Molecular Modeling

of Polymer Structures and Properties

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The Author:
Bruce R. Gelin, Custom Research and Consulting, 105–4 Trowbridge Street, Cambridge, MA 02138, USA

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Preface

While new theoretical and analytical methods are always sought after, their reduction to practice is often difficult, and a considerable space of time elapses before the new techniques are brought into widespread use. This has been especially true of the integration of computers into chemical research. This book concentrates on the topic of detailed atomistic modeling of polymer molecules and materials, with the goal of making this aspect of computer-aided chemical research more accessible to the large audience of polymer scientists.

A very considerable history of such molecular modeling already exists in other fields, most notably in bio/pharmaceutical applications. Small molecule modeling dates back to the 1960s, and major advances in protein modeling followed. The first calculation of the molecular dynamics of a protein was done in 1977, and shortly thereafter, the increasing availability of superminicomputers gave research departments a tremendous boost in their ability to pursue computational modeling. Now, the constant improvement in computing capabilities at all levels—personal computers, graphics workstations, and supercomputers—makes it possible for many individuals to have at their disposal levels of computational power unheard of a decade ago. The combination of experience in bio/pharmaceutical modeling and availability of powerful computers makes this an appropriate time to consider applying molecular simulation methods in other fields such as polymers and materials.

Many more chemists and scientists in other fields would use molecular modeling if it were less of a mystery to them. The goal of this book is to explore the application of molecular modeling to a particular field, namely polymer structures and properties. Detailed, atomistic modeling of polymers is not new; one of the first major simulations of the structure of an amorphous, glassy polymer was published in 1985 (see Ref. 64 in Sec. 4.4.3). Even this study of a static, equilibrium structure involved many points of modeling technique and significant computer resources. The scientist wishing to make a theoretical approach to more advanced problems such as thermal behavior and various physical properties might well be discouraged and dismiss the whole subject as hopelessly complex. Further, the scientist may be unsure of the applicability of the models, the computational requirements of the methods, and the quality of the results. Couple this with the less-than-friendly computing environment which is still all too prevalent, and it is not hard to see why polymer modeling is still generally regarded as the province of experts. This need not continue.

This book intentionally avoids questions of computer operations and programming. Computers and their operating systems change too rapidly, and are best covered by the manufacturer's documentation for each type of machine and operating

environment. As for programming, it is increasingly the case that scientists do not write their own programs—rather they work with large software packages prepared by others, including commercial organizations—and thus do not want nor need to become involved in software development. On the other hand, enthusiastic claims and marketing literature from the software developers sometimes makes it difficult for the scientist to know what to expect in terms of models, methods, and results. What the scientist needs to understand, and what this book covers, are the *models* and the *computational approaches* that are used to study different problems. Both of these, too, will be improved upon constantly as more scientists and companies pursue theoretical studies, but the basics covered here will always remain fundamental to an understanding of simulation approaches.

The method of this book is to explain the techniques in a general way first, followed by accounts of applications to certain areas. A number of simulations recently reported in the literature are used to illustrate the applications in Chapters 4 through 8. The first three chapters present the general idea of modeling as a simplification process, the development and classification of empirical force fields, and how they are applied to perform various basic calculations such as energy minimization and molecular dynamics. Chapter 3 uses a small molecule as an example to make the details of the energy function explicit. Chapter 4 is devoted entirely to the question of model building, since this is not simple for polymer systems, and has consequences for all further computations. Unlike small-molecule or protein modeling, where it is relatively easy to construct a trial molecular geometry or to use an X-ray crystal structure, polymeric systems do not consist of multiple copies of one prototypical molecule; rather there is a distribution of chain lengths, compositions, and conformations. The polymer model-building process itself can involve significant computations.

Chapter 5 concentrates on the characterization of polymer structure, as revealed by model-building and the simulations which follow. In Chapter 6 the deformation of the equilibrium structures is considered. Considerable information about deformation mechanisms is learned even from simple models of single polymer chains. This serves as a preface to simulations with more complex models. The subject of Chapter 7 is diffusion of small penetrants (e.g., gas molecules) within polymeric materials; related phenomena touched on include characterization of polymer surfaces as regards wetting, coatings, and interdiffusion across polymer-polymer interfaces, and the dynamics of energy transfer within polymers. Chapter 8 shows how mechanical models can be useful in the explanation of polymer electrical properties.

Aside from the necessary characterization of force fields and their operations, this book avoids mathematical treatments in favor of qualitative descriptions of the models and results. Ample mathematical background is available in the references, which are also recommended to those wishing to study the simulation methods in greater detail. This orientation reflects the goal of this book to make polymer modeling more accessible to scientists who may have been discouraged in the past by the apparent exclusion of the field to all but experts.

Computational polymer modeling is currently in a state of rapid development, and what is presented here as the start of the art is likely to be revised and superseded

before long. This book attempts to bring the reader to the point from which independent study and evaluation of the current literature are possible. If the book encourages scientists to approach molecular modeling with a critical understanding and realistic expectations, it will have served its purpose.

Bruce R. Gelin

In memoriam Victor M. Gelin (1909–1992)

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Introduction to Molecular Modeling

The purposes of this chapter are to provide a rationale for the use of modeling as a way of estimating polymer structures and properties, and to acquaint the reader with the spectrum of modeling methods available. We begin with a general discussion of modeling as a means of *structure-based design* of molecules. We differentiate between molecular properties and bulk properties, and discuss the role of rational design in the research process. The second part of this chapter considers the various levels of abstraction used in deriving models, and provides our first general view of the hierarchy of computing methods available.

1.1 Purpose of Modeling

Polymer research, like other basic scientific research, is complicated and expensive. Advances in instrumentation, methodology, and theory are always sought after, both for their fundamental scientific value and for their "economic" value, that is, for their ability to make research proceed more efficiently and effectively. The final goal of this research is to develop new materials, processes, products, and applications.

Experiments to learn the details of polymer structure, to measure polymer properties, and to try to establish relationships between the two, can be very time-consuming and expensive. The synthesis of a new polymeric material in laboratory quantities can require weeks of work by highly skilled scientists and technicians, while tying up expensive equipment and using scarce chemicals and catalysts. The analytical laboratory work needed to characterize the newly synthesized material is also expensive to obtain: property measurements vary greatly in complexity, but the total cost of the work, including sample preparation, set-up time of equipment and apparatus, the actual analytical procedure, and sample tracking and reporting, rapidly mounts into many thousands of dollars.

Given these considerations, it is worth investigating methods for property *prediction.* Even if not perfectly accurate, such methods could reasonably indicate whether it might be worthwhile to synthesize the material and do the analytical work; they could also suggest alternative structures to consider. Additional value can accrue

from integrating theoretical calculations with experimental programs. As results from both approaches are compared, insights into the structural and mechanistic basis of phenomena can contribute to better understanding of the material under development, and again suggest new formulations or treatments to improve its properties.

1.1.1 Goals of Predictive Methods

One aim of theoretical methods is to develop standardized procedures to compute structures and properties without synthesizing the actual material. That is, we wish to be able to start with an atomic-level model of a proposed polymer and use appropriate theory and calculations to predict its structural details and its material properties, and to use *design at the molecular level* to create a material with the desired properties [1].

This is a rational approach that has been carried out in some cases. For small molecules isolated in space, highly accurate theories which consider the detailed electronic structure are capable of producing the correct geometry and a number of properties of the molecule. If the molecule is flexible and has several geometric isomers, such theories can predict energy differences between the various states and thus tell which one is the most stable isomer. Energy barriers to transitions between states can also be calculated, permitting accurate estimates of the mix of populations and rates of interconversion at room temperature or any other temperature.

1.1.2 Molecular vs Bulk Properties

For some applications, the consideration of a single molecule surrounded by vacuum is a sufficient theoretical model to obtain the properties of interest. For example, the conformational properties, the heat of formation and other thermodynamic properties, the dipole moment, the polarizability and higher electrical moments, the steric and electrostatic fields, and the spectral properties of the molecule can be directly calculated (Fig. 1.1). Significant research effort is directed toward the perfection of methods for these tasks and their extension to new molecular systems.

In other cases, however, it is not solely the properties of one molecule that determine the behavior of interest. In the design of new drugs, for example, the drug molecule interacts with other molecules to trigger what may be a very complicated scheme of reactions and biochemical processes. It may be possible in some cases (or it may be necessary, when there is no information about the molecules with which the drug interacts) to develop improved drugs simply by considering the drug molecule or a series of similar molecules and attempting to correlate the desired activity with chemical structural features. But if structural information exists about the molecules with which the drug interacts, it may be very advantageous to use this information as part of the detailed molecular model of the drug's activity [2].

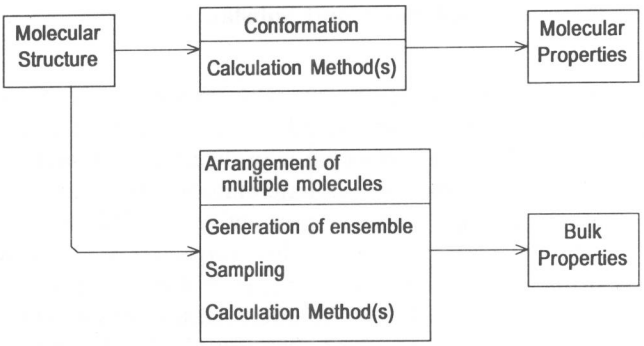

Figure 1.1. Computation of molecular and material properties.

In materials contexts, we are interested in the bulk properties produced by a large collection of molecules, because such properties are the basis of the economic value of the material. The bulk sample may consist of many identical copies of a single molecule, and these may be well ordered as in a crystal, or randomly ordered, as in a fluid or glass; see Fig. 1.2. The sample might also consist of mixtures of several or many different molecules. In the case of long chain molecules, the individual chains may be ordered as in a crystalline domain of an oriented polymer, or they may be very randomly intertwined to form a complicated amorphous network. Further, polymerization conditions usually produce a variety of molecular weights, tacticity, and main-chain branching patterns; these in turn affect how the molecules occupy space and thus what density, permeability, mechanical attributes, and other properties the bulk material will possess. In all of these cases, it is clear that the properties we want to predict must depend on the molecular properties of the component molecules, but the dependence is complex and also involves the arrangement of the molecules. The challenge is to calculate both the individual-chain properties and the bulk material properties.

Figure 1.2. Regularity and order in matter. Some materials consist of many identical copies of one molecule, well ordered as in a crystal (a), or in random relative arrangement as in a gas or fluid (b). Other materials consist of non-identical molecules, with some domains exhibiting a high degree of local order and others disordered (c).

1.1.3 Rational Design of Molecules and Substances

The interaction of molecular-level theory with experimental work in materials research takes two forms that have already been mentioned (see Fig. 1.3). One approach is to think of theory as an initiator in discovery research. In this point of view, the purpose of calculations is to evaluate materials that have not been created, with the goal of distinguishing the most productive possibilities from those which will not have the desired properties. The other approach is to consider theoretical work as part of an integrated program of theory and experiment. Here it is hoped that by providing a structural basis for the interpretation of phenomena, theory will help introduce a rational means for designing new materials. Simultaneously, each experiment serves as a check on theoretical predictions, and it is hoped that the two approaches will complement and strengthen each other.

Such structure-directed design has come to be known as *rational design.* Its proponents see applications in a wide range of research activities where the goals are reached by creation of new molecules and materials. These include at least the following fields: pharmaceuticals, agricultural chemicals, food and cosmetics, flavors and fragrances, polymeric materials, and inorganic materials such as solid catalysts, metals, and composites. The work is not limited to creation of completely new molecules — it also includes designing novel arrangements or aggregates of existing molecules, as well as interpreting the results of materials processing (orienting, annealing, crystallization, etc.).

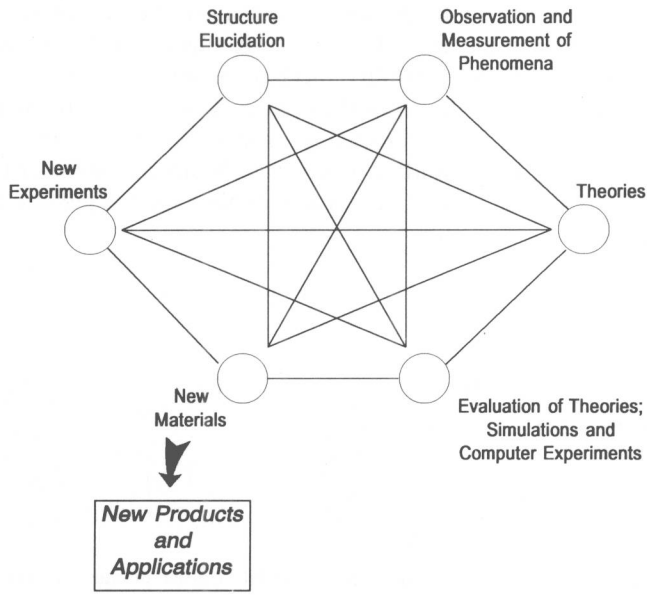

Figure 1.3. The interaction and integration of theory, calculation, and experiment in materials (and other) research.

1.2 Modeling as an Abstraction

Polymer systems are in general highly complex. In all but very specifically synthesized materials, the single chains vary in length (degree of polymerization), the chain compositions may vary in a regular or random fashion, and stereochemical centers along the chains may have regular or random orientations. Furthermore, in real materials many chains are involved, and they are in general not ordered; even in highly crystalline materials, there are usually also amorphous regions. How to treat this mixture of situations and estimate overall properties is a difficult problem. It is not a straightforward process to develop models that include all the material states and interactions present in the sample, and in the proper proportions. Also, models that contain sufficient variety and quantity of local structures may need to be very large and unwieldy.

Accordingly, the first principle of modeling is one of *simplification*, though the degree of simplification varies considerably according to the aspects of polymer structure studied, as discussed later in this chapter.

A dictionary definition of modeling states that it is the act or art of making a copy or imitation of an existing object; implicit is the idea of removing detail and complexity to facilitate concentration on some particular aspect of the object modeled. While the context of this book is computer modeling, it is useful to consider briefly some of the modeling that was done, both in chemistry and other fields, before computers were in widespread use.

1.2.1 Physical Models and Computational Models

A familiar example of modeling in industry is the building of a replica, or a scale model, of a complex manufactured object. For example, exact replicas of cars were built of wood, plaster, or other materials long before the design was committed to manufacturing. In this case, much of the purpose of the model was simply to view it and evaluate the design or aesthetic qualities; a solid model afforded only limited opportunities for making measurements, and evaluating operating characteristics was not possible. In the case of airplanes, scale models were important for wind-tunnel evaluations, a form of operational testing using a model. Nowadays, of course, large and increasing amounts of computer modeling are used in the automobile, aircraft, and many other manufacturing industries.

A somewhat light-hearted but illustrative view of physical modeling is given in Fig. 1.4. The "basic model" shown in the figure is one of the simplest problems in freshman physics, yet it captures much of the reality of the situation. A slightly better model, taking into account sliding friction and wind resistance, is also shown. Another amusing physical model was created from mousetraps and ping-pong balls to show how a chain reaction works [3]. An array of mousetraps is placed on the floor of a large room; each trap is cocked and has two ping-pong balls placed on it. To start the chain reaction, one ping-pong ball is tossed into the room. It hits a trap, sending

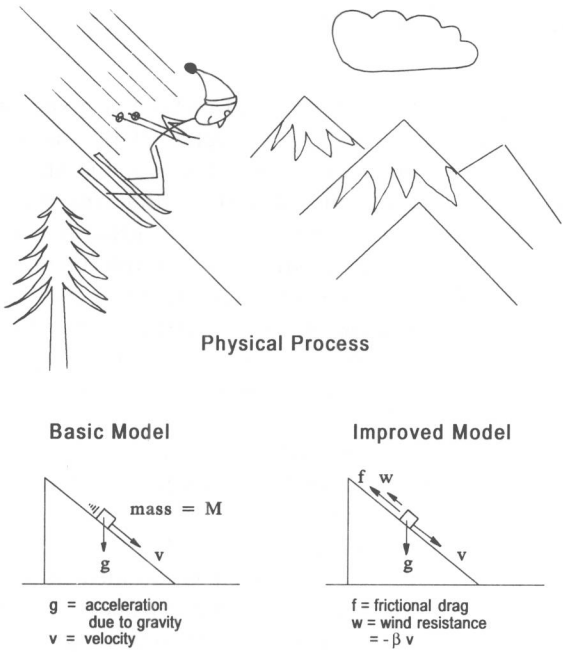

Figure 1.4. Abstraction and simplification make it easier to model physical processes.

its two ping-pong balls into the air; they land on two traps, springing up four balls; and so on. Eventually all the traps have been sprung and the "simulation" comes to an end.

In chemistry, solid models have played a very important role in helping scientists understand the three-dimensional nature and spatial relationships of molecules. The Corey-Pauling-Koltun models [4] are colored solid balls truncated and machined to interlock at the correct angles with the correct scale distances between centers. Numerous chemical researchers relied heavily on these models. One significant example is the Nobel Prize-winning work on molecular complexes by D.J. Cram [5] and others. Even earlier, custom-built models played a major role in Watson and Crick's unraveling of the structure of DNA [6].

But for all their utility, physical models have some disadvantages. Large structures are time-consuming and expensive to build, and they can be difficult to support physically, due to the weight of the model materials. Once such a large model is built, it may be nearly impossible to look inside it to see internal structures of interest. Modification, especially in the interior, could be difficult. While they are accurate representations of molecular structure and geometry, models are incorrect in other respects. They are not flexible, and do not undergo the vibrations that all molecules execute at any temperature. They do not represent nonbonded interactions, such as hydrogen bonds, van der Waals interactions, and electrostatic attractions or repul-