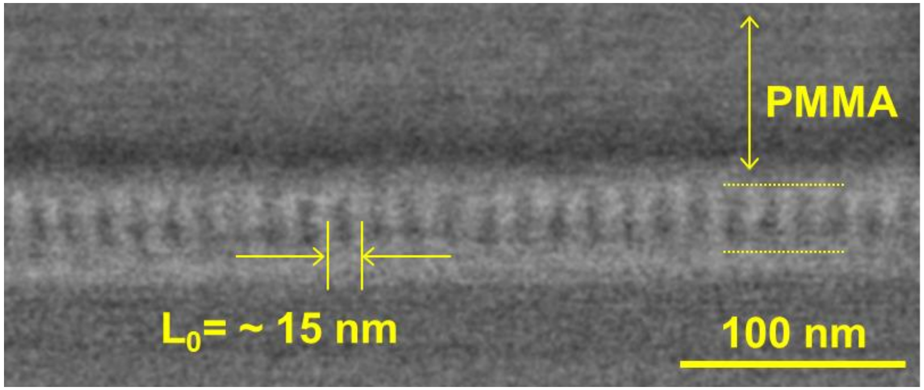
Candidate Materials Systems/ Current Experience with 8 nm Resolution

P2VP-PS-P2VP

Topcoat

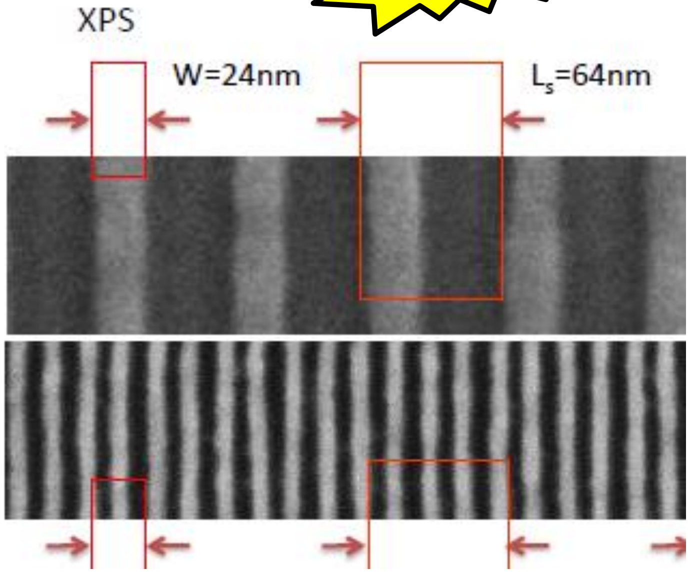
Gen 2 – Target 1



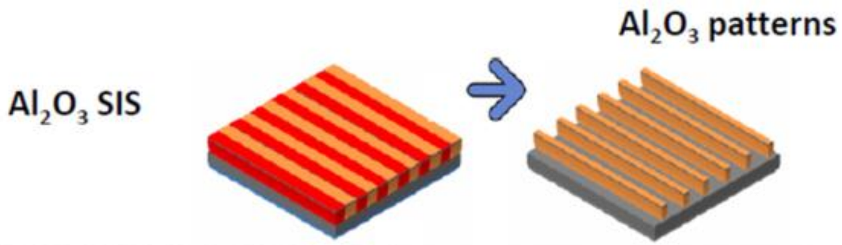


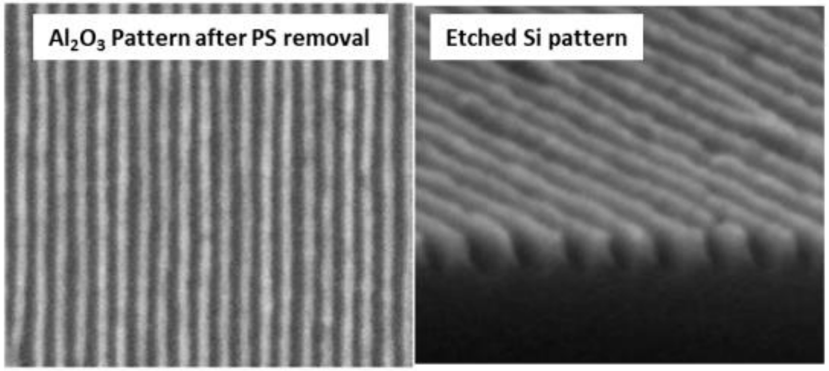
P2VP-PS-P2VP

Solvent Anneal



Pattern transfer by Synthesis In-Situ (SIS)

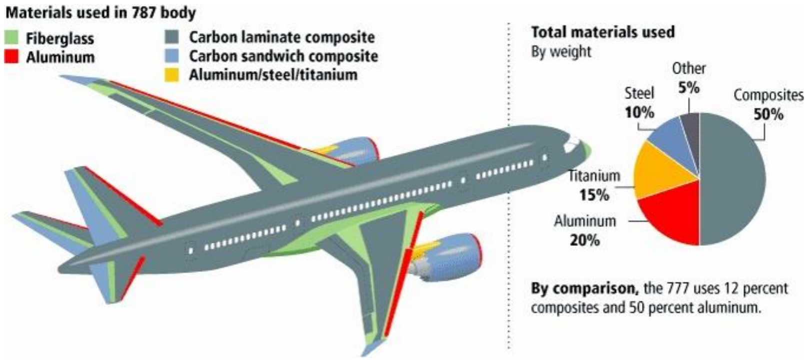




Polymer Matrix Composites

C. Brinson (NU), J.J. de Pablo (UC), Keten (NU), E. Luijten (NU), H. Jaeger (UC)

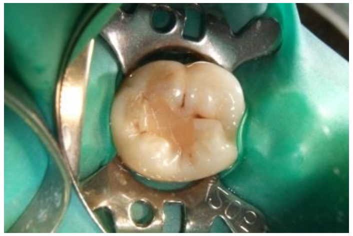
MOTIVATION



- **Composites are lightweight, corrosion resistant, tailorable, low cost**
- **Limited understanding of:**
  - multiphase composite properties
  - simultaneous control of electrical/mechanical properties
  - long-term properties and durability under use conditions

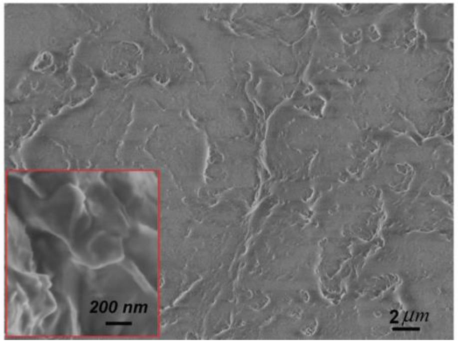
Initial Goals: Comprehensive design of composite materials

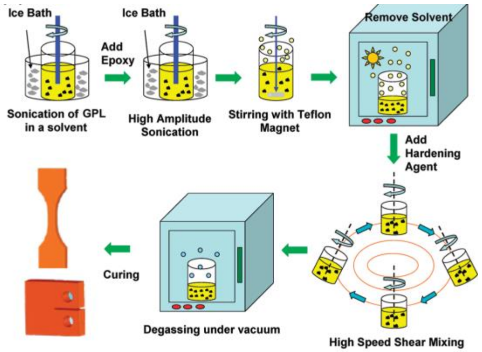
- Control of surface-polymer interactions
- Tune thermomechanical and electric/dielectric properties
- Use of nanofillers for tuning of electrical conductivity, toughness and durability
- Multiscale prediction and design of materials with known electric, dielectric and mechanical properties

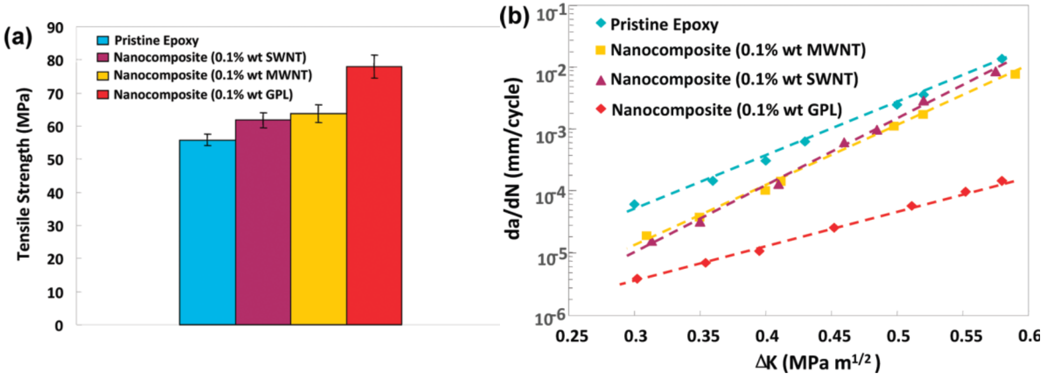


http://siag.project.ifi.uio.no/problems/grandine/Composites01.jpg

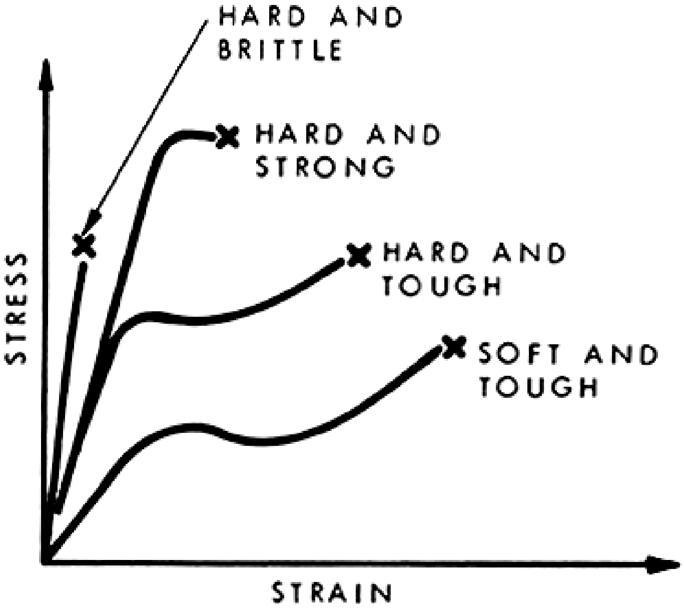
Challenges – processing, ageing, rejuvenation







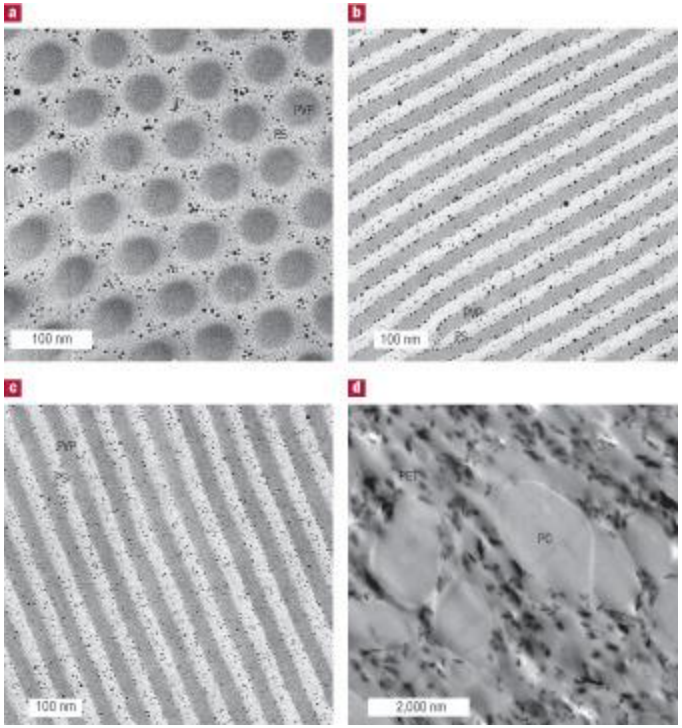
(a) Solution mixed graphene sheets in epoxy and Corresponding tensile strength (b) crack growth rate vs. stress intensity factor amplitude ΔK, from Rafiee et al., *ACS Nano*, 3, 3884 (2009)



Courtesy of Leon Govaerts, Eindhoven U.

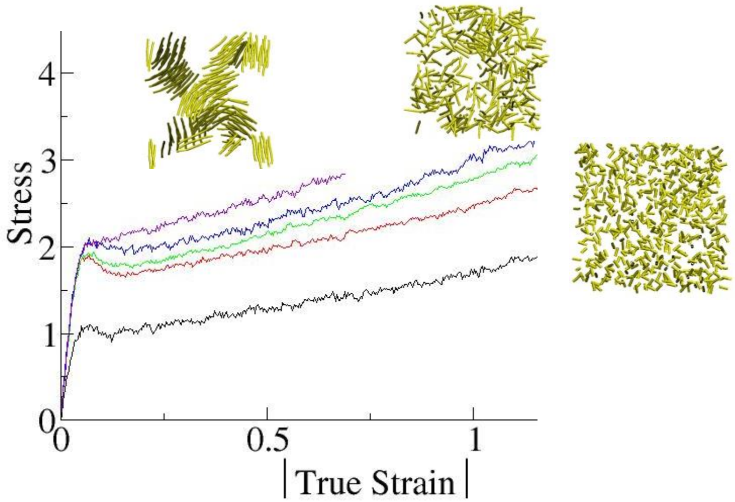
Superior Nanocomposites Through Rational Design

Control of Interfacial Energy

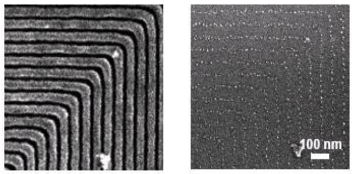


(a-c) Gold nanoparticles in PS-b-PVP
(d) Montmorillonite layered silicates selectively dispersed in the poly(ethylene terephthalate) domains of a poly(ethylene terephthalate)/polycarbonate blend

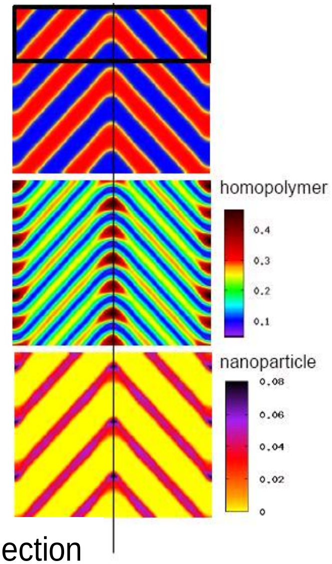
Manias, E., *Nat. Mat.,* 2007



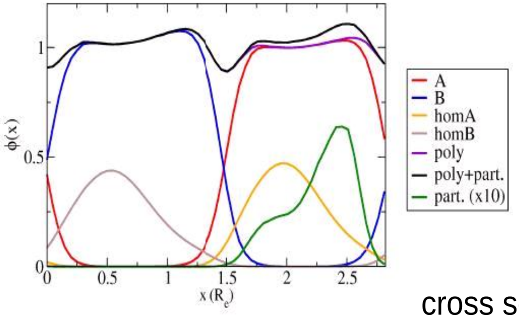
Experiments



Simulations



Density profiles - cross section

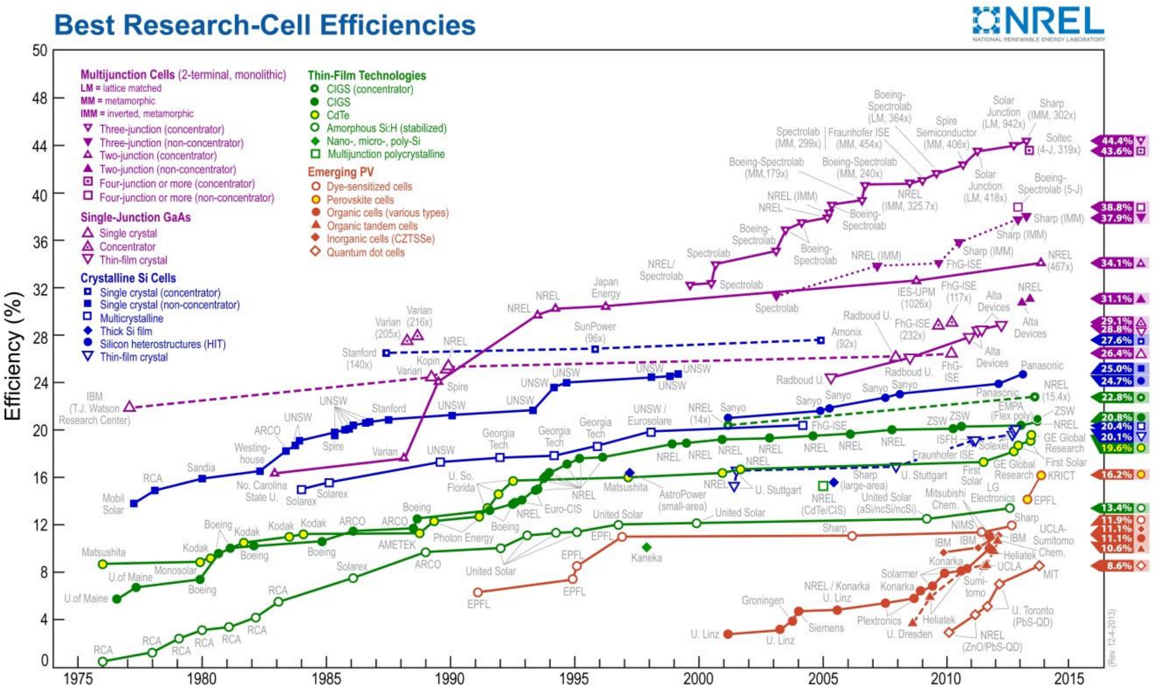


cross section

All-Polymer Organic Solar Cells

L. Yu (UC), J.J. de Pablo (UC), G. Galli (UC), M. Hersam (NU), H. Jaeger (UC), M. Olvera de la Cruz (NU)

MOTIVATION



Energy

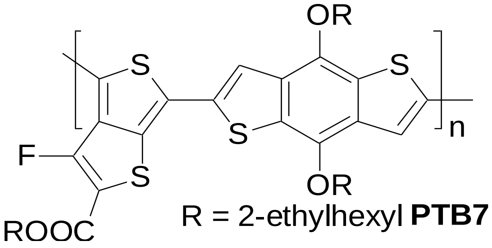
- **Inorganic solar cells currently exhibit higher efficiency**
- **Rapidly improving performance of organic cells**
- **Organic cells made from earth abundant materials, light weight, stable, processing, morphology optimization**

Initial Goals: Create all organic solar cells

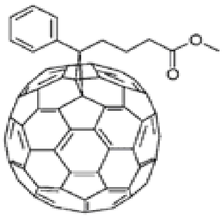
- Search for new design principles for electron accepting polymers
- Generate new materials with greater potential than fullerene derivatives as n-type materials
- Novel accepting polymers w. high mobility for organic electronics

Recent Collaborative Work on Solar Cells

Polymer solar cell materials.



R = 2-ethylhexyl **PTB7**



PC$_{71}$BM

Major conclusion:

Polarizing spectroscopy and GIXD experiments imply only very low content (≈20%) of crystalline donor polymer domains in the active layer of PTB7:PC71BM blend solar cells.

The polarizing spectroscopy experiments support the existence of a majority fraction of amorphous polymer.

Energy-filtered TEM indicated that the addition of DIO to the casting solvent (DCB) causes a decrease in the size-scale of the resulting interpenetrating BHJ structure.

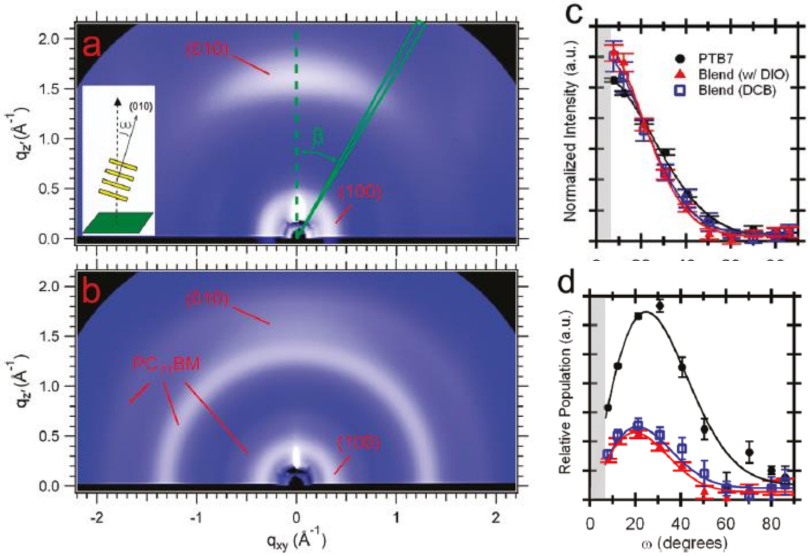


Figure 2. GIXD detector images for (a) neat PTB7 and (b) PTB7:PC$_{71}$BM blend (with DIO) films. Note that the intensity (color) scales for the two images are not the same, and the vertical axes are labeled $q_{z'}$ to reflect the fact that the scattering vector measured along the detector meridian ($q_{xy} \approx 0$) is not exactly parallel to the sample z-direction. The detector angle β is not equivalent to the polar angle ω (diagrammed in the inset). (c) Pole figures for the (010) reflection for neat PTB7 (black circles) and for PTB7:PC$_{71}$BM blend films prepared with (red triangles) and without (blue squares) DIO processing additive. The error bars are calculated from the estimated standard deviations from the peak fitting coefficients. The data are normalized by the total scattered intensity for each given sample. (d) Geometrically corrected orientation distribution functions (symbols the same as in (c)). The data are scaled by the film thickness, beam path length, and polymer volume fraction, showing that the neat film has significantly higher crystalline content relative to the blend films.

Matthew R. Hammond, **R. Joseph Kline**, Andrew A. Herzing, Lee J. Richter, David S. Germack, Hyun-Wook Ro, **Christopher L. Soles**, Daniel A. Fischer, Tao Xu, **Luping Yu**, Michael F. Toney, and **Dean M. DeLongchamp**, *ACS Nano*, **5**, 8248–8257, (2011).
Red: NIST Scientists

Search for Design Principles of Electron Accepting Polymers for All-Polymer Solar Cells

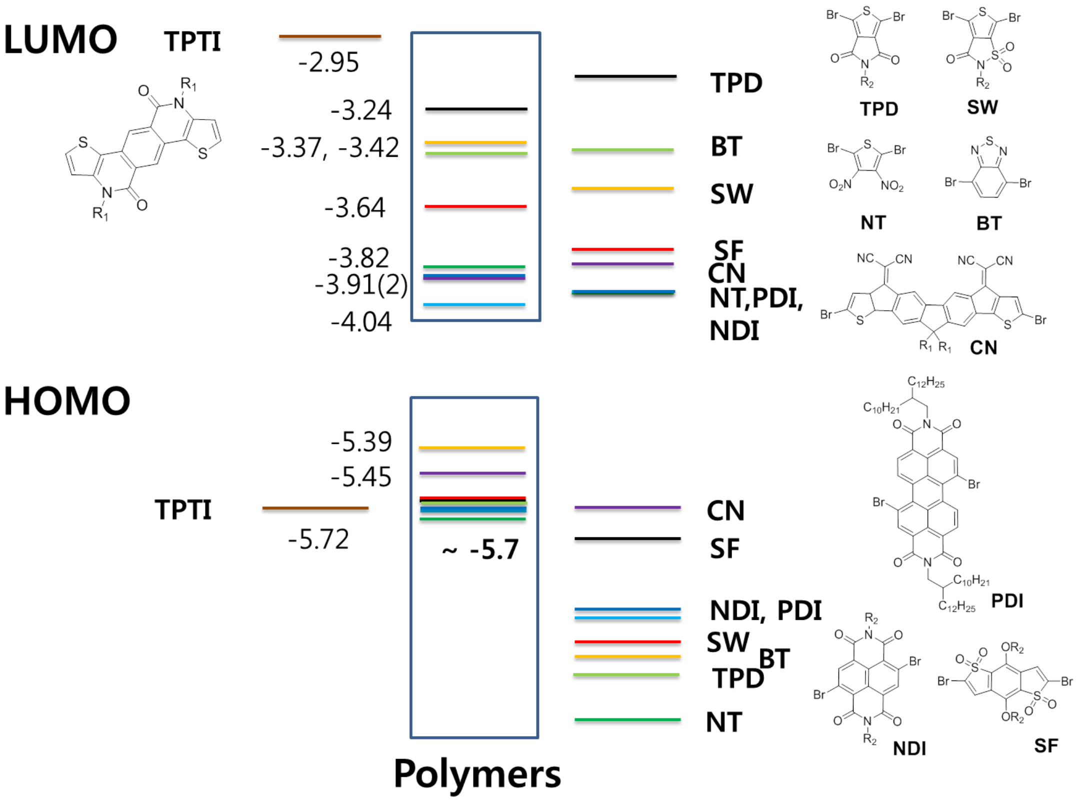
Accepting polymer architectures:

a). Strong acceptor-weak donor, (SA-WD).

b). Strong acceptor-weak acceptor, (SA-WA).

c). Strong acceptor-strong donor, (SA-SD).

Control energy levels of n-types of polymers via proper monomer design and combination

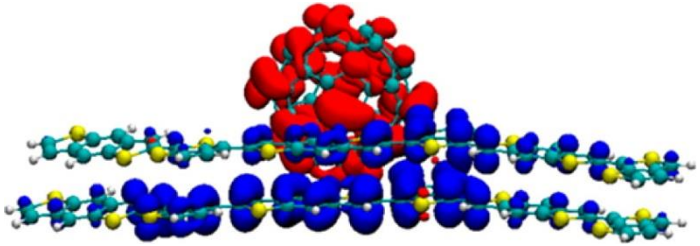


Preliminary discovery:

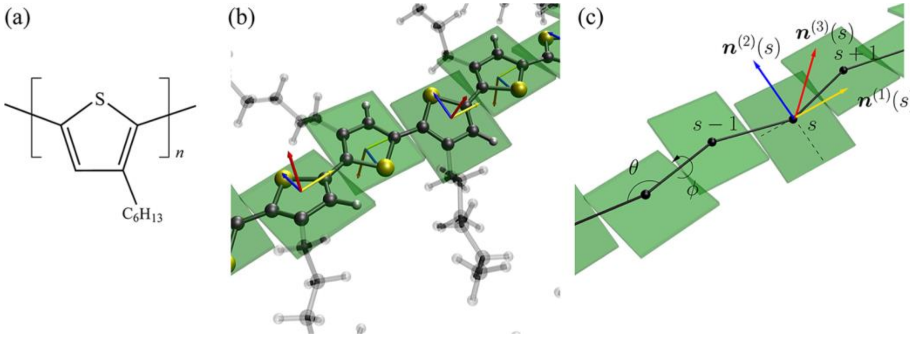
- To control the energy levels and at the same time introduce internal polarization, a weak acceptor-strong acceptor monomer combination is desirable (Red colored).
- LUMO energy levels of the electron accepting polymers are determined by those of stronger electron accepting monomers and the HOMOs are largely decided by the weak accepting (or donating) monomers.
- Internal polarization is important for OPV application.
- high SCLC mobility is crucial to achieve high PCE and polymer backbones with high planarity is thus desired.
- unipolar charge transport is required for solar cell materials.

Materials Design

(1)

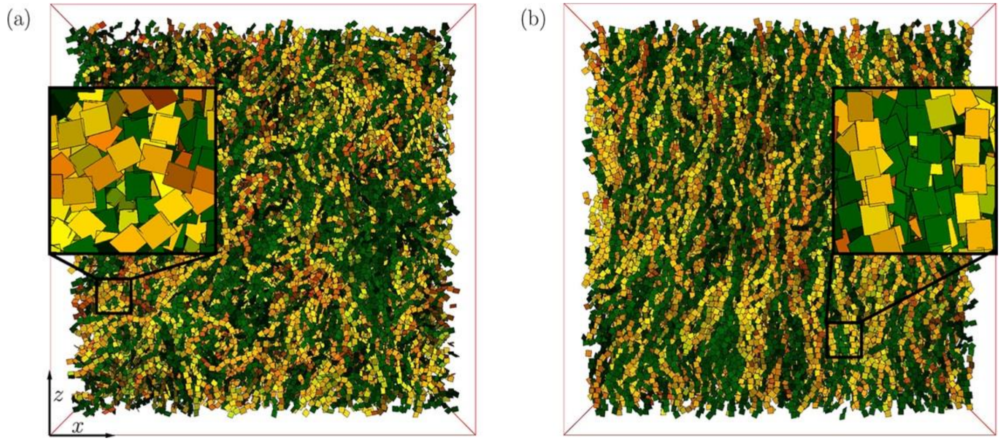


DFT – charge transfer
MC, MD – short-range structure



TICG
Mesoscale structure
External fields

(2)



(1) Borges et al., *J. Am. Chem. Soc.* **2013,** 135, 18252-18255.
(2) Gemuenden et al., *Macromol.*, **2013**, 46, 5762-5774.

Self-Assembly of Biomaterials

M. Tirrell (UC), J.J. de Pablo (UC), E. Luijten (NU), M. Olvera de la Cruz (NU), L. Yu (UC)

MOTIVATION

Military

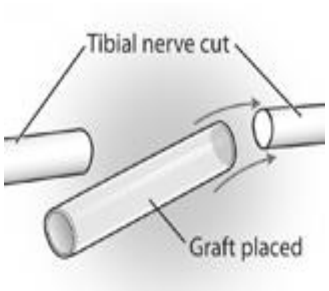
- **Improvised explosive devices (IEDs) cause severe blast and tissue loss injuries**
- **Improved body armor has improved survival rates and increased frequency of injury to limbs/digits**

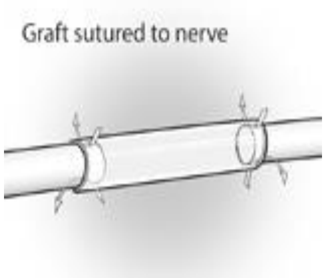
Civilians

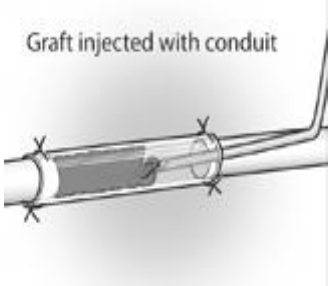
- **2.8% of trauma patients have peripheral nerve damage**
- **Nerve injury costs $7 billion dollars in the US alone**
- **50,000 nerve repair procedures per year**

Initial Goals: Create a self assembled matrix

- Injectable
- In situ gel formation
- Stiffness in range of neural tissue
- Promote growth and activity of Schwann cells





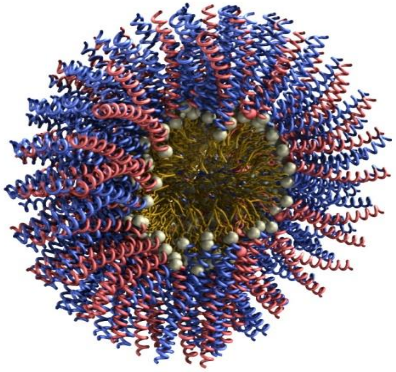


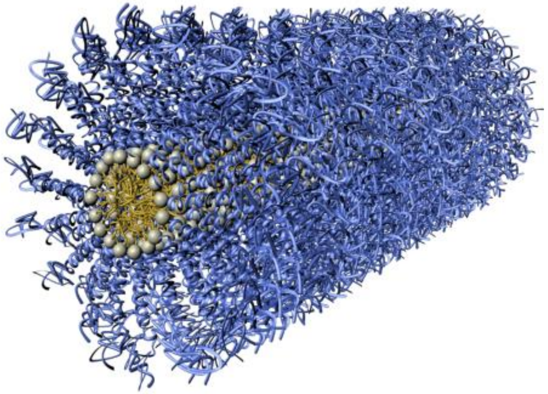
Self-Assembly of Biomaterials

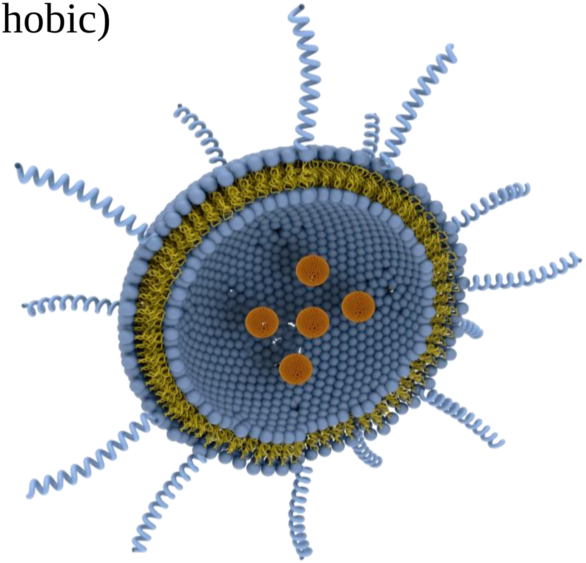
M. Tirrell (UC), J.J. de Pablo (UC), H. Jaeger (UC), E. Luijten (NU), M. Olvera de la Cruz (NU), L. Yu (UC)

Peptide Headgroup (hydrophilic)

Fatty Acid Tail (hydrophobic)





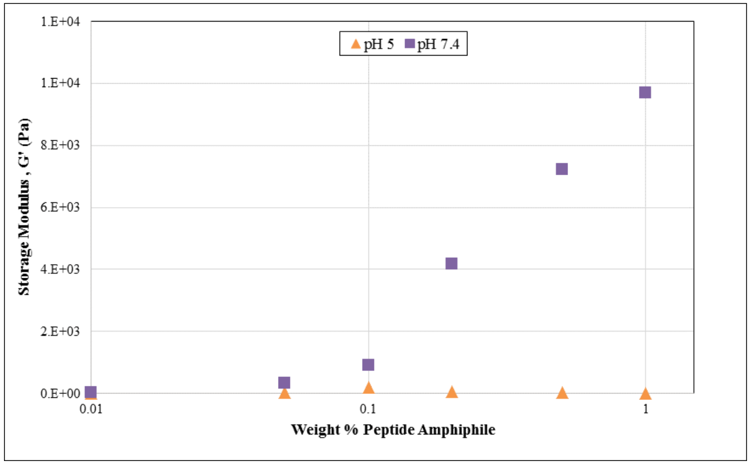


Tirrell, Kokkoli & Biesalski. *Surface Science*, 2002.

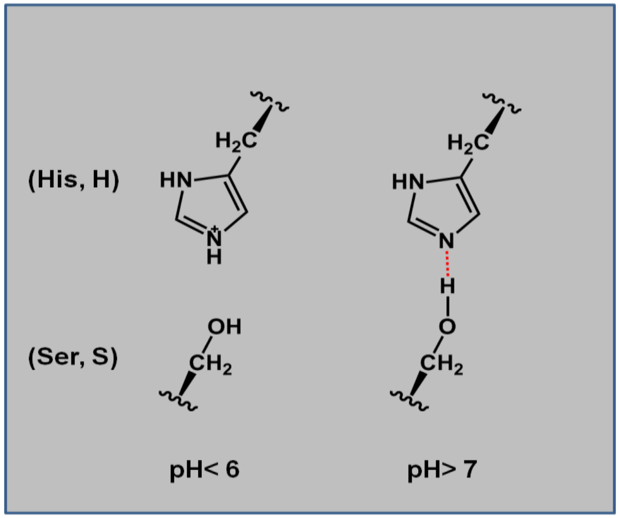
Peptide Amphiphile Design: C_{16}GSH

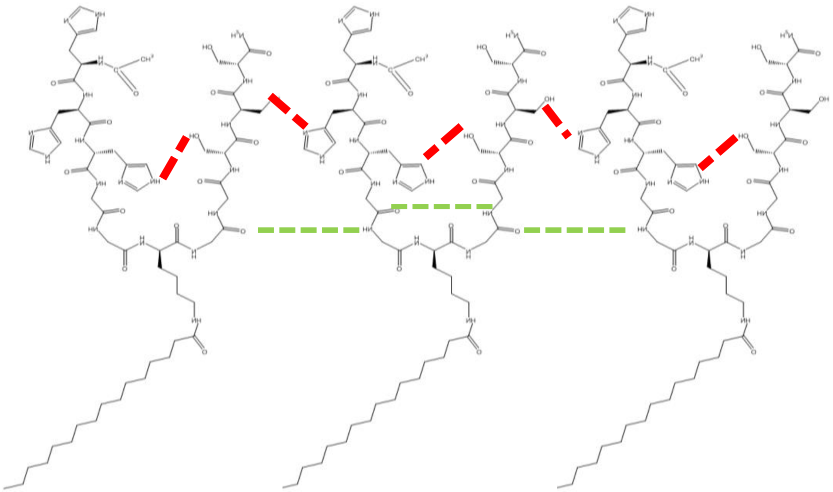
Liquid

Gel



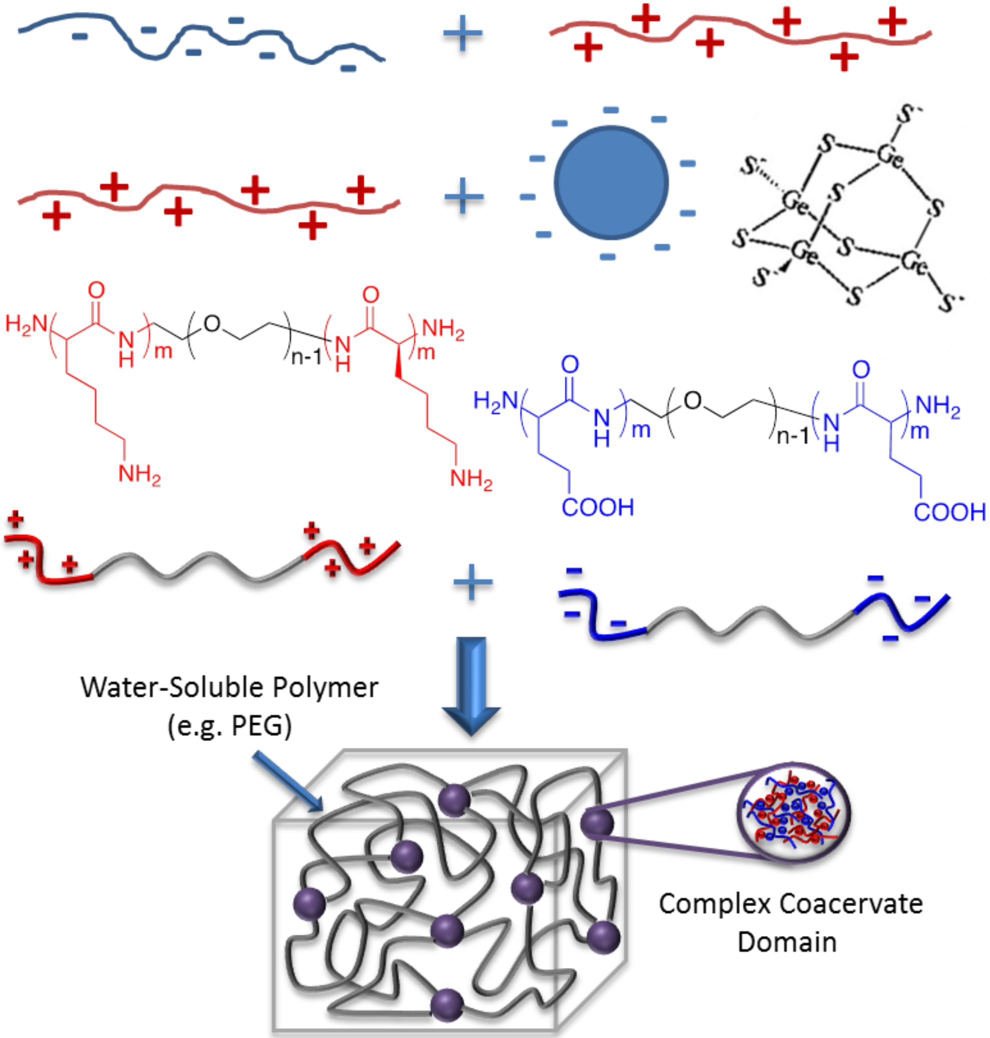
Lateral H-bonding gives physical gelation

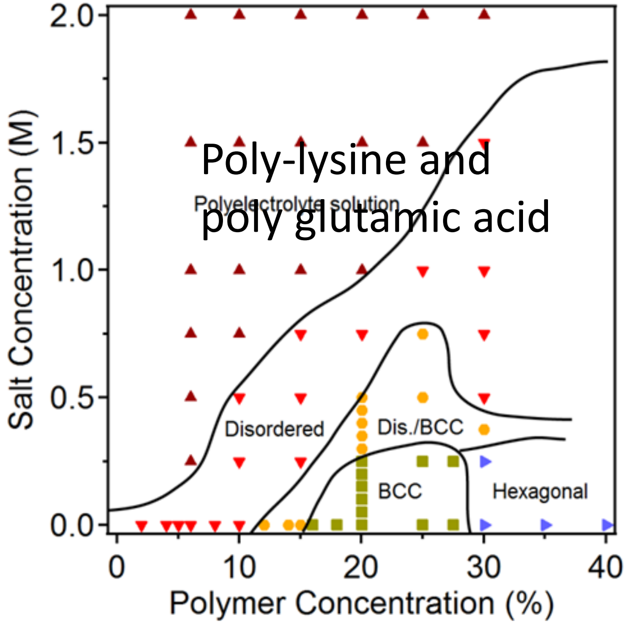




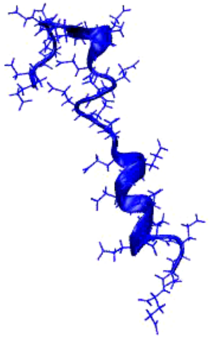
Lin, **Megley**, Viswanathan, Krogstad, Drews, Kade, Qian, & Tirrell. *J. Mater. Chem.*, 2012.

Complex Coacervation in Biomaterials





Poly-lysine and poly glutamic acid

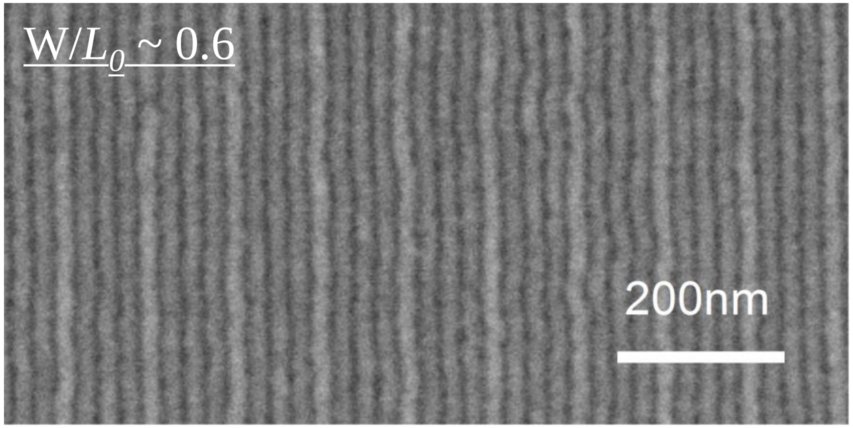


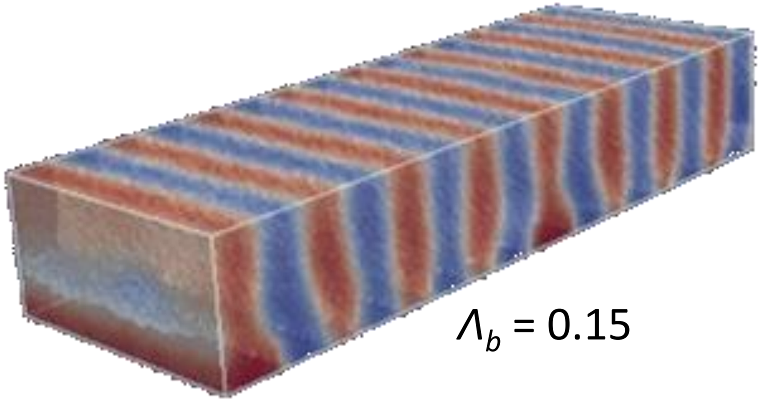
Tools

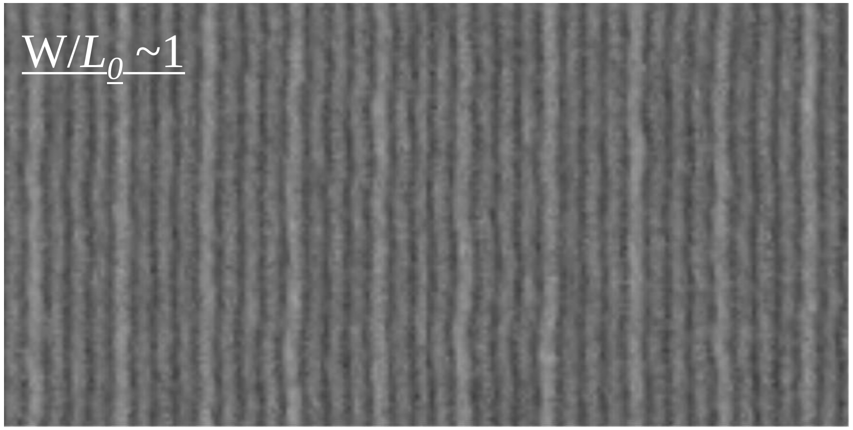
Characterization – GISAXS

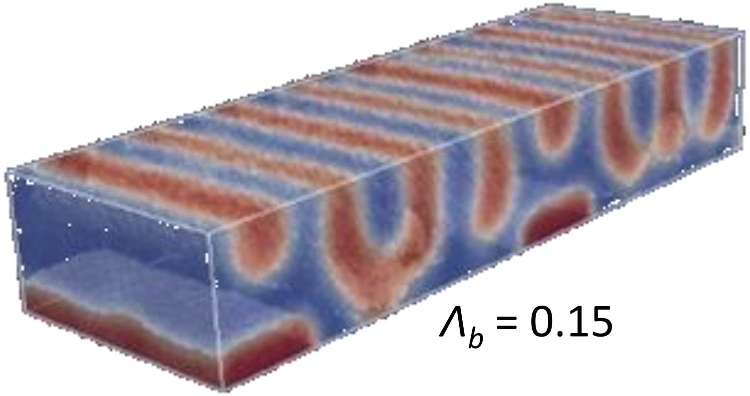
Nealey, Foster, de Pablo, Vorhees, Bedzyk

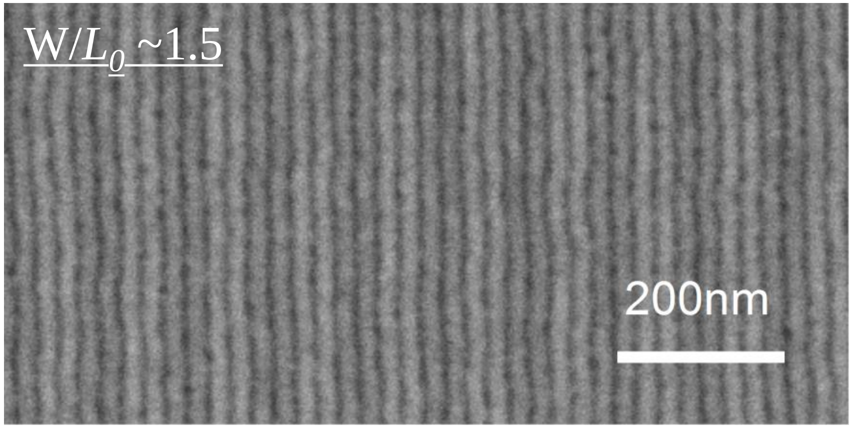
Top-down vs cross-sectional structures for 4X multiplication

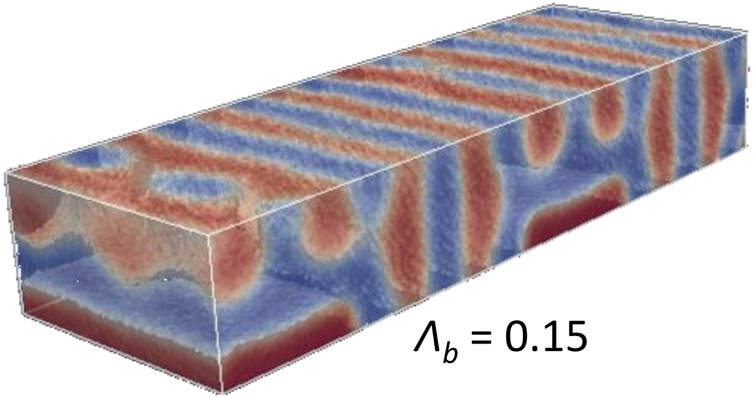






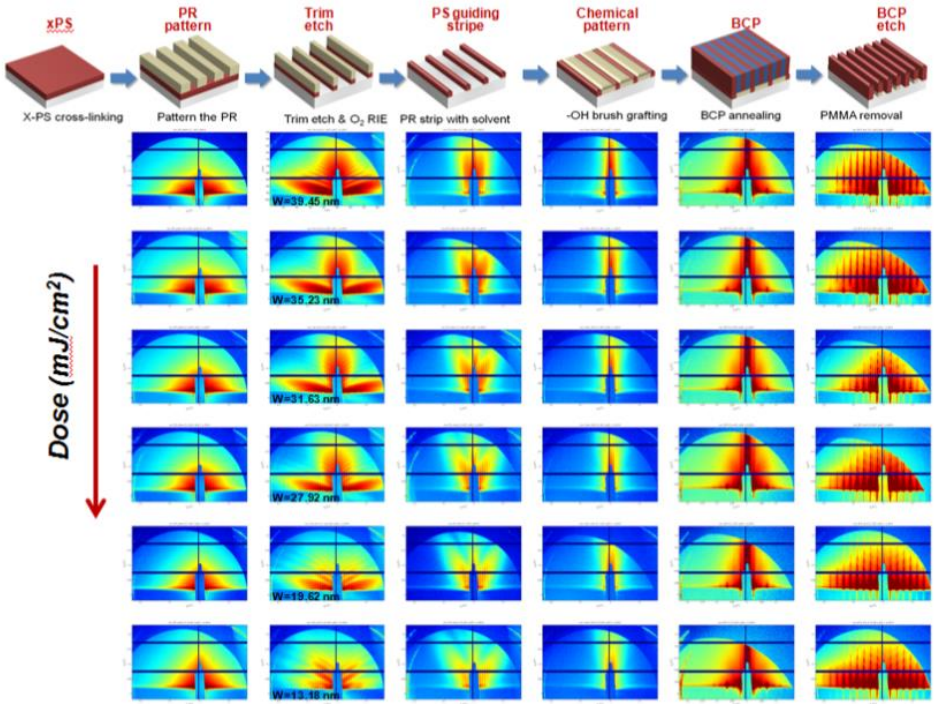




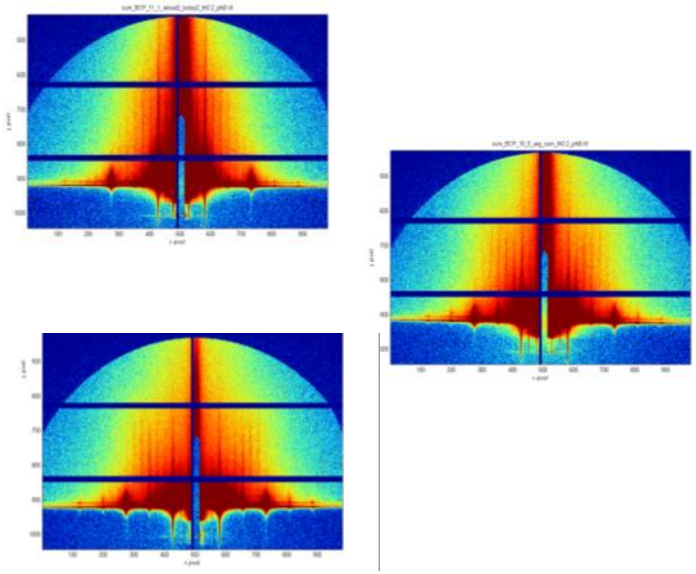


Vision of Integrated Analysis Loop

GISAXS data

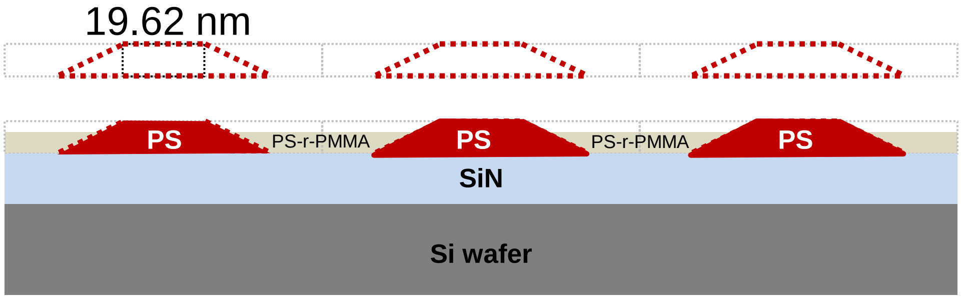


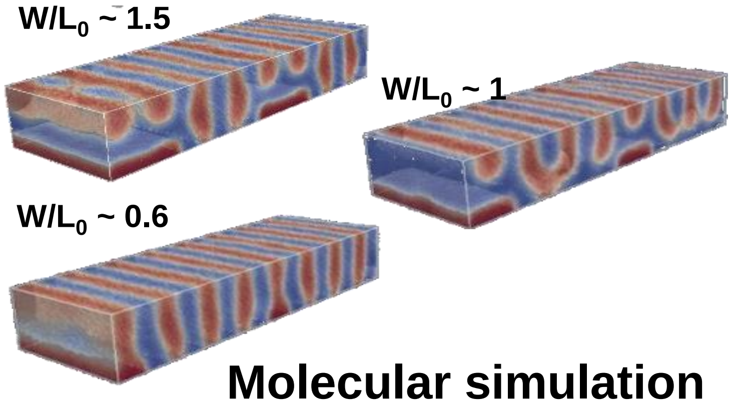
GISAXS from BCP



Form factor and structural factor to generate GISAXS pattern

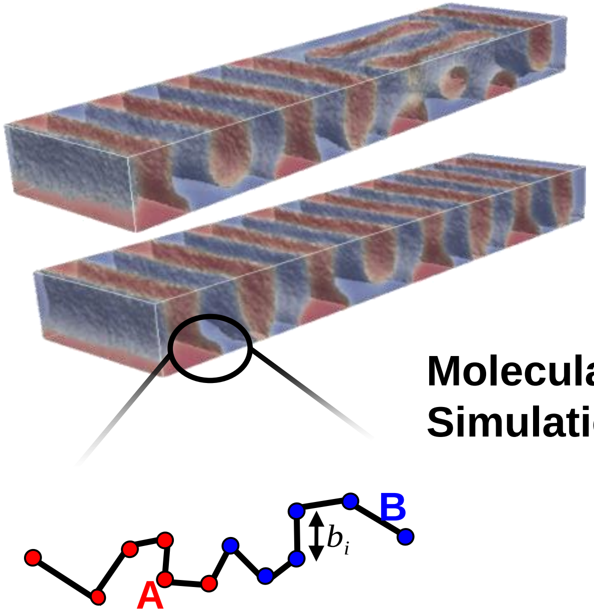
Boundary conditions for DSA



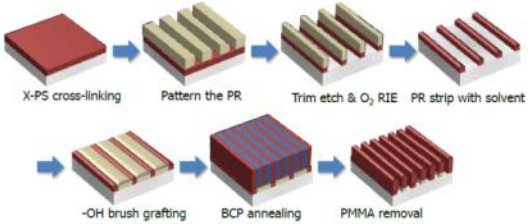


Molecular simulation

Leveraged Resources for 3D Characterization of DSA at ANL



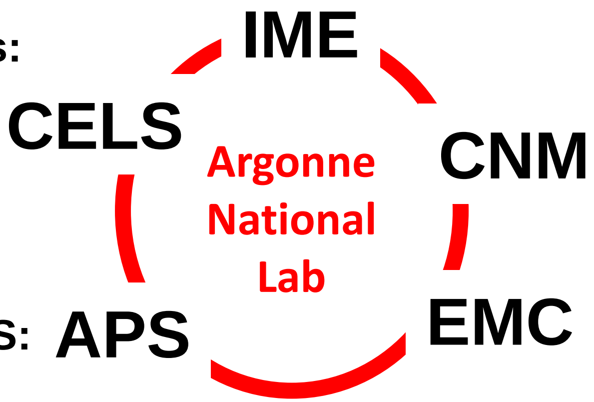
Molecular Simulations:



IME - Directed Assembly:

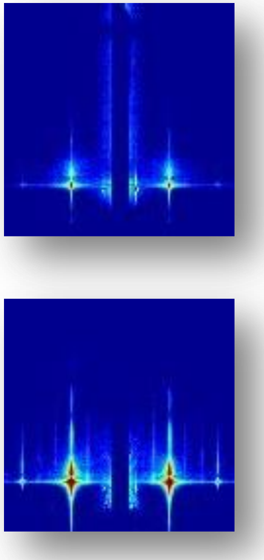
CNM – Nanofabrication:

- Electron Beam Lithography System
- RIE Oxford PlasmaLab 100
- Atomic Layer Deposition



APS - GI-SAXS:

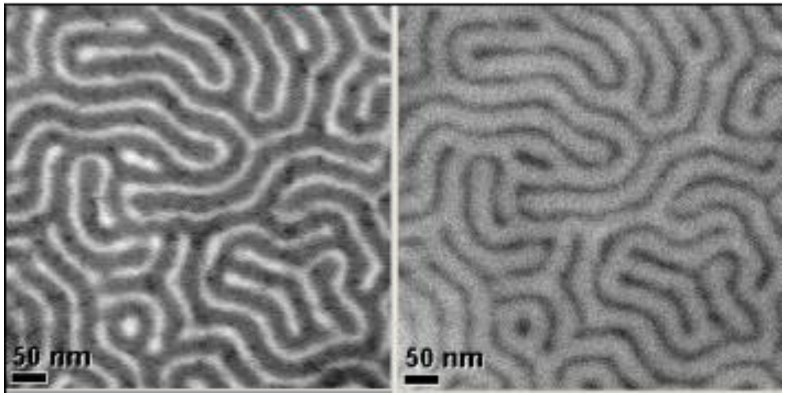
RoSXS



Sector 8, GISAXS, Sector 29, RSoXS

EMC - TEM tomography:

Energy-filtered TEM



Tools

Theoretically Informed Coarse Grained (TICG) Environment

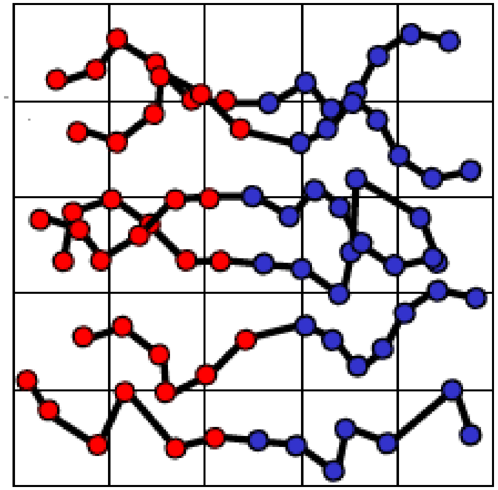
De Pablo, Olvera, Jaeger

TICG METHODS

A fully functional, scalable, general purpose TICG tool for equilibrium and non-equilibrium assembly of structured fluids, including polymers, composites, liquid crystals, etc.

- **Fluctuations**
- **Free boundaries**
- **Swelling**
- **Particles**
- **Charges**
- **Dynamics** →
- **Flows**

Monte Carlo simulations

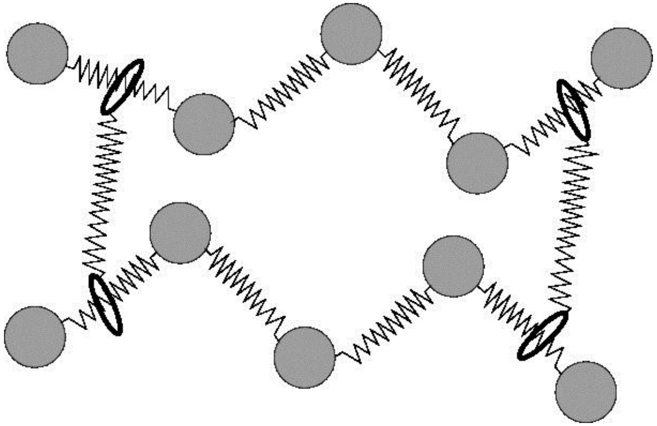


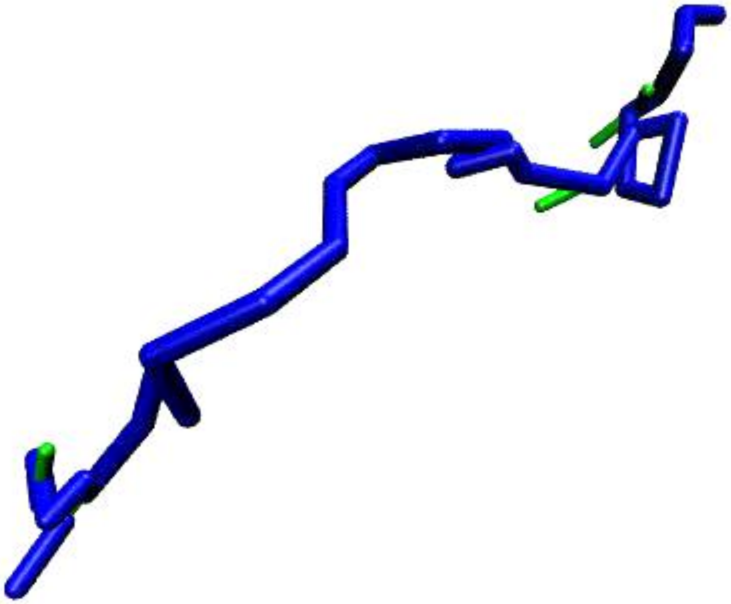
- particle-based
- includes fluctuations
- no fields:
  the local densities and energy are functions of the bead's positions
  traditional MC simulation

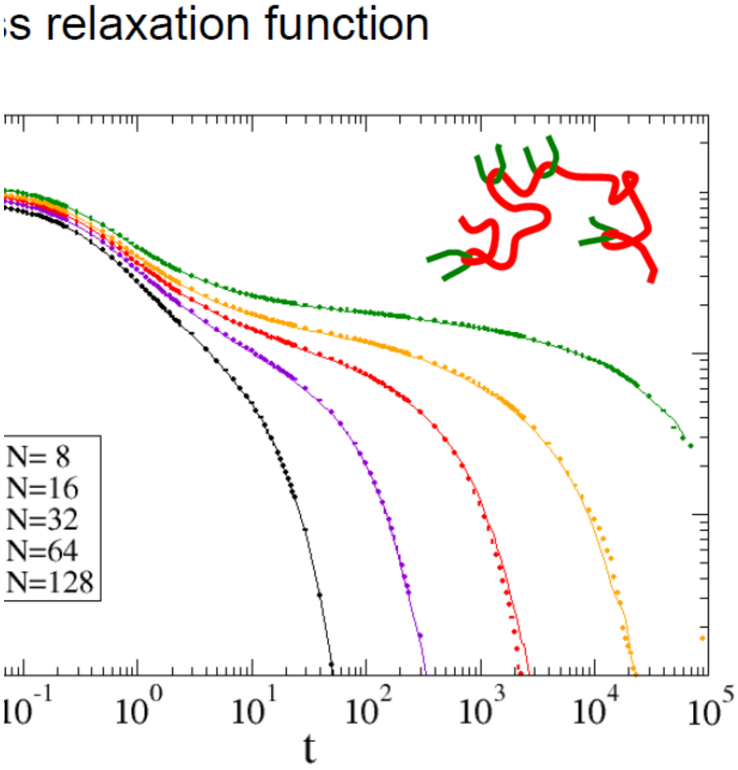
CHALLENGES – Dynamics

- Dynamics of structure formation
- Entanglements via slip-links
- Defects

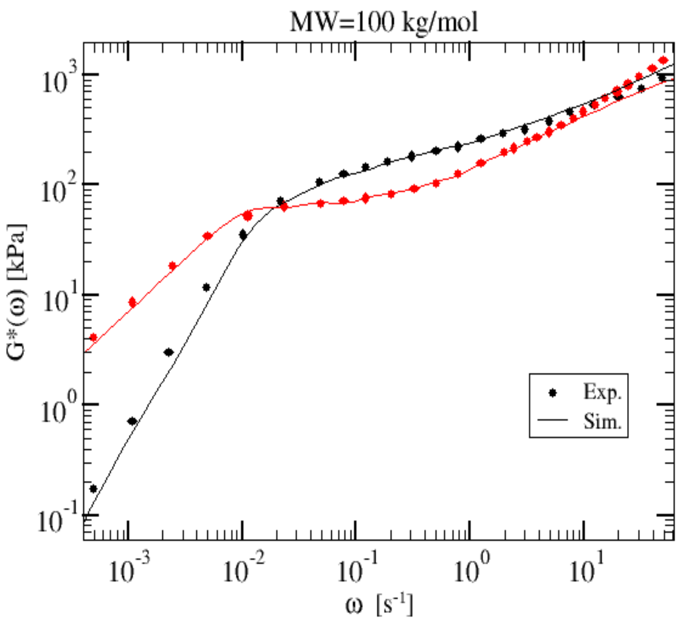
Ramirez, Mueller, de Pablo, *Soft Matter*, 2012

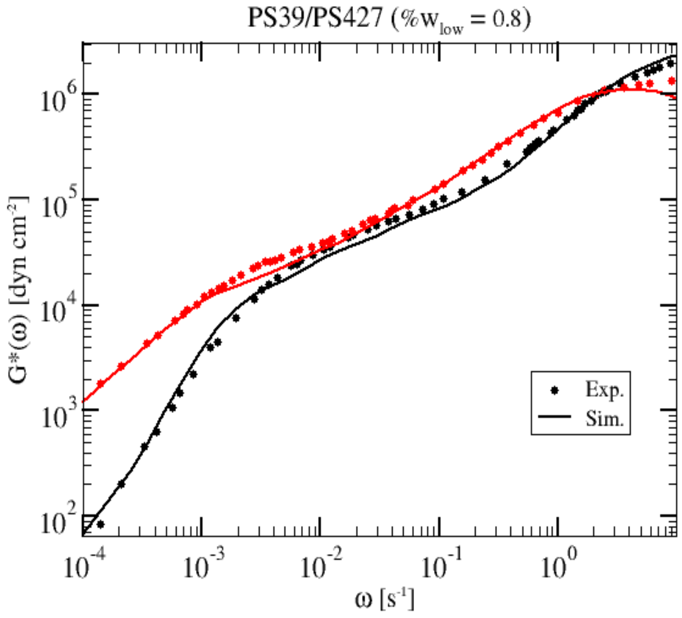




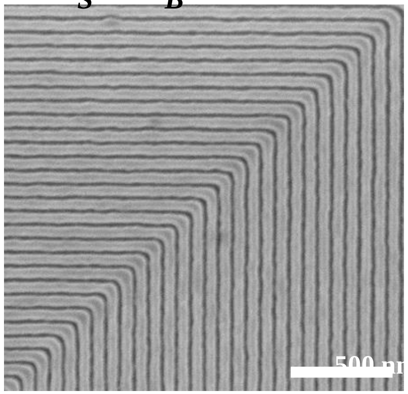


Monodisperse & Bidisperse Polystyrene Blends





$L_S = L_B = 70$ nm

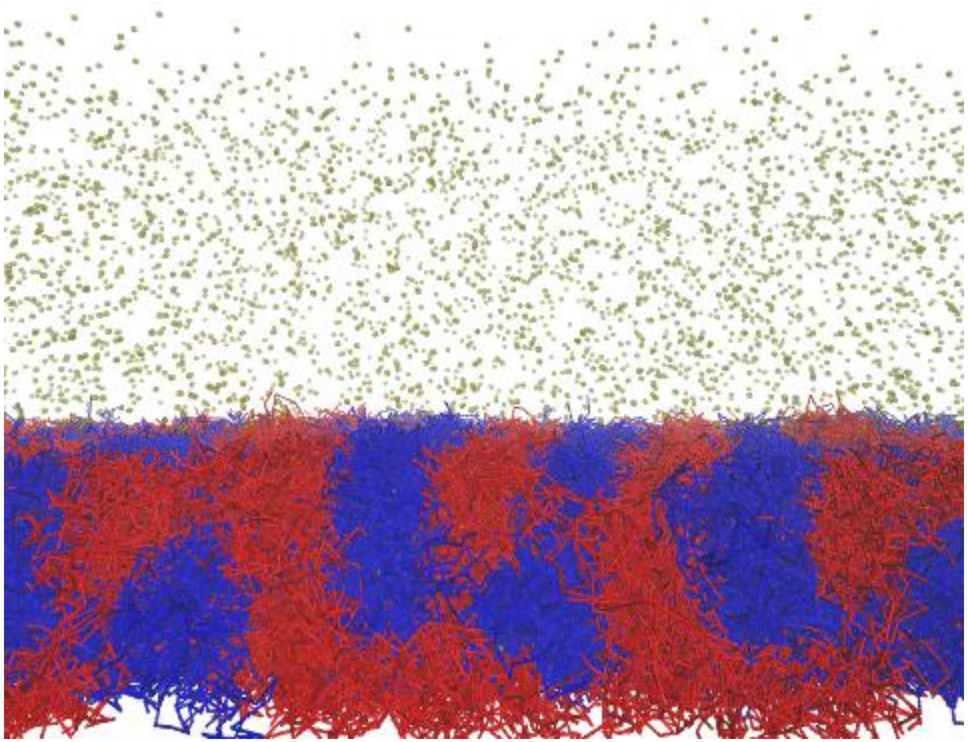


Data taken from:
J. K. Nielsen, H. K. Rasmussen, O. Hassager, G. H. McKinley, *J. Rheol.* ***50***, 453 (2006).

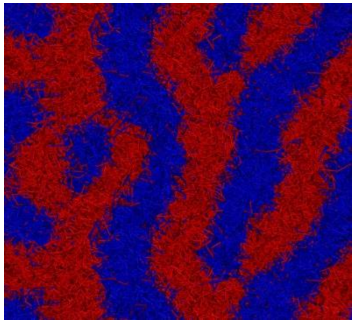
Data taken from:
H. Watanabe and T. Kotaka, *Macromolecules* ***17***, 2316 (1984).

CHALLENGES: Solvent Annealing

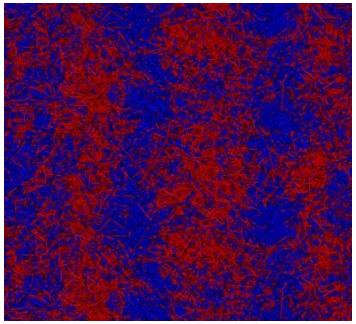
- The Model is able to mimic the experimental solvent annealing procedure
- Defects in self assembly after spin coating are removed by the exposure to solvent vapor



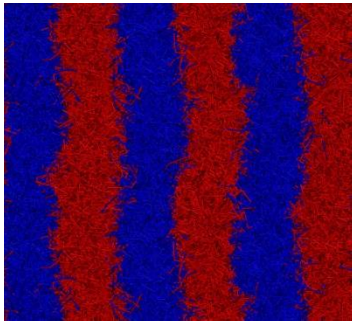
After Spin Coating



After Film Swelling



After Solvent Evaporation



Tools

Evolutionary Strategies

Jaeger, de Pablo, Foster, Olvera de la Cruz

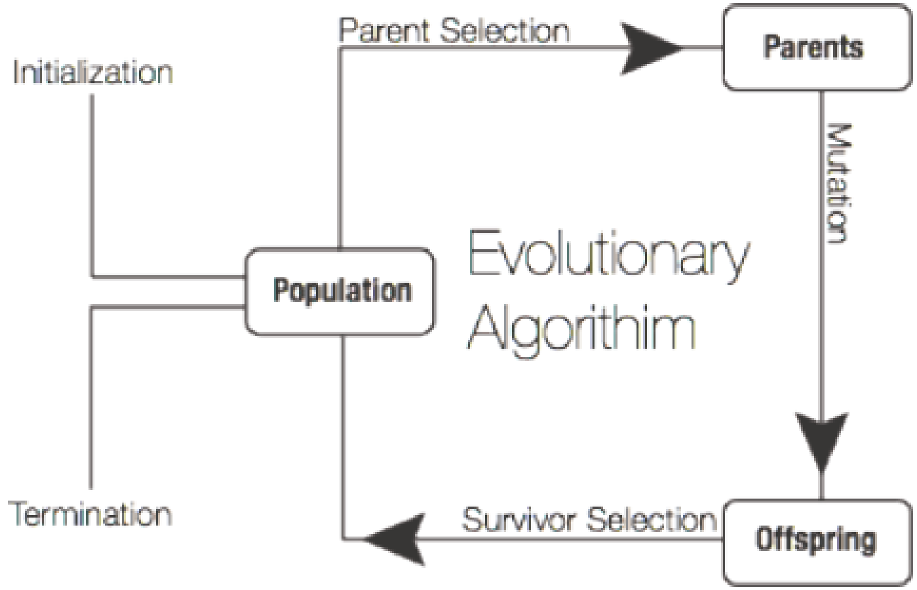
Optimization via Evolutionary Strategies

- **Far from equilibrium assembly**
  - difficult
  - no established pathways
  - processing conditions often as important as materials details
- **Result**: “Materials by design” is not possible because there is no clean way to go from design goals to specific composition or processing conditions → trial and error search for solutions
- **Need:** Multi-parameter optimization engine that can find optima in high-dimensional search spaces efficiently, without need for detailed first-principles knowledge of underlying physics and chemistry
- **Approach:** State-of-the-art evolutionary algorithms to find optimal materials composition and processing conditions

Optimization via Evolutionary Strategies

Artificial evolution is a search & optimization process that **does not** require a priori knowledge of the system

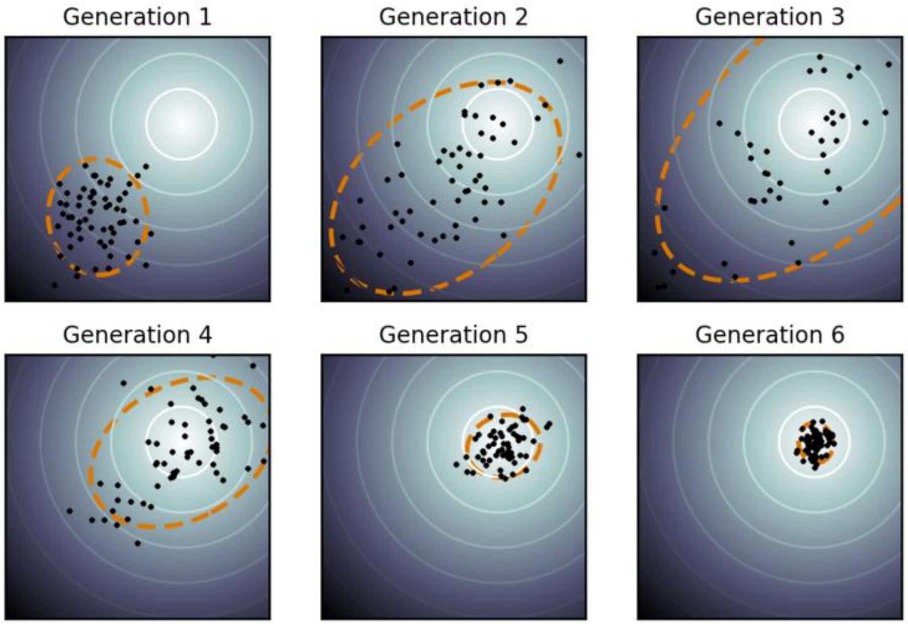
Modern evol. strategies are much more powerful than the genetic algorithms of old

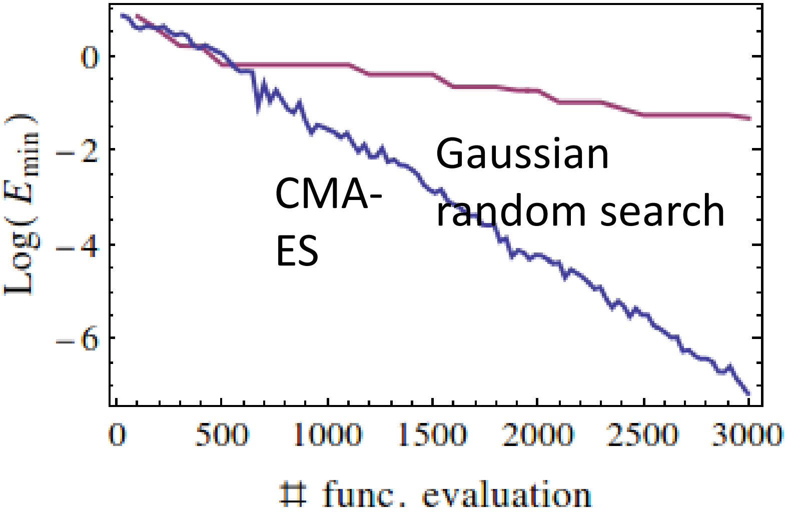


'Black Box' approach, requires only 2 ingredients:

- A way to evaluate if one object is better than another = a **fitness metric**
- A mutatable representation of the structure to be optimized = a **genome**

Pattern Optimization: Evolution Strategy





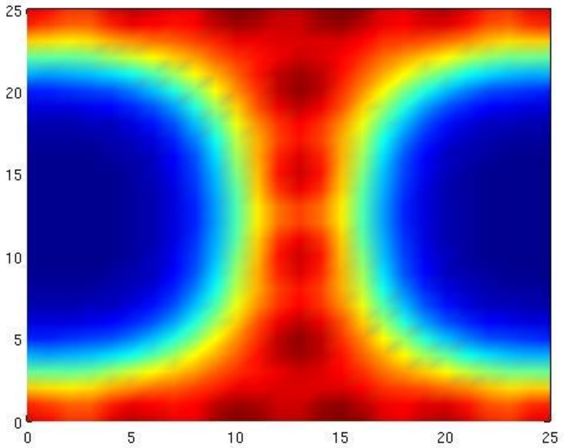
(Test function: 5-d Ackley)

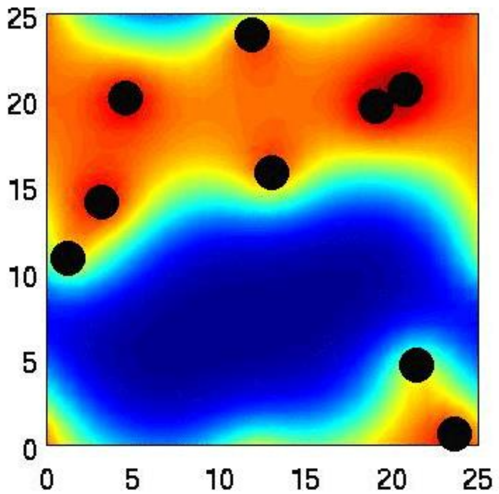
- Evolution strategy (ES) is a generic optimization technique
- Correlated noise is used in a covariance matrix adaptation (CMA) scheme to update a sample population
- Finite population size enables efficient landscape exploration
- No derivative of fitness function is needed

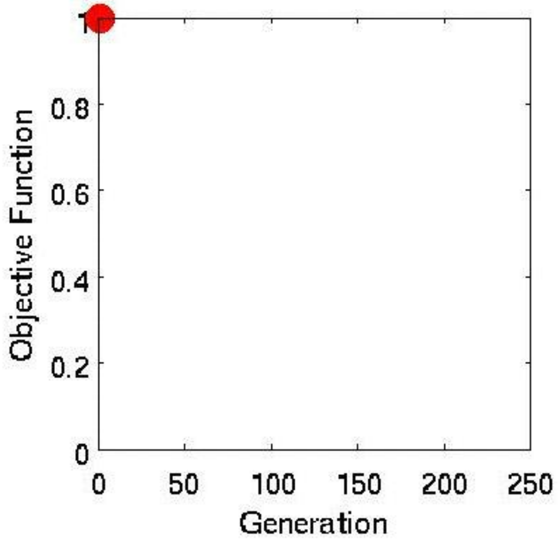
Hansen & Mueller et al., *Evol. Comput.*, 11:1-18, 2003
Eiben & Smith, *Introduction to evolutionary computing*, Springer, 2003

Evolution Towards Known Morphology

Target Morphology and Necessary Underlying Surface Pattern





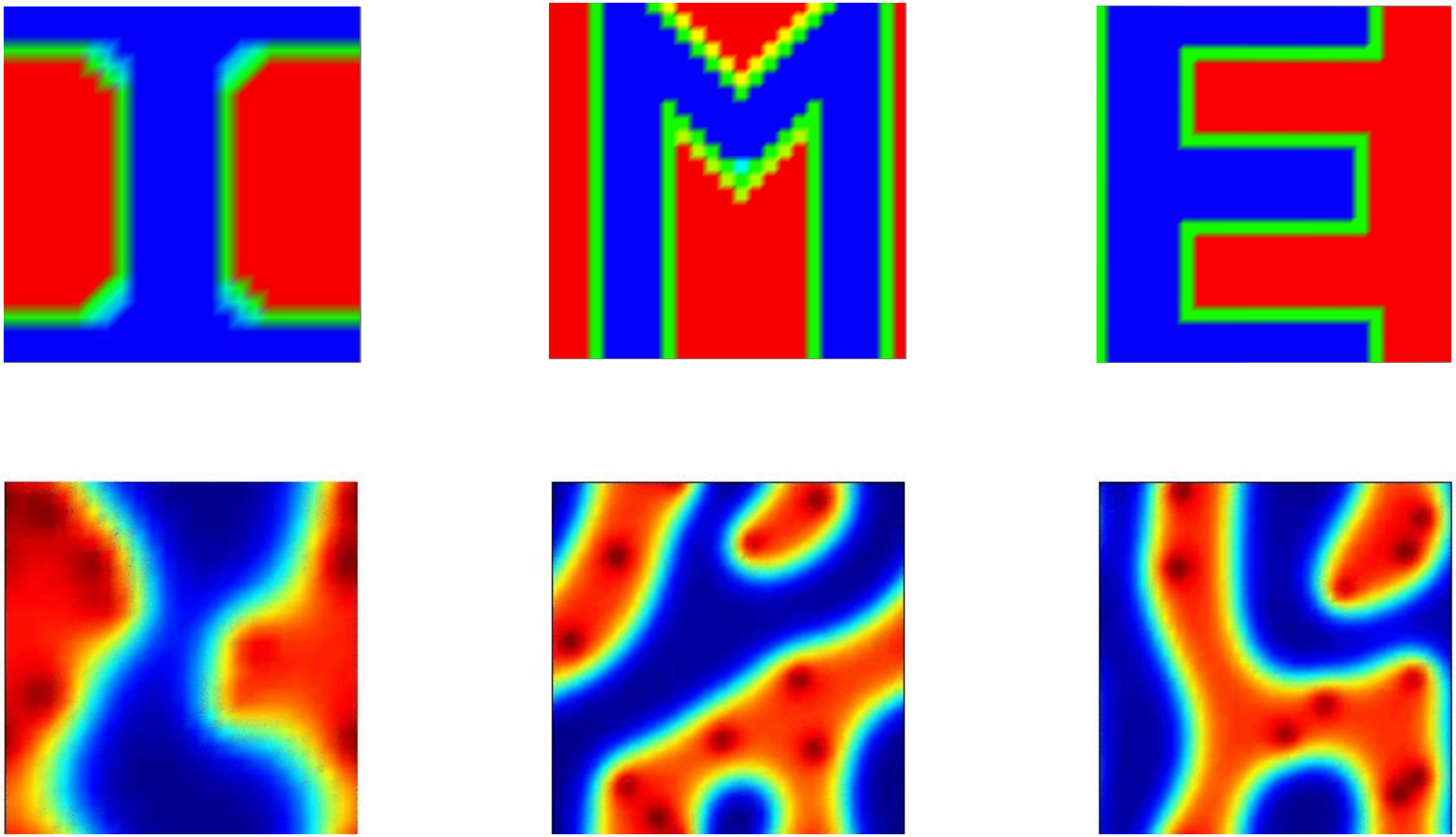


- Target morphology generated from a solution of the C-H equation using surface spots with lamella forming block copolymer

- 9 spots arranged in a periodic box to make an "I" shape

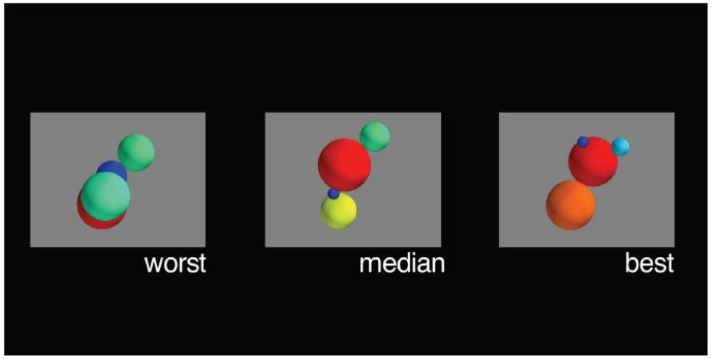
- Objective function is the difference between the target morphology and a current structure

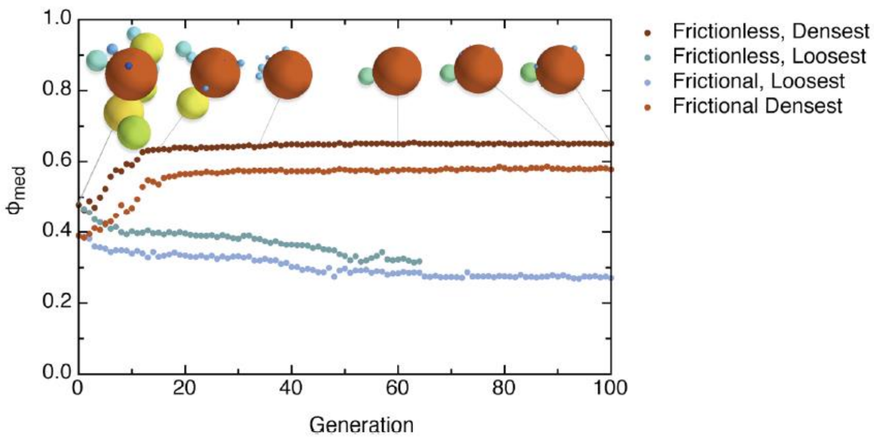
More Examples...



Example 1

Find shape of ‘granular molecule’ that produces densest packing when poured into container under gravity

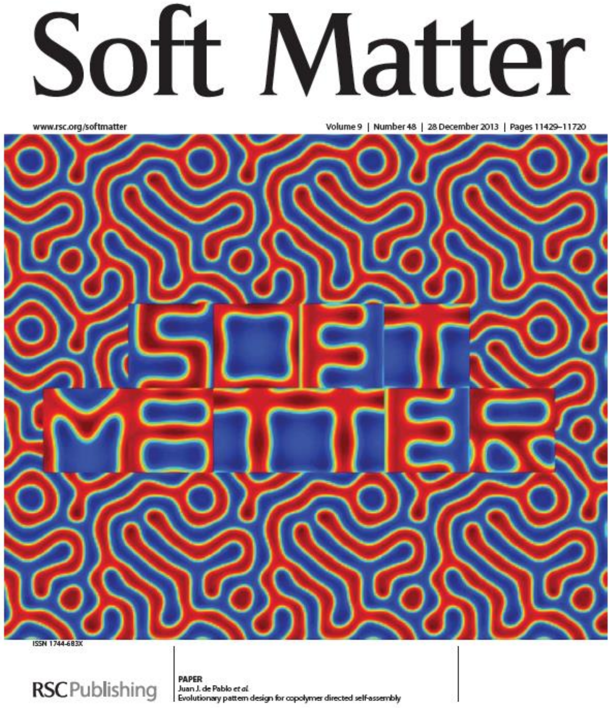




M. Miskin, H. Jaeger, *Nature Materials* **12** (2013) & in prep.

Example 2

Find minimal number, and their spatial placement, of anchoring points to direct copolymer self-assembly into specified pattern



Soft Matter

www.rsc.org/softmatter Volume 9 | Number 48 | 28 December 2013 | Pages 11429–11720

ISSN 1744-683X

RSC Publishing

PAPER
Juan J. de Pablo *et al.*
Evolutionary pattern design for copolymer directed self-assembly

J. Qin, H. Jaeger, J. de Pablo, et al., *Soft Matter* **9** (2013)