

Molecular Dynamics Simulation and Visualization

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Abstract

We have developed atomic-scale material models capable of melting, crystallization and amorphization. These models feature molecular dynamics governed by Langevin equations of motion in which particle interact through attractive covalent forces and short-range repulsion forces. Also, we present an interactive virtual visualization tool for the simulation of atomic scale material behavior. An application of this research is to understand the processes that can control the quality of a single-crystal Si grown from the melt.

1. Introduction

The quality of a single-crystal Si grown by Czochralski method [1] from melted silicon (see Fig. 1) is sensitive on the growth conditions such as crystal growth rates and temperature gradients at the liquid/crystal interface. Production of high quality crystal Si requires understanding of the growth mechanism on the atomic level. One of the experimental techniques is transmission electron microscope which gives direct images of atomic structures of crystals. However, preparation of samples for electron microscopy is a long process. In the approach described herein, the molecular dynamics simulation for large-scale systems (up to 10000 atoms) are used to model the crystal growth. Particles are objects that have mass, position, velocity, and respond to forces, they are easy objects to simulate. Despite their simplicity, they can be made to exhibit a wide range of interesting behavior. For example, the movement of atoms in materials can be simulated by particles with appropriate potential functions defined in the small neighborhood of

each particle. The developed computer system enable us modeling material behavior using the particle objects in an interactive 3D environment. Such environment can be used to facilitate the exploration of a structure in situations that are difficult or expensive to reproduce experimentally.

We calculate the position of the atoms in the material during the process and display atomic images of the crystal structure as a function of time. In addition, several diagnostic imaging techniques that aid the analysis of structure at atomic level: radial distribution function $g(r)$, bond angle distribution function $g(\theta)$, and static structure factors $S(k)$, were developed. This paper proposes the approach for modeling and visualization of large scale molecular models applied on the simulation of a single-crystal Si growth from molten silicon.

1.1. Related Work

There has been extensive research on physically based modeling and dynamic simulations for computer graphics. The basics of mass-spring systems and particle system dynamics including some implementation hints are well described in SIGGRAPH'94 tutorial [2]. Different approaches have been introduced to visually model the physical processes. The physically based models capable of heat conduction, thermoelasticity, melting, and fluid-like behavior in molten state were first described by Terzopoulos, *et al.* [3]. Their model is very simplified and lack of precise physical behavior on atomic level.

Greenspan [4] investigated various N -body systems as discrete models of solid, liquid and gaseous media. Over the years, much attention has been given in the physics and chemistry literature to the development of discrete liquid models involving aggregate molecular dynamics in

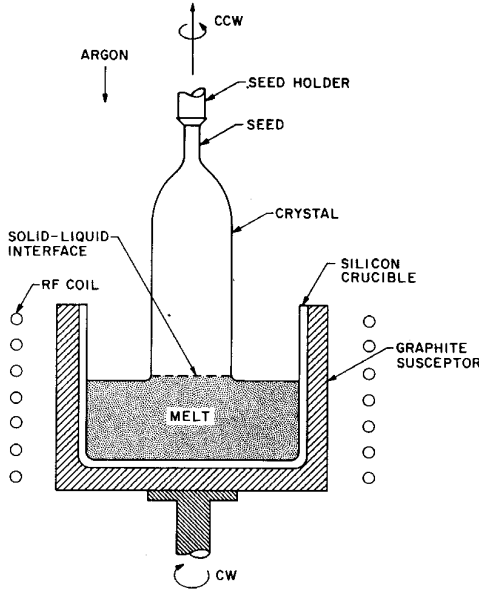


Figure 1. Czochralski crystal puller.

which the molecules are subject to various interaction potentials [5]. A basic technique is to model long-range attraction and short-range repulsion forces between pairs of particles according to potentials of the Lennard-Jones type, which lead to forces involving inverse powers of particle separation distance [6]. Recently Ishimaru, *et al.* [7] demonstrated that in addition to crystal silicon it is possible to simulate the amorphous and liquid state of pure silicon with this type of potential by different heating and freezing methods of melted silicon.

Small molecular models (up to 100 atoms) that may contain multiple types of atoms, can be created with a commercial quantum mechanics package called Gaussian94 [8]. This package falls in to a group of *ab initio* methods when very accurate molecular orbital calculations are carried out for the entire structure with hydrogen termination. Unfortunately, no such system is available for larger molecular models.

Section 2 of this paper introduces the molecular dynamic approach to the simulation of material behavior. Here the equation of motion of a particle system and the total potential energy based on repulsive and attractive forces is defined. Next the numerical implementation using finite differences and stochastic forces is discussed. The modeling and visualization of simulated processes within a time interval is proposed in Section 3. Section 4 proposes the diagnostic techniques of simulated results consisting of multiple 2D graphs continually changing in time as the simulation proceeds. The last section demonstrates the modeling technique applied on the Czochralski crystallization process

from molten silicon.

2. Molecular Dynamics

The motion of the particle i is governed by a pair of the first-order ordinary differential equations (ODE)

$$\begin{aligned} m_i \dot{\mathbf{v}}_i(t) &= -m_i \gamma_i (\mathbf{v}_i(t) + \mathbf{v}_p) + F_i(\{\mathbf{x}(t)\}) + R_i(t) \\ \dot{\mathbf{x}}_i &= \mathbf{v}_i, \end{aligned}$$

where in our model, the explicit systematic force F_i between the N particles was derived from the total potential Eq. 2, stochastic force R_i was introduced to mimic the motion of solvent molecules on the solute, and \mathbf{x}_i , \mathbf{v}_i , m_i , and γ_i are the position, velocity, atomic mass and friction coefficient, respectively. In general, the force F_i may depend on the position of all particles, denoted by $\{\mathbf{x}(t)\}$. Concerning the nature of the stochastic force R_i it is assumed to be stationary, Markovian and Gaussian with zero mean and to have no correlation with initial velocities $\mathbf{v}_i(0)$ nor with the systematic force $F_i(0)$. The pulling speed \mathbf{v}_p is assumed to be constant in time.

2.1. Total Potential Energy

A basic technique is to model attractive covalent and short-range repulsion forces between pairs of particles according to total potentials. The total potential energy of a system of N particles as proposed by Tersoff [6] is defined as a sum of interatomic potentials:

$$\begin{aligned} \Phi &= \sum_i^N E_i, \\ E_i &= \frac{1}{2} \sum_{j \neq i}^N f_c(r_{ij}) [V_R(r_{ij}) - b_{ij} V_A(r_{ij})], \end{aligned} \quad (2)$$

where $f_c(r_{ij})$ is a cutoff function controlling the influence of inter-atomic forces, written as

$$f_c(r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos\left[\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right] & \text{if } R_{ij} < r_{ij} < S_{ij} \\ 0 & \text{if } r_{ij} > S_{ij}. \end{cases}$$

The repulsive and attractive elements denoted by V_R and V_A , respectively depend on particle pairs, while the function b_{ij} includes particle triples in its expression. We used the Tersoff definitions

$$\begin{aligned} V_R(r_{ij}) &= A_{ij} \exp(-\lambda_{ij} r_{ij}), \\ V_A r_{ij} &= B_{ij} \exp(-\mu_{ij} r_{ij}), \\ b_{ij} &= \chi_{ij} (1 + \beta_i^n \xi_{ij}^{n_i})^{-1/2n_i}, \end{aligned}$$

$$\xi_{ij} = \sum_{k \neq i,j}^N f_c(r_{ij})g(\theta_{ijk}),$$

$$g(\theta_{ijk}) = 1 + c_i^2/d_i^2 - c_i^2/[d_i^2 + (h_i - \cos \theta_{ijk})^2],$$

where r_{ij} is internuclear distance between particles i and j , and θ_{ijk} is the bond angle between bonds ij and ik . Following reference [9] the double indexed constants are defined as $\lambda_{ij} = (\lambda_i + \lambda_j)/2$, $\mu_{ij} = (\mu_i + \mu_j)/2$, $A_{ij} = (A_i A_j)^{1/2}$, $B_{ij} = (B_i B_j)^{1/2}$, $R_{ij} = (R_i R_j)^{1/2}$, and $S_{ij} = (S_i S_j)^{1/2}$. All other parameters are constants reported by Tersoff [6] for silicon type of molecules, while their suitability and limitations were delineated by Haliçionglu [9]. Even though, the Tersoff originally derived his potential for a crystal silicon, Ishimaru *et al.* [7] showed that the Tersoff empirical inter-atomic can be adapted for simulation of liquid and amorphous silicon as well. Thus, the potential shown in Eq. 2 is sufficient for our purpose to model the crystal growth from a liquid silicon consisting of three states of silicon. The assumption is made that no impurities are present in the silicon.

2.2. Implementations

Numerical integrations of equation of motion, Eq. 2, were performed under the constant volume within the cubic domain with periodic boundary conditions on side faces and a reflection plane on bottom. At each time step the collision between the particle and the reflection plane is calculated to prevent particle from escaping out of the volume. To simulate the dynamics of our models we provide the initial position $\mathbf{x}(t_0)$, $\mathbf{x}(t_{-1})$, and stochastic vector $X_{-1}(\Delta t)$, systematic force $F(t_{-1})$ of particle i for $i = 1, \dots, N$. At each subsequent time step $t_0, t_1, \dots, t_n, t_{n-1}, \dots$, we evaluate the current velocities, current systematic force, current stochastic vector, and new positions using the explicit Gunsteren and Berendsen [10] stochastic approach. The integration method is of the third order and there is not necessity to assume that systematic force F_i is constant during time interval Δt , because the method includes higher order terms.

We use the units $kJ \text{ mole}^{-1}$ (energy), u (atomic mass), angstroms \AA (10^{-10} m) (length), K (temperature), and time is in ps units. The integration time step Δt and friction coefficient γ were usually set to 0.002 ps and 5 ps^{-1} in our simulations.

3. Visualization

The data obtained from the molecular dynamic simulation can be visualized and processed by the diagnostic techniques. It is not possible at present to run the dynamic simulation in real time and to control the simulation and visualization parameters interactively. However, we can run

the molecular simulation for a given simulation parameters on a parallel workstation and calculate results for several discrete time steps. Finally, the stored solutions can be displayed as a 3D model changing its shape in time while a set of 2D diagnostic functions varying in time can help us to understand the undergoing structural changes.

Each atom in the molecular structure is characterized by five parameters: the atomic symbol, the van der Waals radius (a probability measure of the location of electrons), and x, y, z cartesian coordinates in angstroms \AA . As usual, atoms are represented as spheres, while bonds are drawn as thin cylinders. We note that the number of atoms is constant in time during our simulations. On the other hand, since the presence of a bond between two atoms is determined from automatically calculated threshold value, their appearance and disappearance are discontinuous in time. The view point and the objects in a scene are changing their positions, while the light sources are considered to be stationary.

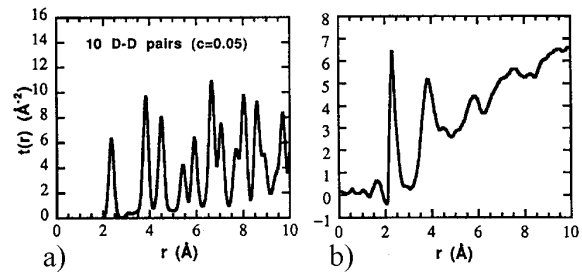


Figure 2. Radial distribution function for a) crystalline silicon and b) amorphous silicon.

4. Diagnostic Techniques

Taking just the direct view of the atoms as shown in Figure 4, it is difficult to determine where the structure is still crystalline but with some disorder. To analyze the different crystal structures in more detail, we plot a time varying radial distribution function $g(r)$, bond angle distribution function $g(\theta)$, and static structure factors $S(k)$.

The radial distribution $g(r)$ gives the probability of finding a pair of atoms a distance r apart, relative to the probability expected for a completely random distribution at the same density. It can be calculated by averaging the number of atoms a given distance away from each atom in the sample. The radial distribution function for a crystal differs from that for an amorphous and liquid sample. Figure 2 shows the plot of $g(r)$ for a crystalline and an amorphous sample. The significant distinguishing feature is the absence of the third peak from Fig. 2a in the amorphous sample. To compare the simulation data with the available data

of neutron-diffraction measurements [7], the static structure factors $S(k)$ defined by Fourier transformation of $g(r)$ are used. In the bond angle distribution function $g(\theta)$, we count the number of bond angles for a given angle from each triple of atoms in the sample, see Fig. 3.

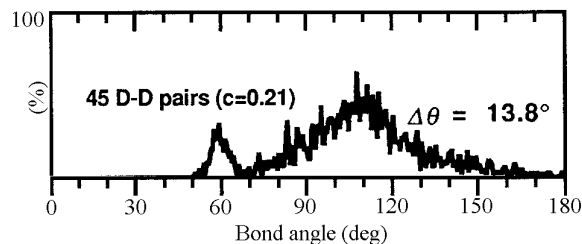


Figure 3. Bond distribution function for an amorphous silicon.

5. Results

In the first example 9216 Si atoms were initially placed on the diamond lattice sites within the volume $62 \times 62 \times 62 \text{ \AA}^3$, i.e. the tetrahedral prism. The entire volume was immersed in a heat bath with the fixed temperature distribution and pulled upwards in z direction for the simulation of crystal growth. In Fig. 4, the pulling speed and temperature gradient were set to 12 m/s and 15 K/\AA , respectively. The singly subscripted parameters such as λ_i from Eq. 2 were set for a silicon molecule as follows: $A = 1830.8 \text{ eV}$, $B = 471.18 \text{ eV}$, $\lambda = 2.4799 \text{ \AA}^{-1}$, $\mu = 1.7322 \text{ \AA}^{-1}$, $\beta = 1.1 \times 10^{-6}$, $n = 0.78734$, $c = 1.0039 \times 10^5$, $d = 16.217$, $h = -0.59825$, $R = 2.7 \text{ \AA}$, $S = 3.0 \text{ \AA}$, $\chi = 1$.

The second example, Figure 5, demonstrates the effect of varying reference temperature. Initially, the cluster of two oxygen atoms placed into a regular hexagonal lattice of silicon atoms, Figures 5a, was heated at room and melting temperature shown in Figures 5b and Figures 5c, respectively. The high disorder observed at melting temperature is due to large stochastic forces applied to silicon atoms.

In the third example, Figure 6, we studied the oxygen and silicon interactions. Here, two oxygen and 37 Si atoms were used in quantum mechanics simulation package Gaussian94, while the visualization and post-simulation diagnostics were done by proposed system. Figure 6 shows the sequence of images from dynamic visualization.

The proposed system implemented on HP9000/800 workstation gives the user choice of displaying all diagnostic variables plotted against time. The program lets the user

orient his view arbitrarily in the 3D environment while observing the pre-calculated molecular dynamics simulations.

6. Conclusion

Applying techniques from physics-based modeling and molecular dynamics, we have illustrated an interactive virtual visualization tool for the simulation of material behavior at atomic level. Also, we have demonstrated the modeling technique of the crystallization process of liquid silicon for large-scale systems. Implementation of multiple types of atoms and their interactions in large-scale systems is under the current investigation.

7. Acknowledgment

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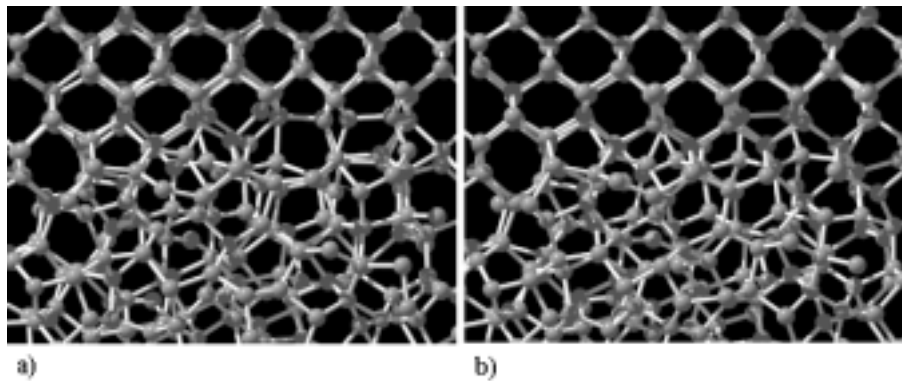


Figure 4. An example of atomic arrangements in crystallization processes after simulation time of a) 300 ps and b) 600 ps.

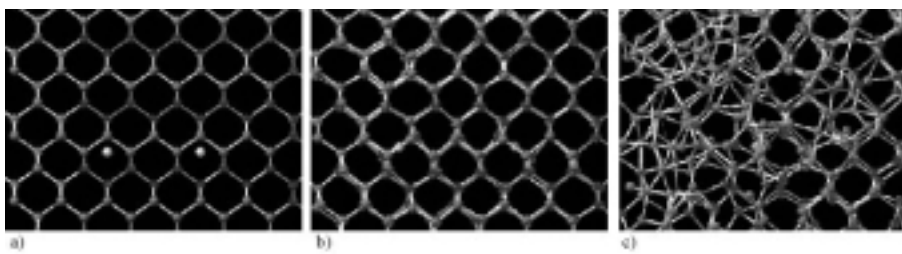


Figure 5. Varying temperature. a) Initial cluster of silicon atoms. b) Cluster after 600 ps at room temperature. c) The same initial cluster after 600 ps at melting temperature.

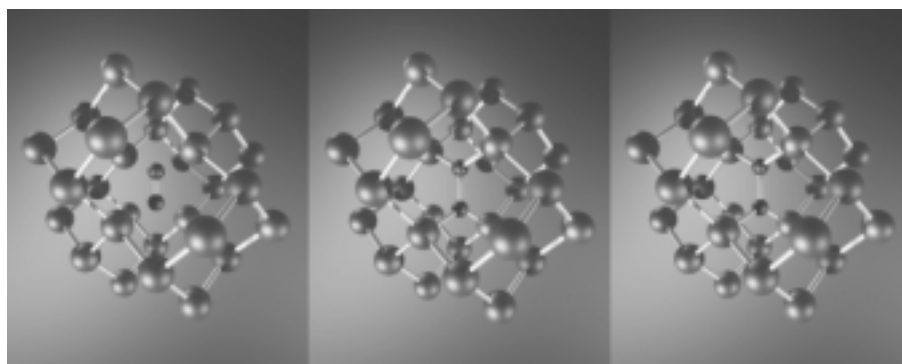


Figure 6. Oxygen and silicon interactions (SiO_2). Two oxygen atoms are located at the center.

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