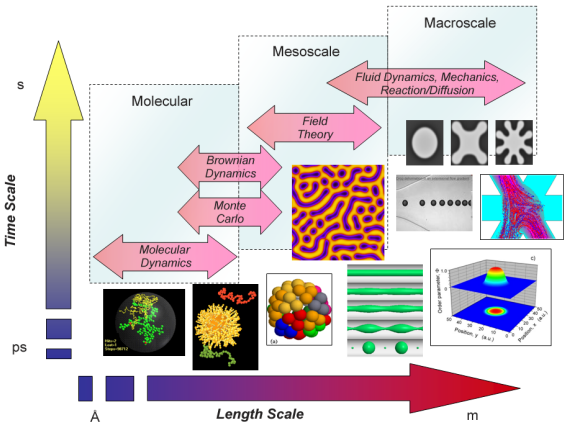
Theory, Modeling, and Simulation

The Polymers Division develops and utilizes theoretical, computational, and conceptual tools to enable the prediction and/or explanation of phenomena relevant to polymer science measurement research. These efforts enable U.S. innovation and industrial competitiveness by advancing polymer measurement science, standards, and technology.

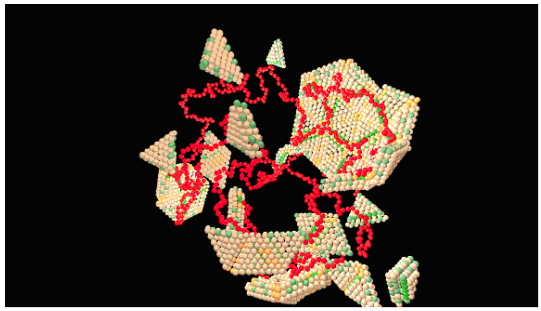


Length and time scales in polymer science.

The methodology used for any given research problem is determined by the spatiotemporal scales of interest. The Theory, Modeling, and Simulation research efforts in the Division span the entire spatiotemporal spectrum relevant to polymer science: Molecular Scale, Mesoscale, and Macroscale.

Molecular Scale

Molecular Dynamics—Molecular Dynamics (MD) simulations are a powerful class of simulations widely used to explore behavior centering on the molecular length scale. MD simulations are unique in that they provide a detailed picture of the dynamics of single molecules as well as groups of molecules. Such a detailed description of molecular motion is essential to providing important insights into physical behavior observable at larger length scales. Current MD projects in the Polymers Division span the entire range of length and time scale typically accessible through MD simulations, from quantum-atomistic (QM) to supramolecular (coarse-grained). While MD simulations demand significant computational resources, they typically require a minimum of simplifying assumptions and conditions, and therefore serve as an ideal complement to analytical and numerical approaches.



Snapshot from MD simulation of virus self-assembly.

Current MD projects under investigation in the Division include a study of glassy dynamics of trehalose-sucrose carbohydrate glasses and the mechanism of protein preservation; the effect of configurational entropy on the association of macromolecules; the competitive binding of molecules to surface-grafted nanoparticles; and the morphology of polymer films of block-copolymers as a function of substrate surface topology.

Path-Integral Methods—The computation of the transport properties of polymers is a classical problem in polymer science, but many problems remain open due to the absence of sufficiently powerful analytical, and even numerical techniques. Although the mathematical problems are often relatively easy to formulate, the solution of these problem is extremely challenging, and requires cutting edge mathematical and numerical methods.

Many transport properties can be effectively calculated with high accuracy by first casting the boundary value problem formally in terms of path integration, and then implementing a numerical solution through the Monte Carlo generation of random-walk paths, and the evaluation of functions evaluated along these paths. This computational method has been applied to the problems of calculating the electrostatic capacity C, diffusion-limited rate constant, electric polarizability tensor α, translational friction coefficient f, and the intrinsic viscosity $[\eta]$ for ideal shapes to test computational accuracy; the method was then applied to polymer and complex-shaped aggregates.

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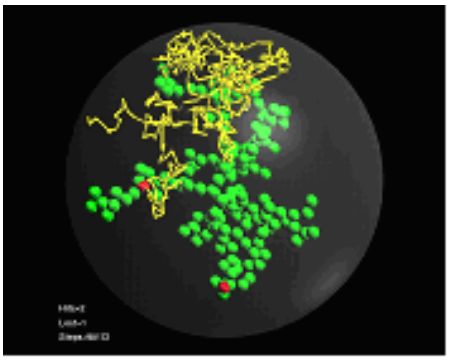


Collection of spheres (green) represents a model branched polymer, and the path (yellow) represents a probing random-walk trajectory. C is determined by the fraction of trajectories that hit the sphere.

Computation of dimensionless ratios of these properties is very promising for the quantification of the shape and topology of complex-shaped objects (e.g., knot type, genus number of surface, determination of surface curvature, etc.). There are many further applications of these energy functions to the properties of dilute particle dispersions and to scattering measurements: virial coefficients for thermal and electrical conductivity, dielectric constant and refractive index, magnetic permeability, and far-field scattering lengths in acoustic and light scattering.

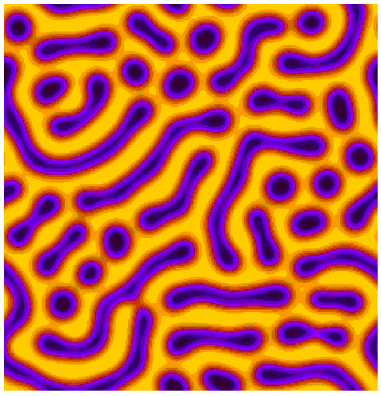
Recent work in the Polymers Division has emphasized the computation of the friction coefficient and intrinsic viscosity of carbon nanotubes, modeled both as rigid rods and conformationally flexible worm-like cylinders.

Selected References J.F. Douglas, H.-X. Zhou, J.B. Hubbard, "Hydrodynamic Friction and Capacitance of Arbitrarily Shaped Objects," *Phys. Rev.* E **49**, 5319 (1994); M.L. Mansfield, J.F. Douglas, E.J. Garboczi, "Intrinsic Viscosity and Electrical Polarizability of Arbitrarily Shaped Objects," *Phys. Rev.* E **64**, 061401 (2001); M.L Mansfield, J.F. Douglas, "Transport Properties of Wormlike Chains with Applications to Double Helical DNA and Carbon Nanotubes," *Macromolecules* **41**, 5412 (2008).

Mesoscale

Coarse-Grained Field Theory—In traditional polymer field theory, one begins with a coarse-grained, particle-based model of interacting polymers. The monomer-monomer interactions are then formally transformed into a field-based framework with a single polymer interacting with an average "chemical potential" field representing the many underlying monomer-monomer interactions. For special situations, polymer field theory is analytically solvable. However, for many physically interesting systems, numerical solution of the underlying equations is necessary.

Mesoscale modeling and simulation using sophisticated coarse-grained, field-theory methods represents an important facet of the Theory, Modeling, and Simulation effort in the Polymers Division. Theorists in the Division have developed mean field and stochastic field theories in order to study a wide range of polymer, copolymer, polymer blend, and related soft-matter phenomena on numerous length and time scales in the mesoscale regime.



Monomer composition snapshot from a mean-field simulation of a copolymer-small molecule blend.

For example, theorists in the Electronics Materials Group have developed an advanced stochastic field theory for studying interfacial fluctuations in block copolymer systems under consideration as a lithographic mask (i.e., a block copolymer resist) for next-generation nanoelectronics manufacturing. Computer simulations based on block copolymer field theory have yielded new and important insights into the physical nature of interfacial fluctuations in block copolymer resists, and theorists are working closely with scattering experts in order to incorporate these new insights into next-generation block copolymer scattering models under development in the Dimensional Metrology for Nanofabrication project.

Selected References: G.H. Fredrickson, V. Ganesan, F. Drolet, "Field-Theoretic Computer Simulation Methods for Polymers and Complex Fluids," *Macromolecules* **35**, 16 (2002); A.W. Bosse, C.J. Garcia-Cervera, G.H. Fredrickson, "Microdomain Ordering in Laterally Confined Block Copolymer Thin Films," *Macromolecules* **40**, 9570 (2007).

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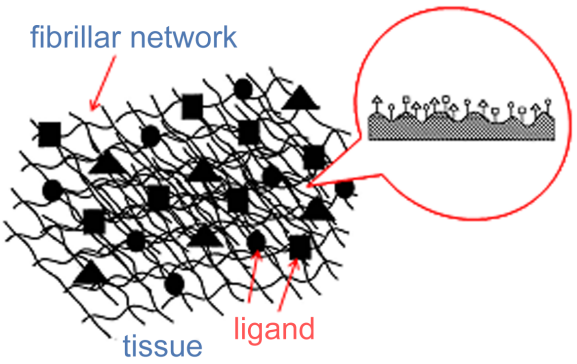
Finite Element Analysis—Finite element analysis (FEA) is a powerful computer-based tool widely used by scientists and engineers for understanding the response of physical systems with complicated geometries to external influences. Finite element analysis is based on the fundamental physical principles that establish a system of differential equations to govern the behavior of physical systems, and can obtain numerical solutions to the governing equations. In the Polymers Division, FEA has been employed for designing measurement apparatus, validating experiment results, and simulating prototype experiments. Specific examples including charactering the fluid flow and heat transfer analyses in material processing, failure analysis of materials interfaces, and understanding cell-material interactions in biological research.



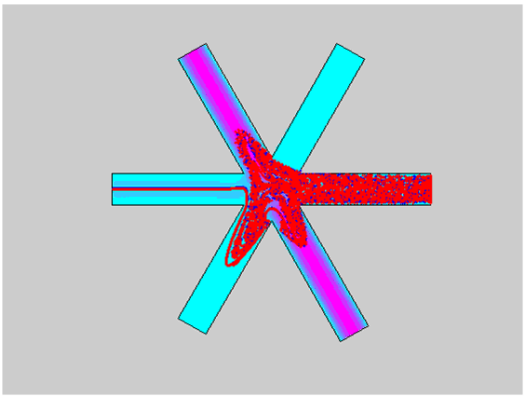
Microtexture of ECM.

Currently in the Polymers Division, a finite element model is being developed to investigate the molecular mechanism of cell adhesion and the spreading process on the extracellular matrix (ECM) protein layer. The adhesion and spreading process is mediated by the interaction of cell receptors and ECM ligands, in which the receptors diffuse along the cell membrane surface and interact with ligands in ECM to form bonds. Upon contact with the ECM substrate, cells spread and the adhesion zone grows as bond formation at the adhesion front increases to a critical level. The model involves coupling of reaction-diffusion processes and mechanical contact between cells and ECM. In our study, the influence of ECM microtexture and stiffness, glycocalyx layer (present at cell surface), mass action kinetics, as well as receptor mobility and stochastics on the cell adhesion development will be addressed. The study is significant for in-situ binding measurement of proteins, and also facilitates rational design and fabrication of the cellular environment with defined biophysical and biochemical properties.

Selected References M.Y.M. Chiang, W.L. Wu, J.M. He, E.J. Amis, "Combinatorial Approach to the Edge Delamination Test for Thin Film Reliability - Concept and Simulation," *Thin Solid Films* **437**, 197 (2003); A.S. Smith, K. Sengupta, S. Goennenwein, U. Seifert, E. Sackmann, "Force-induced Growth of Adhesion Domains is Controlled by Receptor Mobility," *PNAS* **105**, 6906 (2008).

Macroscale

Fluid Dynamics—Fluid flow at a variety of length scales is ubiquitous to both traditional polymer processing and rheology applications, as well as to emerging applications that are currently active research areas in microfluidics and nanotechnology. Fluid dynamics provides the foundational insight necessary to understand the underlying physics and design, as well as improve measurement methods in these types of problems.



Chaotic mixing in the microfluidic "star-cell" continuous mixer is analyzed using a combination of CFD, particle tracking, and chaos theory.

Fluid dynamics methods encompass a variety of numerical, theoretical, and analytical techniques and are often used in conjunction with one another. Computational fluid dynamics (CFD) has emerged as the tool of choice for solving the most complicated problems in both mesoscale and macroscale applications. Flow in complex geometries requiring solution of the full Navier-Stokes or similar equation is generally undertaken using the finite element method.

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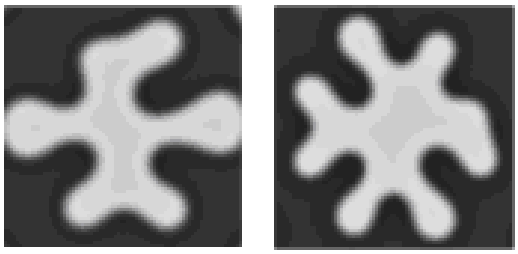
Permeation of textiles to manufacture polymer composites, flow in extrusion dyes, and nutrient flow in bioreactors are prime examples. However, other techniques, most notably the Lattice-Boltzmann method, are also used, and have emerged as powerful tools for analyzing multi-phase flows.

Numerical techniques are often only part of the solution, and must be combined with theory to fully understand and analyze a problem. Analysis of chaotic mixing in microfluidic geometries, as well as Rayleigh instability in multi-phase polymer blends, are recent examples in which theory and simulation are equally important.

Analysis of most fluid dynamics problems is undertaken using the assumption of a continuum fluid. However, a number of emerging problems in nanotechnology require multi-scale modeling in which CFD methods are used in conjunction with discrete particle based methods, such as Brownian dynamics. An example is the separation of single-walled nanotubes using solution based methods. Such hybrid approaches enable continuum problems to be solved, while also capturing small scale dynamics and their coupling macroscale phenomena.

Selected References: F.R. Phelan Jr., B.J. Bauer, "Simulation of nanotube separation in field-flow fractionation (FFF)," *Chemical Engineering Science* **62**, (2007); F.R. Phelan Jr., N.R. Hughes, J.A. Pathak, "Chaotic Mixing in Microfluidic Devices Driven by Oscillatory Cross Flow," *Physics of Fluids* **20**, 023101 (2008).

Thermodynamics — Phase field modeling can be applied to a wide variety of topics, such as phase transitions, chemical reactions, and transport phenomena that are essential in the fields of physics, chemistry, materials science, continuum mechanics, and cell biology. Several mathematical methods are available to obtain solutions to these types of models.



Cell morphologies calculated using a phase-field model based on thermodynamic principles.

In the Polymers Division, a mathematical model using the phase-field method, based on thermodynamic principles, has been developed to elucidate complexities of effects due to mechanical interactions between the cell and substrate on cellular organization, cell adhesion, and migration. This model will provide insights into the dependency of cell morphology and migration on substrate mechanics. These insights cannot be deduced from the experimental observations alone. Through the adoption of phase-field theory, which provides a mathematical description of diffuse interfaces in phase transition problems, our research has focused on how cell morphology is linked to substrate mechanics, how cell migration is guided by substrate stiffness, and mechanisms by which substrate rigidity is translated into cell morphological stability and movement.

Selected References: D.E. Discher, P. Janmey, Y.L. Wang, "Tissue Cells Feel and Respond to the Stiffness of Their Substrate," *Science* **310**, 1139 (2005); Y. Ni, M.Y.M Chiang, "Cell Morphology and Migration Linked to Substrate Mechanics," *Soft Matter* **3**, 1285 (2007).

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