Final Report for Award #ER25586
Integrated Multiscale Modeling of Molecular Computing Devices
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1 Progress Summary

This report outlines results for Award #ER25586, "Integrated Multiscale Modeling of Molecular Computing Devices." In summary, this grant has supported two postdocs, six publications, and seven presentations at meetings, all of which are listed in Section 2. The general theme of this research has been to expand the capabilities of a simulation technique, Kinetic Monte Carlo (KMC) and apply it to study self-assembled nano-structures on epitaxial thin films. KMC simulates thin film growth and evolution by replacing the detailed dynamics of the system's evolution, which might otherwise be studied using molecular dynamics, with an appropriate stochastic process.

One of the principal aims of this work has been to include off-lattice effects in KMC simulations. A specific motive for the off-lattice KMC work is an atomistic study of the Asaro-Tiller-Grinfeld [7, 8] instability, in which misfit stress leads to the formation of a pattern of bumps on the surface of a heteroepitaxial film (a crystalline film of one material grown on a crystalline substrate composed of a second). When the resulting surface structures are sufficiently small, they are often referred to as "quantum dots" due to the hope that they may be useful for electronic applications that exploit their size in a quantum mechanical fashion. Much of the work on this subject is continuum based, but there is much to be gained from atomistic simulation if it can be done efficiently. In a broader context, incorporating elastic effects into KMC simulations in a way that retains the simplicity and speed of the basic method has emerged as a central challenge in the KMC community. Both the quantum-dot problem and other problems that involve significant elastic deformation of a crystal require some relaxation of the one of the fundamental assumptions many KMC models for crystal growth are based on: Atoms can only occupy predetermined lattice positions.

My initial attempts to address this issue were in collaboration with Weinan E (Princeton), who is a co-PI on this project, and my first postdoc Weidong Guo. We have recently published a paper "Simulation of Impurity Diffusion in a Strained Nanowire Using Off-lattice KMC," *Communications in Computational Physics* **2** (2007) 164-176 [9]. In this work, collections of atoms interact via two-body empirical potentials, as they do in many molecular dynamics simulations, but are only allowed to occupy states that are, to a good approximation, minimizers of the potential in the configuration space. The rates for transitions between states are determined using the harmonic approximation to transition state theory [10], by the finding approximate locations of saddle points that separate minimizers. Locating minimizers and saddle points of the potential is computationally expensive. To make large scale computation feasible, we chose to examine a system where the locations of these points in configuration space would be close to their positions in a perfect lattice. Specifically, we examined interstitial diffusion in a weakly strained geometry.

In a more recent attempt to address the quantum-dot problem, I have begun a collaboration with Peter Smereka (Michigan), who had been working on this problem using a model put forward earlier by Lam, Lee and Sander [11, 12]. In this model, the interactions between atoms are modeled using an array of linear springs that attempt to restore atoms to their equilibrium configuration. In this approach, one tracks the displacement of atoms from equilibrium rather than allowing an arbitrary off-lattice configuration, interactions are nearest-neighbor, and neighbors are pre-defined. Together with a simplifying assumption that transition state energies for single-atom moves correspond to system energies with the atom removed, one is able to substantially reduce the computational

complexity of the problem. My role in this work has been principally aimed at a method for locally updating the elastic configuration when a single atom is either removed or moved to an adjacent lattice site. We completed a paper "An Energy Localization Principle and its Application to Fast Kinetic Monte Carlo Simulation of Heteroepitaxial Growth," Journal of the Mechanics and Physics of Solids 57 (2009) 521 - 538, that presents a remarkably efficient algorithm for doing this. The algorithm relies on a surprising theorem that allows one to obtain very accurate estimates of energy differences based on local calculations.

In a third approach to introducing off-lattice effects into KMC simulations of crystal growth, I have been collaborating with Shaun Hendy (Industrial Research Ltd. and Victoria University, Wellington NZ) and his student, Peter Zoontjens, on combining lattice-based KMC simulations with molecular dynamics (MD) simulations in a spatially decomposed, hybrid simulation. This project was motivated, in part, by some earlier work I had done on hybrid simulations that coupled KMC to continuum models for crystal growth [13, 14]. In this work, we have focused on the competition between face centered cubic (FCC) and hexagonally close-packed (HCP) packings on an FCC facet of a growing/evolving crystal. It is possible for both types of packings to nucleate on an existing layer. When these grains impinge upon one another, they meet up in a way that leaves a gap that neither lattice type can fill. Our simulations use MD to simulate the region surrounding such gaps and KMC to simulate regions that are well separated from such gaps. In order to do this, considerable effort has gone into developing KMC simulations that can accommodate both FCC and HCP lattices. We have published this work in a paper "Hybrid Method for Modeling Epitaxial Growth: Kinetic Monte Carlo plus Molecular Dynamics," *Phys. Rev. B.* **76** (2007): Art. No. 245418 [15]. In a developing collaboration with Shaun Hendy, Art Voter (Los Alamos) and his postdoc Abhijit Chatterjee, we are planning to perform a hybrid KMC-accelerated MD simulation of screw-dislocation mediated epitaxial growth, where the dislocation core is simulated with accelerated MD techniques developed by Voter's research group.

Returning to the theme of producing thin films with self-assembled patterns, a final activity related to this project has been to examine patterns that form during continuous coating processes. In earlier work supported by this grant, I examined patterns resulting from step-edge meandering instabilities [16] and published a paper "Morphological Instability during Directional Epitaxy," *Journal of Crystal Growth* **295** (2006) 188-201 [17]. In this paper I examine the role of both Erlich-Schwoebel barriers [18] and imposed deposition gradients in producing meandering instabilities in monolayer films using both KMC and a linear stability analysis of a the Burton-Cabrera-Frank (BCF) [19] continuum model. Together with a new postdoc, Mike Saum, I have more recently extended this work to look at multi-layer growth. This work, "The Role of Processing Speed in Determining Step Patterns during Directional Epitaxy," has been published in *Discrete and Continuous Dynamical Systems B.* Mike Saum and I continue to work on pattern formation by self assembly during epitaxial growth. Most recently, we have collaborated with Christian Ratsch (IPAM) where we applied some of our new KMC algorithms to restudy a pattern formation problem that Ratsch had previously explored using level-set based simulations of the BCF model. This work was published as: M. Saum, T.P. Schulze and C. Ratsch, "Inverted List Kinetic Monte Carlo with Rejection applied to Directed Self-Assembly of Epitaxial Growth," Communications in Computational Physics 6.(2009).553 - 564.

2 Students/Postdocs, Publications, Presentations

2.1 Students/postdocs supported by this grant:

1. Postdoc Dr. Weidong Guo from January 2004 through June 2005
2. Postdoc Dr. Mike Saum from August 2006 through June 2008

2.2 Publications supported by this grant:

1. T.P. Schulze, "Morphological Instability during Directional Epitaxy," Journal of Crystal Growth. 295 (2006) 188-201.
2. W. Guo, T.P. Schulze and Weinan E, "Simulation of Impurity Diffusion in a Strained Nanowire Using Off-lattice KMC," Communications in Computational Physics. 2 (2007) 164-176.
3. P. Zoontjens, T.P. Schulze and S.C. Hendy, "Hybrid Method for Modeling Epitaxial Growth: Kinetic Monte Carlo plus Molecular Dynamics," Phys. Rev. B. 76 (2007): Art. No. 245418.
4. M. Saum and T.P. Schulze, "The Role of Processing Speed in Determining Step Patterns during Directional Epitaxy," Discrete and Continuous Dynamical Systems B. 11 (2009) 443–457.
5. M. Saum, T.P. Schulze and C. Ratsch, "Inverted List Kinetic Monte Carlo with Rejection applied to Directed Self-Assembly of Epitaxial Growth," Communications in Computational Physics 6.(2009).553 - 564.
6. T.P. Schulze and P. Smereka, "An Energy Localization Principle and its Application to Fast Kinetic Monte Carlo Simulation of Heteroepitaxial Growth," Journal of the Mechanics and Physics of Solids. 57 (2009) 521 - 538.

2.3 Presentations supported by this grant:

1. PI Schulze, invited presentation, workshop on "Nanoscale Material Interfaces: Experiment, Theory and Simulation," National University of Singapore, November 2004.
2. Postdoc Weidong Guo, poster presentation, the AICHE Annual Meeting, Austin, November 2004.
3. Postdoc Weidong Guo, contributed talk, SIAM Conference on "Computational Science & Engineering," Orlando, February 2005.
4. PI Schulze, invited presentation, IPAM Multiscale Analysis & Computation Workshop, IPAM, Univ. of California, Los Angeles, November 2005.
5. PI Schulze, invited presentation, IPAM "Bridging Time & Length Scales in Materials Science & Bio-Physics Reunion Conf.," Lake Arrowhead, June 2007.
6. Postdoc Mike Saum, contributed talk, 6th International Congress on Industrial & Applied Mathematics, Zurich, July 2007.
7. PI Schulze, 6th International Congress on Industrial & Applied Mathematics, minisymposium, Zurich , July 2007.

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