Perspective

Structure, Dynamics and Thermodynamics in Complex Systems: Theoretical Challenges and Opportunities

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Introduction

Dynamics and equilibrium thermodynamics have traditionally been treated as separate subjects in chemical engineering. However, as the focus of our profession continues to evolve from processes to products, and from simple fluids to structured materials, a close coupling between dynamics and thermodynamics will become an ever more distinctive feature of our discipline's research landscape. The products that we design, be they nanostructured coatings or targeted drug delivery devices, are characterized by increasingly tight structure specifications at ever-shrinking length scales. At the fundamental level, microscopic structure is the result of the interplay between driving force (thermodynamics) and formation rates and mechanisms (kinetics). In this article I use selected examples to illustrate some of the exciting opportunities that the interplay of dynamics and thermodynamics presents for theoretical and computational research in chemical engineering.

Prediction and quantification of structure

Many of the products in whose design and manufacture chemical engineers are involved possess complex structure. An important question is, therefore, to predict the equilibrium structure of a complex material. This information is useful even when thermodynamic equilibrium cannot actually be attained. Fredrickson and coworkers have developed powerful field-theoretic methods for polymeric fluids and other soft condensed matter systems that capture polymer architecture, composition variations, and polydispersity while smearing out atomic details[1] (Figure 1). This approach can account for chemical reactions, it can equilibrate systems with very wide ranges of length scales, and allows for continuous adjustment of spatial resolution through spectral, finite difference, or finite element representations. In so doing, these mesoscopic computer simulations provide a seamless connection to continuum property modeling. The approach involves integrating out particle coordinates in the partition function and replacing the high-dimensional configurational problem by a functional integration over fluctuating density and chemical potential fields. Equilibrium structures correspond to saddle points of an effective Hamiltonian, and the problem then becomes one of nonlinear optimization. Recent examples of the application of field-theoretic methods to structure prediction in polymer fluids include the determination of the equilibrium morphology in an (ABA triblock + A) alloy that resolves structure over five orders of magnitude,[2] and the calculation of potentials of mean force between nanoparticles in block copolymers.[3]

Field theoretic methods allow the formulation of models at the atomistic, mesoscopic or macroscopic scales, and they can be derived from conventional particle-based models of fluids.[1] The approach appears particularly promising for the study of concentrated polymer systems, such as multiphase blends and copolymer melts; systems with soft, long-ranged interactions, such as polyelectrolytes and electrolyte solutions; and colloidal suspensions, including systems with surface charges, grafted polymers, and counterions.[1]

A well-developed framework exists for quantifying the structure of crystalline solids. Much less is understood about the quantification of structure in amorphous materials.[4] The importance of amorphous materials (e.g., biological materials, such as tissue; porous rocks; soil; dispersions) makes the quantitative description of their structure a subject of considerable scientific and technical importance.[5] Progress in this direction has recently been made by Torquato and coworkers, who introduced the idea of an order phase diagram. [4,6] They defined metrics quantifying translational and orientational order in the hard-sphere system, and mapped fluid, crystalline, and glassy states onto a plane whose coordinates are the order metrics (the order phase diagram). They found that nonequilibrium states occupy a distinct region of the order phase diagram, which suggests the intriguing notion of a geometric criterion for distinguishing equilibrium and glassy states. Furthermore, glassy states were found to lie along curves parametrized by the quench rate, [4,7] making this representation a valuable tool for understanding the relationship between structure and processing history. Subsequent work has demonstrated the usefulness

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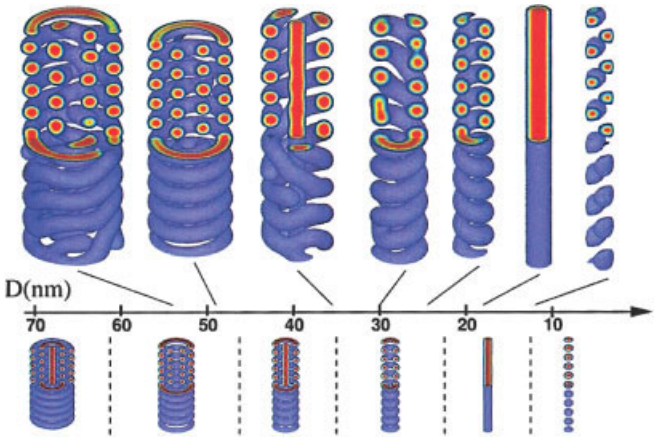

Figure 1. Simulated structures of self-assembly of a diblock copolymer + homopolymer blend in cylindrical confinement.

Calculations show the effect of the confining cylinder's diameter (D) on the resulting mesostructures. The bottom row shows results obtained using cylindrical coordinates. In tight confinement, hexagonal packing of the cylindrical micelles running parallel to the pore would impose stress on the system. This stress can be relieved by arranging the system into a set of concentric shells. In each shell the cylinders bend and tilt with respect to the pore axis, thus, forming helices or doughnuts. These calculations were performed using self-consistent field theory. [1-3] Reprinted, with permission, from ref. 56, copyright Nature Publishing Group, http://www.nature.com.

of the order phase diagram for understanding the relationship between structural order and dynamic and thermodynamic properties of network-forming fluid systems.[8,9]

Mechanisms and rates of phase transitions

A common route to structure formation is phase separation. The mechanisms of phase separation are generally thought to fall into two basic categories: nucleation and spinodal decomposition.[10] Such established notions need to be refined or reconsidered altogether when phase transitions involve complex mixtures, such as polymer solutions, colloidal suspensions, and protein solutions. This is illustrated by recent small angle neutron scattering (SANS) experiments by Balsara and coworkers on phase separation in polymer blends,[11-15] and by optical microscopy studies of liquid-liquid phase transitions in concentrated protein solutions by Vekilov and coworkers.[16] These experiments challenge established theoretical predictions on the evolution from stability to instability, and on the very nature of the fluctuations that grow spontaneously into the stable phase (critical nucleus). Improved theories of phase separation in complex fluids and soft condensed matter must incorporate the effects of fluctuations,[17,18] and viscoelasticity.[19,20] Although initial steps in these directions have been taken,[17-20] this remains an important area for future fundamental theoretical work.

The computational study of transitions between stable equilibrium states presents considerable difficulties, stemming from the fact that, microscopically, such transitions are rare events. The usual approach to such calculations is based on transition state theory, and involves running short dynamic trajectories starting from the appropriate transition state. The rate constant is then calculated as the product of the probability of observing the system in the transition state times a transmission coefficient obtained from the dynamic trajectories.[21] In complex systems possessing many degrees of freedom, the transition state is not known at the outset, and often it may not even be specified in terms of a small number of variables.[21] Chandler and coworkers have developed the transition path ensemble method, which allows the study of rare events without prior knowledge of either the transition mechanisms or the transition states.[21] The method involves a stochastic sampling of transition paths. It has been used to study a number of complex processes, such as cavitation of liquids between solvophobic surfaces,[22] ion pair dissociation in water,[23] and the unfolding of protein domains.[24] The method offers great promise for the investigation of transitions between stable states in complex systems of interest in chemical engineering.

Dynamics and thermodynamics in glass-forming liquids

The glassy state is ubiquitous in nature and in technology. It is key to food processing and to the pharmaceutical stabilization of labile biomolecules. Most engineering plastics are amorphous solids, as are some metallic glasses of interest because of their corrosion resistance and soft magnetism. Optical fibers are made of very pure amorphous silica, occasionally carefully doped. The most common form of water in the Universe is believed to be glassy. The silicon used in many photovoltaic cells is amorphous. Most of these examples entail cooling a viscous liquid fast enough to avoid crystallization (supercooling). Although this route to the vitreous state has been known for millennia, the molecular mechanisms whereby liquids acquire amorphous rigidity upon cooling, as well as the microscopic origin of the distinguishing properties of glass-forming liquids, such as dynamic heterogeneity or the breakdown of the Stokes-Einstein equation, are not well understood.[25] Dynamic heterogeneity[26] refers to the emergence of spatially separated regions, typically several nanometers in size, whose relaxation dynamics differ from each other by orders of magnitude. Understanding these canonical features of glass-forming liquids impacts our ability to predict, control and engineer reactions, mixing and transport processes in this ubiquitous and technologically important type of liquid matter. From a fundamental viewpoint, the very nature of the glassy state is one of the important unanswered scientific questions in contemporary science.[27]

A distinctive aspect of supercooled liquid behavior is the apparent connection between dynamics and thermodynamics. The thermodynamic viewpoint of the glass transition originated with Walter Kauzmann's classic review article,[28] which pointed out the dramatic loss of entropy with respect to the stable crystal that accompanies deep supercooling of many liquids. The nature of this impending "entropy crisis" has since been clarified,[29] but the notion that liquids form glasses because they run out of configurations to explore remains a basic underpinning of several current theories of the glass transition.[30,31] Experimental support for this viewpoint is provided by numerous measurements of relaxation rates showing an intimate connection between dynamics and configurational entropy,[32] in agreement with the Adam-Gibbs theory of structural relaxation.[33] Alternative approaches to the glass transition view this phenomenon as purely kinetic.[34,35]

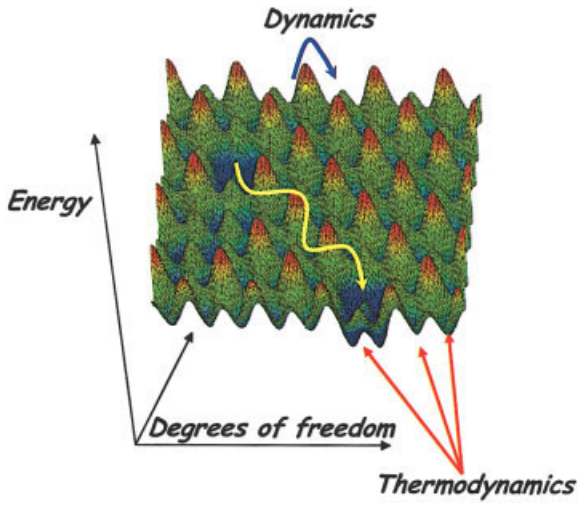

Figure 2. The energy landscape perspective.

Schematic representation of a system's potential energy as a function of its degrees of freedom. In this topographic viewpoint of glass-forming systems, thermodynamics is obtained from the statistics of the depth distribution of potential energy minima. Sampling of distinct saddles and potential energy minima defines a system's dynamics.

The energy landscape formalism[36,37] provides a topographic viewpoint of viscous slowdown (Figure 2).[38] In this approach, one seeks to understand the manner in which a liquid explores its multidimensional potential energy surface as a function of temperature[39] and density. This perspective has proved to be insightful, versatile, and powerful, and is being applied to the study of protein folding, atomic clusters, protein engineering, and macroeconomics.[37,40] Because of the high dimensionality and complexity of landscapes, a taxonomic enumeration of all potential energy minima is impossible. Instead, a statistical description allows the calculation of thermodynamic quantities (e.g., entropy) from knowledge of the depth distribution of potential energy minima. Such a basin enumeration function describes the number of potential energy minima within a certain depth range about a specified value of energy. Knowledge of the basin enumeration function allows access to a complex system's thermodynamics.[25] Accordingly, the theoretical and computational study of landscape statistics is a very active area of research.[41] Landscape-based equations of state and phase diagrams have recently been obtained.[42,43] This route to the low-temperature thermodynamics of glass-forming systems offers considerable advantages with respect to conventional approaches. First, it avoids the calculation of multidimensional configurational integrals, which are replaced in the theory by one-dimensional (1-D) integrals over the basin depth. Second, the parameters in landscape-based equations of state or free energies provide direct information on such interesting quantities as the range of basin depths and the total number of potential energy minima.

Although significant progress has been made in using the energy landscape formalism to understand the thermodynamics of glass-forming systems, relating relaxation dynamics to landscape properties remains a major challenge. Computational investigations have yielded useful insights into the relationship between dynamics and landscape sampling,[39,44] but a coherent formalism that would allow the calculation of transport coefficients and relaxation times has not yet emerged, recent theoretical progress notwithstanding.[45] In addition to their scientific interest, answers to such questions should provide currently lacking predictive capability for designing and controlling rate processes (reactions, mixing) in glass-forming matrices over wide operating conditions.

Jarzynski's equality

In 1997 Chris Jarzinsky published a seminal article containing what is arguably the most important result in thermodynamics in decades.[46] It consists of an equality linking the free energy difference between two states of a thermal system, ΔA, to the ensemble average of the actual (finite rate, irreversible) work, W, performed in taking the system from one state to the other

$$\langle exp(-W/kT)\rangle = exp(-\Delta A/kT)$$

where the angle brackets denote thermal averaging, and k is Boltzmann's constant. This result is remarkable because it relates a thermodynamic quantity, the free energy difference, to a nonequilibrium one, the finite-rate work, in the form of an *equality* (as opposed to an inequality).

Jarzynski's equality offers rich opportunities for obtaining fundamental thermodynamic information in biological systems (as illustrated by single-molecule RNA stretching experiments[47]), and complex fluids. The investigation of its theoretical implications[48-50] and computational possibilities[51-53] will be an active and important area of research for many years to come. Although it is a general thermodynamic result, and as such not limited to structured fluids, Jarzynski's equation illustrates, at a deep and fundamental level, the connection between dynamics and thermodynamics that is the subject of this article.

Perspective

In the complex fluids and soft condensed matter systems that are increasingly central to modern chemical engineering, driving forces and kinetic constraints often interact in an inextricable manner. This mandates a comprehensive approach where equilibrium and time-dependent phenomena are treated together.[54,55] The selected examples discussed in this article illustrate some of the numerous exciting opportunities for theoretical and computational work that arise from this perspective. Problems, such as the prediction and quantification of structure in disordered materials or the accurate prediction of rates of phase separation in complex mixtures are both scientifically interesting and technically important. They are likely to be a distinctive feature of our discipline's evolving research agenda for many years to come.

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