

Profile of Glenn H. Fredrickson

Farooq Ahmed, Science Writer

Soft matter theorist Glenn H. Fredrickson has been studying how polymers behave and assemble for more than four decades. His work has influenced the engineering of materials so commonplace they are often taken for granted: from hair care products and microelectronic films to adhesives and tennis shoes. The key to his research is an understanding that complex systems can be numerically simulated not only by using the positions of their component molecules but by interacting fields. This breakthrough, called field theoretic simulation, has allowed Fredrickson to make inroads into polymer science, cellular biology, and quantum mechanics, among other fields. In his inaugural article (1), Fredrickson, who was elected to the National Academy of Sciences in 2021 and is a professor of chemical engineering and materials at the University of California, Santa Barbara, uses field theoretic simulations to tackle free-energy estimation in classic and quantum many-body systems.

Cooperative Transitions

Fredrickson was born in Washington, DC, and grew up in eastern Florida. He was greatly influenced by his father, who worked as an electrical engineer for the US Air Force before joining the private sector. “He developed the first integrated computer systems for the publishing industry,” says Fredrickson.

Fredrickson excelled in mathematics and completed his undergraduate degree at the University of Florida in Gainesville in 3 years. “I thought I was going to be pre-med, but I concluded that I would be a much better chemical engineer than a doctor,” he says.

In 1980, Fredrickson enrolled at Stanford University for a doctorate in chemical engineering. After taking an elective course from chemical engineer Curtis Frank, he joined Frank’s group, which studied polymer photophysics. “At that point, I hadn’t made the decision [to become a theorist], but the connection between polymer science and statistical mechanics fascinated me,” he recalls.

After several frustrating months running experiments, Fredrickson convinced Frank to let him become the theorist in the group. “Curt was incredibly generous to allow a young graduate student to just come in and do this,” he says. Fredrickson also enlisted the help of Stanford theoretical chemist Hans Andersen, and by the end of his PhD, he was effectively Andersen’s student.

One of Fredrickson’s earliest breakthroughs came from his work with Andersen. It described a model of glass transitions, which can occur when a liquid transforms into a solid (2). As the disordered molecules in a liquid cool, they “jam” together in the solid form while retaining the initial disorder. “We introduced a class of kinetic Ising models that describe the dynamics of this transition,” he says.



Glenn H. Fredrickson. Image credit: Lillian McKinney (College of Engineering, University of California, Santa Barbara, CA).

“Mathematicians and theoretical physicists are still playing with these models.”

Bell Labs

After he earned his doctorate in 1984, Fredrickson’s mentors expected him to continue on a traditional academic research path. However, an opportunity at AT&T Bell Labs drew him to the New Jersey institution. “I just fell in love with the place,” he says, “and there was an established path to rejoin academia.” Moving to Bell Labs temporarily freed him from having to apply for grant funding and introduced him to researchers across a variety of disciplines.

Fredrickson initially worked on glass transitions at Bell Labs, but he also began investigating block copolymers. The simplest example of block copolymers are di-block polymers, which are formed by bonding two dissimilar polymers at their ends. By linking polymers that have differing chemical properties—hydrophilicity and hydrophobicity, for example—the resultant molecule can act in unexpected ways.

“Block copolymers can self-assemble into a fascinating array of ordered nanostructures, which are soft solids that are highly tunable,” explains Fredrickson.

This article is distributed under [Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 \(CC BY-NC-ND\)](https://creativecommons.org/licenses/by-nc-nd/4.0/).

This is a Profile of a member of the National Academy of Sciences to accompany the member’s Inaugural Article, e2201804119, in vol. 119, issue 18.

Published April 26, 2022.

This tunability, conferred by varying chemistry or polymer architecture, has led to the widespread deployment of block copolymers in products as different as pharmaceuticals, semiconductors, asphalt, and sporting goods, such as shoe soles and skateboard wheels.

One of Fredrickson's most-cited articles from this era examined phase transitions in block copolymers (3). He and Bell Lab's colleague Eugene Helfand showed how composition fluctuations in di-block copolymers influence their transition from disordered to ordered structures. In doing so, Fredrickson and Helfand relied on a method developed by condensed matter theorist Serguei Brazovskii that had previously been applied to much larger systems, such as neutron stars. "There weren't good physical examples of systems where you could see this Brazovskii-type transition until we made the connection with block copolymers," he says.

At Bell Labs, Fredrickson also began a longstanding collaboration with experimental polymer physicist Frank Bates, now at the University of Minnesota. Their combined work has provided a comprehensive analysis of block copolymers, from basic physical questions to the theoretical underpinnings of how the polymers assemble and interact (4). As the collaboration evolved, Fredrickson and Bates investigated polymer structures of increasing complexity. This progression has helped them make connections between chemical engineering and protein science (5).

"Proteins are incredibly diverse because each residue can be selected from 20 different amino acids and the variability grows exponentially with the length of the polypeptide," Fredrickson says. "Synthetic multiblock polymers are the same. Each copolymer can have multiple blocks, each with a different chemical identity. You have the same combinatorial complexity in terms of materials design."

"The difficult question is," he adds, "what do you want to make?"

Return to California

After 6 years at Bell Labs, Fredrickson returned to California, joining the University of California, Santa Barbara, in 1990. At the time, the university had been expanding its chemical engineering and materials science departments by recruiting from corporate laboratories. "When I joined," says Fredrickson, "it was already being referred to as Bell Labs West. We quickly established ourselves as a place with a strong interdisciplinary character and very good connections to industry."

For example, a brief conversation with Santa Barbara materials chemist Galen Stucky led to the discovery that triblock copolymers could be used to synthesize SBA-15, a mesoporous form of silica with hexagonal pores. The material is now widely used in catalyst supports, drug delivery systems, biosensors, and absorbents (6).

Fredrickson's facility with mathematics and statistical mechanics allowed him to use the language of theoretical physics to create field theory models of complex polymer systems. These models replaced atom-by-atom representations of interacting molecules with one or more fields.

"The particle-to-field transformation is exact, so no approximation is involved," he explains. "Nonetheless, the field

representation allows for more efficient numerical investigations, a subject we now call field-theoretic simulations."

Fredrickson credits Sir Sam Edwards with laying the foundation for this methodology. Edwards, a Welsh physicist, first applied quantum field theory to polymer science in the 1960s.

Numerical Horsepower

Over the years, Fredrickson has further advanced field-theoretic simulations and moved away from the "pencil-and-paper" calculations that he had been using to study polymer assembly and properties. This transition required adapting complex Langevin methods introduced in nuclear physics to dynamically evolve fields in polymer models (7). "It's a whole different way to approach dense macromolecular assemblies," he says, "and we finally reached a point where we had enough numerical horsepower to do it."

In a 2006 monograph, Fredrickson codified the use of field theory in polymer physics with an emphasis on inhomogeneous systems such as block polymers (8). He described the work as a "missing piece" that filled a void in the field.

"Edwards and [Nobel laureate] Pierre-Gilles de Gennes had both written classic monographs on polymer statics and dynamics, but they dealt almost exclusively with systems that were uniform," he says. "Also, they didn't address computer simulation techniques."

Computational power allowed Fredrickson to push field theory into areas of interest to those outside of chemical engineering and material science. One study looked at coacervation, a process that occurs when an aqueous solution of oppositely charged macromolecules separates into a dilute phase and a polymer-rich, dense liquid phase (9). Coacervation occurs inside living cells to form minute droplets of protein-rich material.

"People are trying to understand the biological role of condensates formed by coacervation. There was little rigorous theory in this space, and our methods were well suited to understanding their formation and structure," Fredrickson says.

Sustainable Materials

In addition to his research at Santa Barbara, Fredrickson has also had a long-term connection with Mitsubishi Chemical Holdings, one of the world's largest chemical companies. He has served as its chief technology officer and as the executive director of its Kaiteki Institute, a think-tank that promotes sustainable development.

"It was a fantastic experience, and even now I stay involved with leadership and strategy decisions," he says.

Fredrickson is excited about using advances in polymer science to focus on sustainability. A large fraction of plastic waste, for example, remains unusable due to incompatibilities between polymer types, mostly polyethylene and polypropylene.

"If you try to combine them, you end up with a really brittle plastic because they have very narrow interfaces," he explains. "But if you put opposite charges on each polymer, ion-mediated interactions could allow for some remarkable, upcycled plastics."

Fredrickson's work on supramolecular polymer complexes may help spur the development of self-healing, reusable, and environmentally friendly materials (10). Supramolecular complexes consist of polymer assemblies that are reversibly and noncovalently linked. The research relied on resurrecting a vulcanization theory developed by Edwards and chemist Karl Freed in the 1970s. "We picked up this old theory, which had been ignored for 30 years, and realized it could be used to marry supramolecular chemistry and polymer science," says Fredrickson. Edwards and Freed had devised the vulcanization model using quantum field theory, and Fredrickson's calculations on supramolecular polymer complexes led to the realization that field-theoretic simulations could be applied to interacting quantum particles, specifically bosons (11).

Quantum Pivot

The boson research gave Fredrickson the idea that his methods could be used to directly explore other physical phenomena. In his inaugural article (1), Fredrickson demonstrated how field-theoretic simulations simplify the task of calculating free energies in molecular simulations of both classic and quantum systems. Free energies are valuable because they enable the mapping of phase transitions

in complex fluids, such as block polymers and biomolecular condensates, as well as quantum phase transitions in inorganic materials.

In a standard approach that relies on particle coordinates, free energies can be determined only by laborious methods, such as thermodynamic integration. Fredrickson showed that switching to a field theory representation provides direct access to a solution. "This article (1) shows a path to directly computing the free energy. It's something we should have seen 15 years ago when we first started doing this type of work, but we only realized it recently," he says.

Fredrickson says the pivot toward quantum phenomena is an unexpected change. However, he believes his polymer-inspired computational tools could aid multiple applications, including materials for quantum computing and studies of quantum magnetism and quantum turbulence.

"I'm like a kid in a candy store learning all this new stuff," he says. "I have been fortunate throughout my career from Stanford to Bell Labs to Santa Barbara to work with fantastic collaborators and in nurturing environments. Without them, I wouldn't have been able to accomplish [much]."

1. G. H. Fredrickson, K. T. Delaney, Direct free energy evaluation of classical and quantum many-body systems via field-theoretic simulation. *Proc. Natl. Acad. Sci. U.S.A.*, 10.1073/pnas.2201804119 (2022).
2. G. H. Fredrickson, H. C. Andersen, Kinetic Ising model of the glass transition. *Phys. Rev. Lett.* **53**, 1244 (1984).
3. G. H. Fredrickson, E. Helfand, Fluctuation effects in the theory of microphase separation in block copolymers. *J. Chem. Phys.* **87**, 697 (1987).
4. F. S. Bates, G. H. Fredrickson, Block copolymer thermodynamics: Theory and experiment. *Annu. Rev. Phys. Chem.* **41**, 525-557 (1990).
5. F. S. Bates *et al.*, Multiblock polymers: Panacea or Pandora's box? *Science* **336**, 434-440 (2012).
6. D. Zhao *et al.*, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **279**, 548-552 (1998).
7. G. H. Fredrickson, V. Ganesan, F. Drolet, Field-theoretic computer simulation methods for polymers and complex fluids. *Macromolecules* **35**, 16-39 (2002).
8. G. H. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers* (Oxford University Press, Oxford, 2006).
9. J. Lee, Y. O. Popov, G. H. Fredrickson, Complex coacervation: A field theoretic simulation study of polyelectrolyte complexation. *J. Chem. Phys.* **128**, 224908 (2008).
10. G. H. Fredrickson, K. T. Delaney, Coherent states field theory in supramolecular polymer physics. *J. Chem. Phys.* **148**, 204904 (2018).
11. K. T. Delaney, H. Orland, G. H. Fredrickson, Numerical simulation of finite-temperature field theory for interacting bosons. *Phys. Rev. Lett.* **124**, 070601 (2020).