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Challenge in polymer physics*

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Abstract: One of the challenges in polymer physics is to predict the structure and properties of polymeric materials from their microstructures and processing conditions by integrating various theories and simulation methods. We have been involved in such a challenge through a governmental project involving computational modeling of polymeric materials. This article discusses how we tackled the challenge and describes the system we developed.

INTRODUCTION

Polymer physics in the 21st century has many challenges. Here, I discuss one challenge in which I have been involved—the computational modeling of polymeric materials, that is, modeling the behavior of polymeric materials by mathematical equations and then using it to predict the material properties by computer simulation. This is a natural extension of the computer-aided design (CAD) technology that has proven useful in many industries such as mechanical and electrical industries. Similar technology is strongly needed in materials manufacturing industries. Indeed, the term "computer-aided material (or molecular) design" has been used for many years, but the concept is difficult to realize, especially for polymeric materials.

The difficulty comes from the fact that the properties of polymeric materials depend on many factors, which range from monomeric to macroscopic level, such as monomer sequence, tacticity, short-chain and long-chain branching, molecular weight, molecular weight distribution, degree of chain orientation, degree of crystallization, and the states of the crystal-amorphous interfaces. The problem becomes even more difficult in the case of polymer blends or composites where the dispersion conditions and the interfacial structures change the material property drastically. Computational modeling of such complex systems is a challenge in physics and computational science.

From 1998 to 2002, we conducted a governmental project of computational modeling of polymeric materials. Here, I discuss how we tackled the problem and describe the system we developed.

SEAMLESS ZOOMING PROJECT

Aim of the project

The aim of our project is to construct a computer simulation system that bridges the microstructural (or molecular) characteristics of polymeric materials with their macroscopic properties. Ideally, the system we would like to have is one by which we can "zoom in" to the internal structure of the target material at any length scale, and see and test the phenomena occurring there by computer simulation. We called this a "seamless zooming" system. It is easy to envision such a system, but the question is how to realize it.

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Design problem

Clearly, the "seamless zooming" system requires two components. One is a set of programs that can simulate the phenomena at various length scales, and the other is a mechanism for integrating such simulation programs.

Designing such simulation programs is not a simple task, but the objective of the task was clear. Polymer physicists have proposed many theories and have written many programs to model the dynamics of polymers at various length scales. These programs are written for research purposes only and are not in a form to be used by other people. Our task was to make these theories and simulation programs available to general users. We called the simulation programs "engines" since their role is to repeat calculations many times. We chose to build four engines corresponding to the typical methods used in polymer physics, i.e., molecular dynamics, reptation dynamics, self-consistent field theory, and various continuum models. The detail of the functions of these engines will be described later.

The difficult part of the design problem was how to integrate such engines. It is not enough to build these engines separately. We needed some software that integrates these engines and supports the activity of zooming. The software was called the simulation platform. The difficult part is the design of the simulation platform.

Zooming is a procedure of going from one engine to the other engine which deals with the phenomena of different length scale. Conceptually, this operation is possible. "Zooming out" can be done by coarse graining (i.e., by reducing the information of the system by some statistical averaging), and "zooming in" can be done by generating microstructures based on the local equilibrium assumption. However, the computational implementation of such an idea is not easy. The difficulty has two origins—the first is a software design problem, and the second is a physics problem.

The software design problem involves how to let different engines share information they have. To do zooming, different engines have to share physical information on the materials, such as monomers, degree of polymerization, branching type, etc. To achieve this, we first tried to set a terminology specialized for polymers: we tried to define data structures for typical terms used in polymer science (such as "monomers", "polymers", "block-polymers", etc.), but this approach turned out to be impossible. The engines are based on different physical models and have different views for the definitions of "polymers". Settling the terminology was difficult, and settling the data structure was even more difficult. After long discussions, we realized that even if we were able to invent some data format, nobody would be happy, and nobody would use it.

The problem of physics is how to ensure the validity of the zooming procedure. Zooming depends on some theoretical models, and their validity must be studied in the scientific community over a long time. We can propose certain ways of zooming, but they may not be correct, or there may be better ways. Different people will have different ideas for zooming. Our software must be independent of the way of zooming.

These problems made us think that our system must be open and flexible. As it is clear that "seamless zooming" is a grand challenge, we thought that we should develop software that will grow and expand after our project ends. Therefore, the integration must be done not by force, but by voluntary collaboration. This made us think that it is quite important to set up a framework for such collaboration. In fact, we realized that the collaboration of various simulation programs is not easy even within a group of people working together, especially at the stage of development, where the data structures are constantly changed as more functions are added to the programs.

Thus, we had a dilemma. To ensure the flexibility of the system, we wanted to remove any constraints for the engine programmers. On the other hand, we had to impose some constraints for them in order to set up a framework of collaboration.

User-definable format

To resolve the dilemma, we invented a data format called UDF (user-definable format) [1]. The basic idea of UDF is that simulation programmers can determine the structure of the input and output files of their programs, but they should state it in a certain format. UDF thus consists of two parts—structure description and data. Figure 1 shows a very simple example of the UDF file.

The part between \begin{def} and \end{def} is the structure description part, which defines the name, type, and unit of the data. This simple example shows an input file of a program that calculates the trajectory of a ball thrown in the air. The program needs gravity and the initial conditions as you can see in the UDF file. The actual data is written between \begin{data} and \end{data}. From this definition, one can understand that the number 3.0 written after "initial_condition:" has the name "initial_condition.vx" and represents 3.0 [m/s].

This is a very simple example, but it illustrates the essence of the UDF file. The structure description part has other options to express the logical structure of the data, but the most important thing is to give names and units for each data item. Due to the structure description part, all data (or numbers) in the UDF file have their own names and can be quoted by their names. In fact, the UDF file is a kind of database file; any data in the file can be read or rewritten in any order.

To encourage people to use UDF, we made program libraries to read and write the data in a UDF file by C and Fortran programs. We also made a program called a simulation platform, which handles the UDF file in a graphical way. With this program, users can browse, edit, and process the data, extracting certain information from one engine and transferring it for other engines. This provides a base for the collaborative operation of various simulation programs, which is the starting point for our challenge of seamless zooming. The details of this program will be explained later.

```
\begin{def}
    gravity: float [m/s^2]
    initial_condition:{
            vx: float [m/s]
            vy: float [m/s]
            vz: float [m/s] }
\end{def}
\begin{data}
    gravity:9.8
    initial_condition:{3.0,10.0,3.0}
\end{data}
```

Fig. 1 An example of UDF.

OCTA SYSTEM

The system we developed is called OCTA (Open Computational Tool for Advanced Material Technology) [2,3]. It is open and free; the programs, source codes, and manuals can be downloaded at <http://octa.jp>. Figure 2 shows the overall structure of the OCTA system. OCTA consists of four simulation engines (COGNAC, PASTA, SUSHI, MUFFIN) and a simulation platform (GOURMET). These programs are explained in the following.

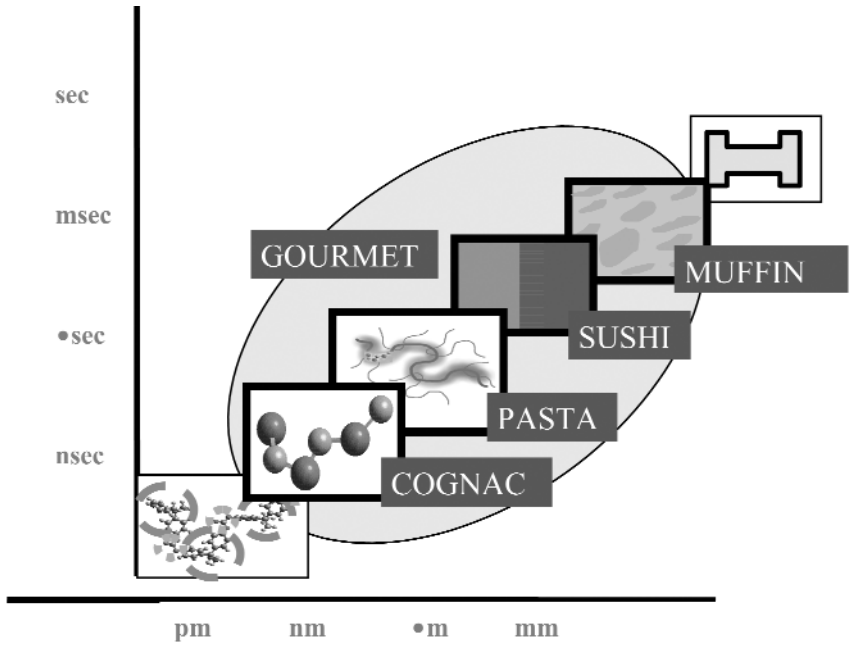

Fig. 2 The OCTA system.

Simulation engines

Coarse-grained molecular dynamics simulator, COGNAC

COGNAC (Coarse-grained Molecular Dynamics program by Nagoya Cooperation) is a general molecular dynamics simulation program that covers a large class of molecular models, ranging from full atomistic models to bead-spring models [4]. Many potential functions used in coarse-grained models such as Lennard-Jones, Gay-Berne, and Coulombic potentials are available, and new potential functions can be implemented easily. COGNAC can deal with various conditions such as under constant temperature, under deformation (elongation and shear), and under external fields. COGNAC has a special function, called zooming, which generates the equilibrium molecular configuration for a given density profile of atoms.

Rheology simulator, PASTA

PASTA (Polymer Rheology Analyzer with Slip-link Model of Entanglement) is a stochastic simulation program that calculates the rheological properties of polymeric liquids of polydisperse linear and star polymers [5]. For given molecular weight distribution, the program calculates the stress response for any history of deformation (shear and elongation). The program is based on the slip-link model, in which polymer molecules interact only through the creation and release of binary entanglements. The three important relaxation mechanisms (i.e., reptation, contour-length fluctuation, and constraint release) are taken into account.

Interface simulator, SUSHI

SUSHI (Simulation Utilities for Soft and Hard Interfaces) calculates the equilibrium and nonequilibrium structures in polymer blends and block copolymers by solving the self-consistent Edwards equation [6]. SUSHI can deal with a variety of polymers—linear polymers, branched polymers with any topology, copolymers with any monomer sequence (block, random, tapered random) and the polymers grafted on solid surfaces. SUSHI can be used to study the surface modification caused by polymer grafting or adsorption, and the self-assembly of block polymers (micellar formation).

Multiphase simulator, MUFFIN

MUFFIN (MUlti-Farious FIeld Simulator for Nonequilibrium Systems) is a general solver for the continuum models for the dynamics of soft materials based on finite difference method (FDM) or finite element method (FEM). MUFFIN includes six packages—Elastica, ElaDyna and GelDyna [7], Electrolyte, MEMFluid, and PhaseSeparation—and can deal with various problems in soft materials, such as the elasticity of multiphase materials, swelling and de-swelling of gels, ion transport in charged colloids, reaction and diffusion in narrow channels, phase separation and droplets deformation in shear and electric field. MUFFIN can take the multiphase structure obtained by SUSHI and calculate various properties such as the effective elastic modulus of the system.

Simulation platform

GOURMET

GOURMET is the simulation platform of the OCTA system [1]. It is a work space for making the input file and analyzing the output file. The user can browse and edit the UDF file, process the data by script language, do plotting, and make 3D animations. Also, the user can use GOURMET to run simulation engines; the user can start simulation engines, monitor certain parameters, and handle the engines interactively.

Figure 3 shows how the UDF file shown in Fig. 1 is handled by GOURMET. Users can see the data structure and the data as it is seen in the top left of the figure. Users can write simple scripts as shown in the bottom left of the figure. This script calculates the trajectory of the thrown ball and displays it in 3D graphics (top right). Other simple script can do plotting the trajectory.

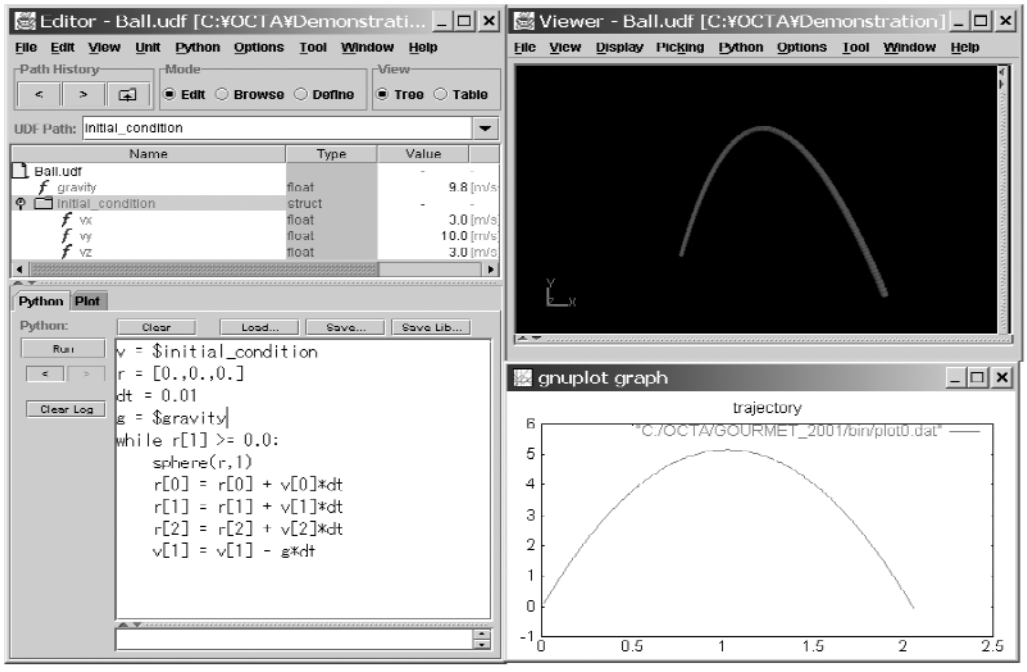

Fig. 3 Viewing the UDF file shown in Fig. 1 by the simulation platform (GOURMET).

Figure 4 shows an example of the user interface of GOURMET for the UDF file used by the molecular dynamics program (COGNAC). The molecular dynamics program needs many data items, such as the molecular structure, interaction potential, simulation condition, and initial configurations. Such

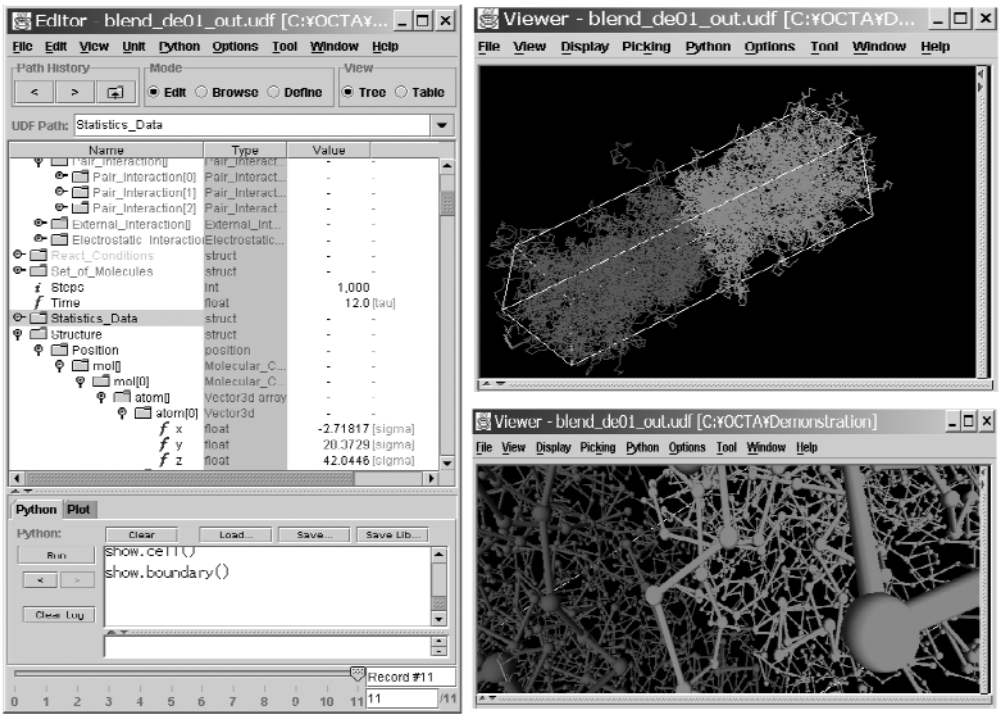

Fig. 4 Viewing the UDF file used in the molecular dynamics program (COGNAC) by the simulation platform (GOURMET).

complex data is shown in a structured way as seen on the left part of the figure. The right part of the figure shows an example of the 3D graphics of the current molecular configuration. Users can display all molecules or selected molecules by simple script. Users can also see the time evolution by moving the slide bar. Notice that the serious simulation program such as COGNAC can be operated by the same interface as that for the simple program for the thrown ball.

COLLABORATIVE OPERATION OF ENGINES

The platform can be used as a base for operating various engines collaboratively. Such activity may be regarded as a prototype of zooming, namely, going from one level of description to the other. In our project, we made several prototypes of zooming. Here, I describe just an example, which is to predict the mechanical properties of block polymers [8]. Other applications can be seen in the home page of OCTA.

Block polymers form various micro domain structures of lamellar, cylindrical, spherical, and bi-continuous forms. These structures depend on many parameters such as the monomeric characteristics (the so-called chi parameter, bond length, specific volume, etc.), the connectivity of the blocks, and the mixing ratio, etc. Predicting the equilibrium structure by molecular dynamics alone is practically impossible since the ordering takes place in an extremely large time scale (ca. 10^3 s) compared with the characteristic time scale of molecular dynamics (ca. 10^{-12} s). To overcome the difficulty, we first used the interfacial engines (SUSHI) to calculate the spatial distribution of monomer density at equilibrium. We then passed this information to COGNAC and generated the equilibrium configuration of polymer chains. An example is shown in Fig. 5. We then calculated the stress-strain curve of the block-copolymers by molecular dynamics (Fig. 6), and studied the structural change taking place during the elonga-

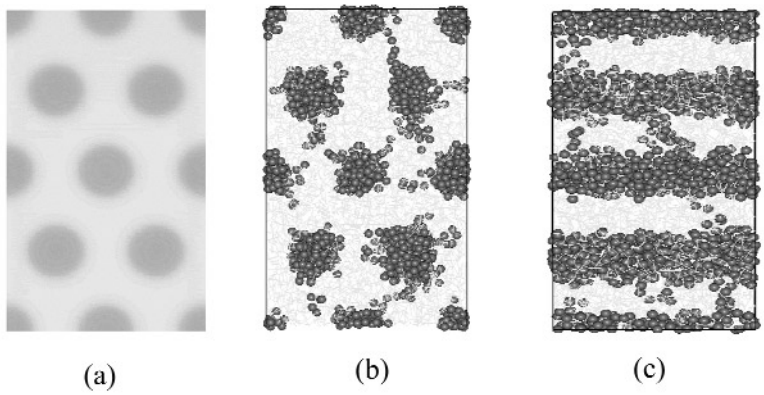

Fig. 5 Cylindrical microphases of ABA tri block polymers. (a) Structure obtained by the self-consistent field calculation; (b) and (c) Corresponding.

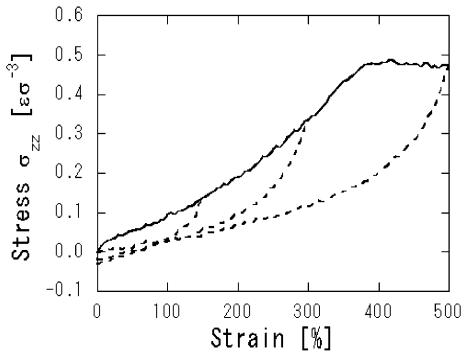

Fig. 6 Calculated stress-strain curve for the spherical microphase of ABA tri block polymers.

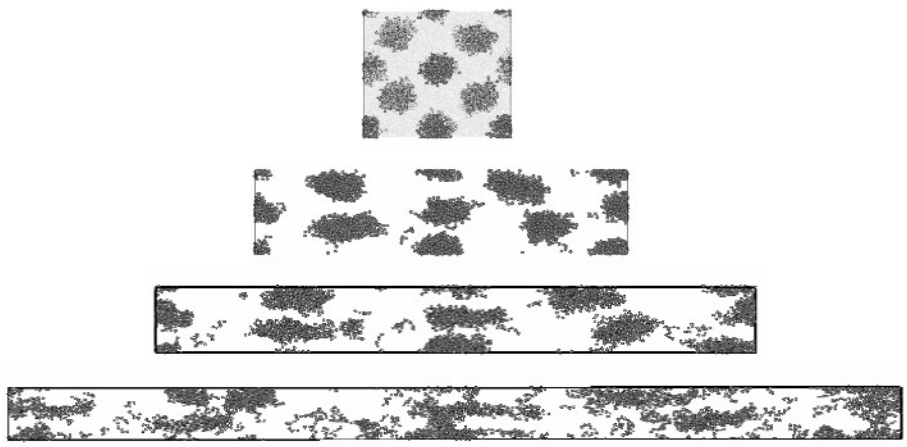

Fig.7 Structural change of the microphase of ABA tri block polymers under elongation. The elongational ratio is 1,2.5,4,6 from top to bottom.

tion (Fig. 7). We can also study the permeability of gas molecules through such structures using the function of MUFFIN.

CONCLUSION

The challenge I discussed here is to bridge the microstructural characteristic of polymers with their material characteristics by theory and simulations. The idea of "seamless zooming" is easy to envision, but very difficult to achieve. In striving toward the objective, we realized that what is actually needed to this end is to integrate various theoretical models in a form available to general users. The OCTA system is a prototype.

In OCTA, the operation of zooming is entirely left for users. We did this deliberately as we believe that the "zooming" is an operation that needs deep understanding of the problem, and that much validation work needs to be done before the operation is automated. Users can customize the system to do automatic zooming. If such experience is accumulated, the seamless zooming will be a reality. Seamless zooming is difficult to achieve, but it is not impossible to achieve.

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