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OVERVIEW OF MULTISCALE SIMULATION METHODS FOR MATERIALS

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Modeling has increasingly become a tool for better proactive design, besides being a method to explain phenomena. In these functions it must be validated with experimental observations before its results can be applied with confidence. Modeling at the continuum scale is well understood, and the accuracy, precision, and robustness of results using continuum methods have been analyzed. Numerous methods, including finite-element analysis, finite-difference methods, and boundary element methods, are now used routinely in a variety of areas, including flow visualization, design of materials and structures, and in industry for automotive design, construction and structure applications, and plant design.

Modeling at the atomistic scale has also begun to be accepted as part of routine research protocol. Results from such methods are now accepted with a reasonable understanding of their accuracy and robustness. Quantum mechanical calculations are now used to understand the properties of semiconductor materials. Atomistic calculations have been used to better understand phase behavior of components and mixtures for the chemical industry. Numerous process design tools used routinely in the chemical industry include information based on atomistic calculations. Increasingly, however, design of materials comes up against phenomena that are in the mesoscale: too large for atomistic simulations and too small for continuum analysis. This is the scale where one cannot use continuum-scale assumptions, yet the system is often larger than can be modeled tractably with atomistic methodologies. How do we study systems that are made of clusters of

thousands of molecules that interact in specific ways? How do we take results from atomistic simulations and correlate them with parameters we need for continuum studies?

1. MESOSCALE MODELING

Examples of mesoscale phenomena include engineering of molecular clusters or of functionalized nanoparticles, crystals, and liquid-crystalline structures [such as clathrates¹ and micelles] that are used as templates for porous membranes,² materials with specific enzymatic,³ or catalytic properties,⁴ control of flow behavior,⁵ nanocontainers with controlled release,⁶ or materials with specific thermal, electromagnetic,⁷ or mechanical properties.⁸ Since a number of these materials are designed by self-assembly of atoms or molecules to form nano-sized clusters, modeling becomes a critical tool in engineering such materials. Modeling is also used to understand conditions to optimize processes to functionalize or engineer aspects of these structures, such as size of cluster, surface properties, or charges. Figure 1 shows some examples of nanoscale ordering and self-assemblies. Modeling mesoscale phenomena in materials design has thus become increasingly significant as mesoscale engineering of materials becomes critical in developing superior materials.

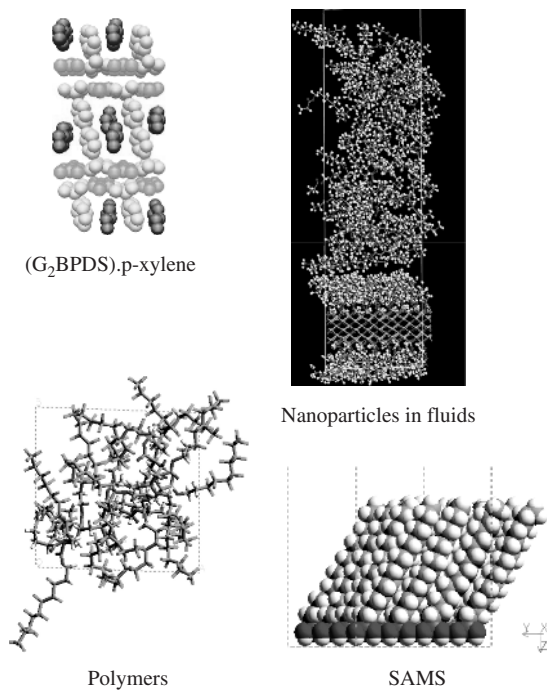


Figure 1 Mesoscale phenomena. (See insert for color representation figure.)

From a modeling perspective, there are a number of aspects to be addressed. Modeling helps to translate macroscopic observations based on nano- or mesoscale phenomena. Judicious use of simulations helps demonstrate why certain behavior is seen which is critical knowledge for engineering such behavior. For example, how can one predict the behavior of silicon nanoparticles whose surfaces have been modified with specific functional groups when they are in a polymer matrix;⁹ or alternatively, how can one engineer the surfaces of nanoparticles so that polymer-particle composites may manifest a certain set of desired properties? Similarly, what types of structures do micelles made up of specific amphiphiles form, and how do they behave at different concentrations; or alternatively, what additives and amphiphiles could one use to engineer and design certain rheological properties in fluids, specific surface properties, or specific micellar structures?¹⁰ How do molecules cluster in various environments,¹¹ and how does that affect their thermodynamic properties and mobility? Similar questions have been addressed for chromonic systems.¹² Another area with significant modeling effort is that of biomolecules.¹³ Simulations have been used to understand the binding mechanisms of biomolecules on surfaces¹⁴ and with each other, enzymatic pathways, mobility of molecules, and design of encapsulants—all with the aim of engineering drugs for specific action as well as methods of targeted delivery. Nano- and mesoscale models can be used not only to look at the equilibrium behavior of materials but also to study the mobility of particles and the rupture behavior of adhesives (essentially nonequilibrium phenomena).

Modeling mesosystems is difficult since the phenomena of interest are neither atomistic (so that solutions can be grasped by understanding the behavior of a few to hundreds of atoms or molecules) nor macroscopic (so that continuum properties of the material can be assumed without losing events occurring in the smaller-scale regime). Modeling phenomena that span different orders of length and time requires the use of multiscale models¹⁵ (schematic in Figure 2). Yet mesoscale phenomena often define macromolecular properties (Figure 3). It is necessary to understand the mechanisms of the phenomena at these length scales

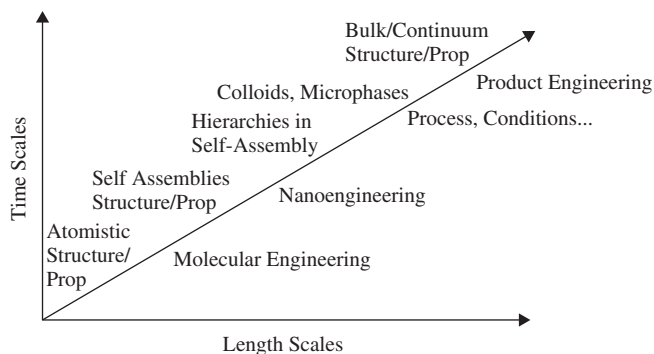


Figure 2 Modeling methods for various length and time scales.

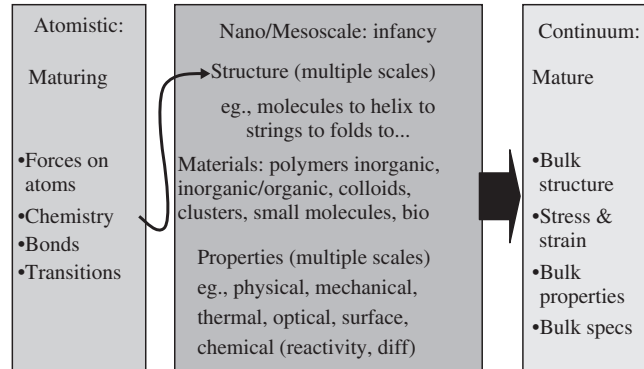


Figure 3 Modeling methods: development status and properties encompassed.

and to characterize them in order to understand or predict the macro properties that emerge.

For example, the specific folding of proteins can affect their macromolecular reaction rates. The manner in which a polymer configures itself in a stress field may define the mechanical properties of the material. Often, these systems are even more complex-showing hierarchies of phenomena. For example, the configuration of small molecules defines how they self-assemble and hence the structure of a cluster. The structure of the cluster will define its interactions with solvent that may surround it or with other clusters. These clusters may aggregate to form networks. The interacting networks in a solvent or without a solvent will have properties related to transport, absorbency, or chemical or physical reactivity, depending on phenomena at all these length scales (Figure 4).

There are additional difficulties with modeling phenomena in the mesoscale. First, it is often difficult to measure them experimentally. Often, the self-assemblies or clusters that form in solutions are transient. In addition, the exact

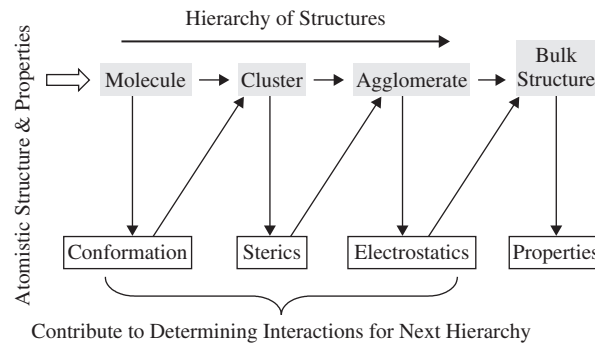


Figure 4 Examples of effects of different time and length scale influencing specific properties and next hierarchical structures.

configurations of the molecules in the clusters are not always visualizable directly, although they can sometimes be estimated from nuclear magnetic resonance, infrared, or other analysis. The effects on continuum properties of these mesoscale phenomena are also nonlinear or nondeterministic, and hence cannot be estimated easily from continuum properties. Thus, validation of models of these mesoscale events is difficult at best.

2. SIMULATION METHODS

Two types of multiscale methods—hierarchical and handshake—have provided feasible solutions to real problems. Approximating a number of polymer repeat units or solvent molecules as single beads with tunable interactions is an example of a hierarchical model.¹⁶ Such models use information lumped from a smaller size scale or a shorter time scale to predict phenomena at the scale of simulation and/or to predict parameters or observations at larger scales. The parameters of the bead, in this case, are obtained from atomistic or quantum calculations on the molecules. In turn, the beads and chains are used to predict viscosity and material properties, which can then be used in flow models or structure/stress models to predict the macroscopic behavior of the material. Such methods are used to study equilibrium structure of polymers¹⁷ and composites as well as nonequilibrium processes such as relaxation and/or fracture.¹⁸ More complex versions of this algorithm have also been used in the study of nanoparticle interactions with polymers as well as a variety of solvents.¹⁹

Lattice models consist of spanning the system of interest by meshes or nodes.²⁰ Molecules that are moving or reacting are lumped into coarser particles, and the nodes or meshes keep track of the extent of mobility or reaction. Examples include curing of polymers,¹⁷ diffusion in porous structures, and stress calculations in materials.

Handshake methods describe the problem by identifying one area where continuum assumptions hold while focusing on atomistic or mesoscale models to solve another aspect such that these two regions influence each other. Dynamic fracture is a very good example.²¹ Energy from large-scale elastic fields is concentrated on the angstrom scale of the electrons that participate in atomic bonding. A simulation of this phenomenon requires an accurate description of atoms bonding at the crack tip and at the same time requires a proper description for very large volumes of strained material, the resolution varying with distance from the crack tip. Far away, it is adequate to use the equations of motion for a macroscopic-averaged continuum field. This spatial decomposition makes it possible to combine various simulation methods describing the different physical regions into a single, powerful simulation tool. Another example is the use of a handshake model to predict micelle free energies: An analytical solution suffices in the continuum assumption of the hydrocarbon core, whereas molecular simulations are required to understand the head groups and their interactions with the solvent.²² Alternatively, different molecular models may be used in different

regions. The combination of quantum mechanics (close to the docking site) and molecular mechanics (in the rest of the protein)(QM/MM) methods allows one to predict the behavior of molecules docking on proteins.¹³ Particular attention must also be paid to an accurate joining of the two regimes at the boundary region.

Today, a significant fraction of related literature is of model systems which explain trends and behavior of ball–spring models but are of little use in predicting the behavior of systems with specific chemistry. Although there is a growing effort to solve real systems of industrial importance, this certainly is an area of challenge requiring development in the modeling toolbox today.

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