Dynamics of Materials Processing at the Molecular Scale

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Abstract—Stochastic simulations based on nonequilibrium statistical mechanics describe the interactions among many discrete atoms or molecules, and thus describe the dynamics of materials processing in applications ranging from inorganic crystalline films to amorphous polymer melts. In general, nonequilibrium thermodynamics does not yield a closed, low-dimensional dynamic equation, although such a model would be desirable to analyze the dynamics and to optimize and control the process. An approach is described here in which targeted simulations are combined with systematic tools to elucidate the dynamics in a computationally tractable manner.

1. Introduction

Molecular simulations can be divided into catagories that include molecular dynamics, molecular mechanics, and Monte Carlo simulations, and all describe the interactions among many discrete atoms or molecules [1, 2, 3]. These simulations provide predictions of material structure and properties based on known interactions among the atoms. Describing long simulation times for processing dynamics is difficult with molecular dynamics because the time scales of atomic vibrations must be resolved, but Monte Carlo simulations can provide predictions over macroscopic time scales. For that reason the examples in this work are modeled using Monte Carlo simulations. Although molecular simulations can be computationally intensive, they are needed because closed form low-order equations are generally not provided by nonequilibrium thermodynamics [4].

One important issue in this presentation is to define the state of the system. In a molecular dynamics simulation, the state is the position and momentum of each particle, while in a Monte Carlo simulation it based on the spatial position only. However, because the simulations and their initial conditions are stochastic, two simulations run under nominally the same conditions will yield completely different *states*. A more physically meaningful way to characterize the simulations is through overall system statistics like densities and distributions. The simulations provide predictions for such quantities, but the differential equations and simulation algorithms are not expressed in terms of them.

Analyzing the dynamics of molecular simulations is difficult because the simulations are computationally intensive and stochastic and they do not have a well-defined
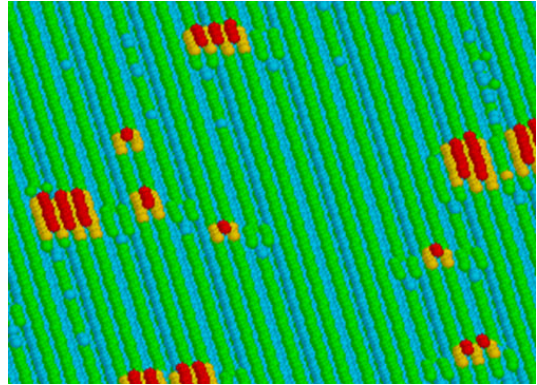

Figure 1: A Monte Carlo simulation of gallium arsenide film processing.

state. One approach to dynamic analysis and systems engineering is that of equationless computing, in which derivatives are computed as they are needed from the detailed simulation, after postulating a low-order state based on physical quantities of interest [5]. The approach described here has the goal of automating the process of finding the state and of constructing an *explicit* dynamic model, using simulation data to identify the state and the model.

2. Examples

A goal of this research is to develop general methods for dynamic modeling that apply in a wide range of molecular simulations. We focus on materials processing applications that are characterized as batch processes. In continuous processing, linearized models are often sufficient for controller design, but in batch processing, nonlinear models are required that describe a range of states and operating conditions. Two examples of batch processes are discussed in this section: thin film processing and polymer reaction engineering. Results are then presented for the thin film application.

2.1. Thin film processing

Gallium arsenide is one of many III-V semiconductor compounds that are used in high-performance optoelectronic devices for fast communication. Detailed Monte
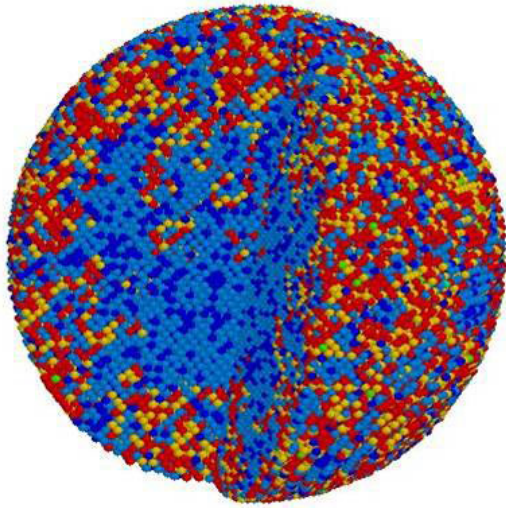
Figure 2: Polymer colloid processing. The particle is 100 nm.

Carlo simulations have been developed to describe the surface evolution during thin film deposition of GaAs, using scanning tunneling microscopy measurements and density functional theory computations. We use the model of Itoh and co-workers here [6]. Figure 1 shows a Monte Carlo simulation of film evolution. The initial surface structure has regular trenches, and as Ga is deposited, clusters form in and on top of the trenches. The clusters then split after reaching a width larger than the intertrench distance. This model system was chosen for our study due to its complicated surface structure and the past research in developing the detailed model.

2.2. Polymer colloids

A second example we are studying is particle evolution in polymer colloid processing. One of our simulations is shown in Figure 2, as motivated by Chern and Poehlein [7]. While the surface area of an actual GaAs film is macroscopic, the polymer particles have nanometer scale dimensions. This distinction becomes important in analyzing the dynamics. A deterministic model may be desired for the film roughness, while a probabilistic model may be required for particle size distribution.

3. Approach

The goal of this work is to develop general and automated methods to represent the dynamics of molecular simulation in a compact manner. We divide this work into two steps—identification of the state and development of a dynamic model.

3.1. Identification of state

Although the goal is to develop systematic methods, it is unrealistic to think that no physical understanding would be needed (especially in *developing* the approach). Spatial correlation functions are often used to describe densities and distributions in molecular simulations, and we use this perspective here. Instead of using spatial *positions* to describe the current state of the system, a spatial *correlation* function should be used that captures the spatial relationship between material structures of interest. In the GaAs film simulations, the surface structure is of interest, so we characterize the surface by a step-step correlation function. It describes not only the number of surface steps, but also the distribution of distances between steps. Our hypothesis is that the spatial correlation function does uniquely specify the state of the system. However, this representation is high-dimensional and noisy. Additionally, no dynamic equation exists to describe the evolution of this state.

Systematic tools are applied to search for a reduced representation for the spatial correlation function. As a first step, principal component analysis is used. Because the dynamics are highly nonlinear, the coordinate dimension may not be optimally embedded in a linear subspace of the spatial correlation function. However, due to the extremely high dimension of the correlation functions (almost 2000 in our example), principal component analysis is used to reduce the dimension down to a level that is tractable for other tools.

Two additional tools we have applied are nonlinear principal component analysis (NLPCA) [8] and self-organizing map (SOM) [9]. NLPCA is used to search for nonlinear manifolds which contain the data, and can be implemented using autoassociative neural nets. The methods must be trained in an iterative procedure, but then provide an explicit coordinate map between the high dimensional space and the reduced-dimensional manifold. An application of NLPCA is presented in [10]. Self-organizing map is another approach that uses training data to identify structure in high-dimensional data. The dimension of the map is typically two-dimensional, with the data projected from the original higher dimension. The training data is organized by the map such that similar snapshots are nearby on the two-dimensional surface. In contrast to NLPCA, no explicit coordinate map is provided by SOM.

3.2. Dynamic modeling

Several approaches are possible in constructing a compact dynamic model. The molecular simulations do not necessarily provide any clear mathematical structure for the model, and one approach is black-box nonlinear system identification. The molecular simulations can be used as the *experiment*, with coefficients in the dynamic model estimated using this data. This is a research direction of interest to us, with results presented elsewhere [12].

An alternative approach is to exploit the reduced-order

state representation and construct a vector field at discrete positions in this space. In constructing such a vector field, one must establish the type of dynamic model that is desired. Should the space be discrete or continuous? Should time be discrete or continuous? Should the model be stochastic or deterministic? The examples of Section 2 motivate the importance of the later choice. Although molecular simulations are inherently stochastic, the noise might be viewed as an artifact due to the finite simulation domain (film growth) or it may be an important part of the dynamics due to the small physical dimension (polymer colloid particles).

Cell-to-cell mapping provides a framework in which to model dynamics that are discrete in space and time [13]. The space is discretized into cells, and simulations are performed beginning in each cell, over some period of time. A deterministic model may be created if each cell is mapped to one cell only, while a Markov chain [14] is computed if a cell is mapped to multiple cells with nonzero probabilities. An application of Markov models to molecular simulations has been presented by one of the authors [15], in which the space is discretized, and in which time may be either continuous or discrete.

4. Results

Results are presented here for the application of principal component analysis and self-organizing map to the gallium arsenide film processing example. Although this study is primarily associated with the identification of the reduced state, the SOM procedure organizes the state space into typical surfaces or groups, which can then be used as the cells in a cell-to-cell map.

The first step is to select a spatial correlation function to represent the surface. Because the surface (pictured in Figure 1) is dominated by atomic height steps, we describe the surface in terms of the number of steps and the distances between the steps. Because the surface is anisotropic, the distances between steps on this 120x120 site surface must be computed separately in the directions along the trenches and perpendicular to them. The resulting step-step correlation (SSC) function has a dimension of 1920. A portion of a step-step correlation function is shown in Figure 3. The peaks represent common surface features, such as a typical cluster size represented by an up-step followed by a down-step at some distance.

Ten simulations are performed and averaged for each snapshot to reduce the effect of noise. Simulations are performed up to a deposition of 0.20 mL, with snapshots taken at increments of 0.01 mL. Simulations are also performed over a range of gallium deposition rates, from 0.06 to 0.20 mL/s. The SSC functions for the resulting 161 snapshots are combined in a single PCA analysis, yielding six dominant modes of the SSC. The six mode reconstruction is shown in Figure 3 along with the original SSC. The PCA reconstruction matches the original well, and additionally
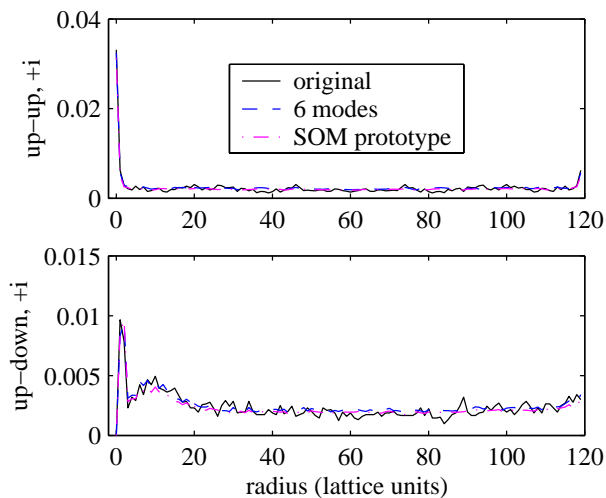

Figure 3: Reconstruction step-step correlation function of one snapshot (flux of 0.16 mL/s at 0.20 mL deposited). The original SSC is obtained by averaging over 10 realizations.

appears to have a positive effect of smoothing out noise.

The PCA procedure thus reduced the dimension from 1920 to 6. This six-dimensional state is then used to train the self-organizing map. After the training, each of the 60 map nodes has a prototype vector representing a typical SSC function. Each snapshot is matched with some prototype vector, and snapshots that are matched to the prototype vector are then considered to be in the same *group*, or cell. Figure 3 also shows the prototype vector for the snapshot, which is difficult to distinguish in the figure due to the similarity between the snapshot and the prototype vectors.

A second comparison is made in Figure 4. In this Figure, a prototype vector for one of the SOM nodes is compared to the two snapshots that were matched to it. These snapshots are thus viewed to be in the same group, because their surface features are similar. Note that they were generated under the same gallium flux (0.20 mL/s) and that they are associated with adjacent coverages of 0.18 and 0.19 mL, so it is physically realistic that they would be grouped together.

5. Conclusions

This presentation describes a general approach to understanding and modeling process dynamics from molecular simulations. Spatial correlation functions are first used to describe the state of the system, and then systematic methods are used to search for low-dimensional dynamics. A low-dimensional representation then enables the brute-force construction of a vector field or cell-to-cell map on the state space, using the molecular simulations to construct the vector field. The computational feasibility of the method has been demonstrated in a few preliminary examples. Further work continues on assessing the tractability of
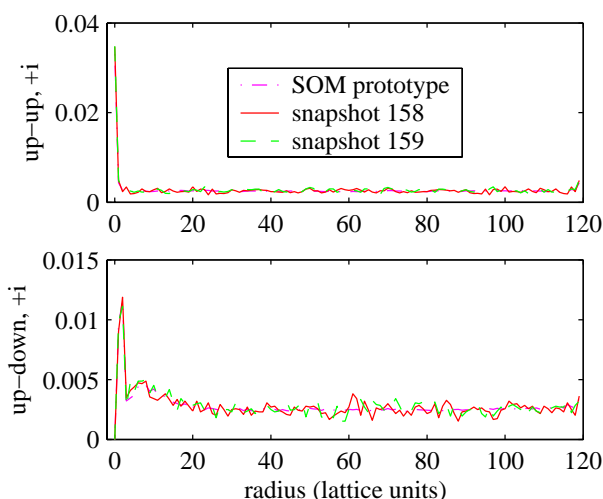
Figure 4: Step-step correlation functions of two snapshots that are matched to the same SOM prototype vector. The original SSC functions are the average over 10 Monte Carlo simulations. A flux of 0.20 mL/s was used for both snapshots, with coverage levels of 0.18 and 0.19 mL.

the method and its general applicability in molecular simulations.

Acknowledgments

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