Simulation of Crystal Growth in Solution by Hybrid Modeling

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A crystal growth model based on hybrid modeling is introduced to examine the experimental conditions of the crystal growth process in solution. This hybrid model is a simulation method across physical length and time scales characteristic of atomistic, microstructural, and continuum models. We simulate the behavior of the liquid during the solidification process by hydrodynamics and the atomistic behavior of the surface of the initial crystal by s ballistic model. Several growth morphologies are obtained and the relationship between macroscopic and microscopic morphologies during solution growth is examined.

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I. Introduction

Multiscale phenomena play an essential role in the dynamics of various complex systems, which consist of interacting subsystems of very different scale. For example, phase transitions, crystal growth processes, self-similarity, self-organized, chaotic, turbulent behaviors are only a few concepts (scale of physical phenomena) which have been developed to characterize the structure of such complex systems6. Quite often the elementary rules which control the interaction among the constituents of a complex system are well known. However, despite of this, the collective behavior of the system as a whole cannot easily be described by an analytical method. Often the complicated dynamics of these systems can be studied only through numerical simulations. In many cases the computational requirements are so large that quantitative studies of the behavior of the system is not feasible. For computer simulations in the field of materials science, supercomputers will never be sufficiently fast enough since the number of atoms in bulk state is the order of 10²⁴, the order of Avogadro's constant. In fact, in the experimental study or practical use, the material consist of the order of 10²⁰-10²⁴ atoms. Therefore, we can not treat all atoms under the experimental condition in computer simulation. Numerous attempts have been made by researchers to avoid this situation by multiscale simulation (hybrid model). However, only few researches have so far been made at simulation by multiscale, because of this limitations of the computer power and the difficulty of combination between each models. In the last few years, several articles have been devoted to this multiscale simulation, such as the study of the solidification process of a eutectic alloy9, growth of coral morphology9, synthesis process of CVD10,11, cluster growth and cluster deposition process12-13, and the progress of a crack in a bulk system14,15. These studies are grouped into the same category because these simulations treat some atoms or particles and combine the macro scale method to examine the whole system. This point is the essence of multiscale method.

The purpose of this paper is to investigate solution growth with this multiscale method, because it is still important to optimize growth conditions of high quality crystals by solution growth. However, the research of crystal growth by simulation often fails to grasp the relationship between the liquid flow in macroscale and the quality of crystal in atomistic scale. For example, quartz bulk in hydrothermal synthesis16, its quality depends on chemical impurities (e.g. OH distribution), inclusion (iron, sodium etc.), and crystal defects which have a relation with macro scale. In other words, the first question to be discussed is that relationship between macro- and microscale mechanisms. These problems should be discussed by multiscale method. So, we applied a hybrid model to the precipitation process and we obtain as a result that the morphology of the crystal depend strongly on the dynamics in solution growth.

II. Model and Numerical Method

Detailed numerical simulations have been performed based on the hybrid model, which consists of hydrodynamics as macro- and lattice-gas model as microscale simulations. The reasons for choosing this approach are threefold: the present lattice-gas model in microscale is suitable for dealing with flows around complex objects17, and it is straightforward to model a solute as lattice-gas particles, and finally this combination is suitable for multiscale calculation. At first, necessary steps of the hydrodynamics simulation are performed, in the present simulation. For the latter, the tagged particles are released to accumulate on right-hand plate from the source plane, i.e. the concentration in the left-hand plate is set to a constant. (See Fig. 1) The information of tagged particles, for example, the directions
of movement and the particle concentration is given by macroscale simulation. The information of the macroscale are defined by averaging over the tagged particles. For example, the number of the tagged particles used by macroscale simulation is given by the concentration value on the mesh in macroscale simulation.

1. Macroscale

The liquid region is suspended between two plates with different temperatures as shown in Fig. 1. The temperature difference between two plates is set to $\Delta T$, and horizontal and vertical lengths are the same as $L=1$. The liquid is assumed as a Newtonian fluid with constant kinematic viscosity and the Boussinesq approximation for an incompressible fluid is used. The top and bottom plates are idealized as adiabatic from the surroundings. The direction of gravity is downward. The governing equations of incompressible Newtonian fluid are made dimensionless with the following scalings; vertical coordinate $\tilde{x}=x/x^*$, horizontal coordinate $\tilde{y}=y/y^*$, velocity $\tilde{v}_x=v_x/v^*$, $\tilde{v}_y=v_y/v^*$, temperature $\tilde{T}=(T-T^*)/(T^*-T^{**})$, pressure $\tilde{p}=p/p^*$, and time $\tilde{t}=t/t^*$. Therefore, the non-dimensional governing equations are as follows\(^{(13)}\):

$$\tilde{v}_{\tilde{x}} \frac{\partial \tilde{v}_{\tilde{x}}}{\partial \tilde{x}} + \tilde{v}_{\tilde{y}} \frac{\partial \tilde{v}_{\tilde{y}}}{\partial \tilde{y}} = 0$$

$$\frac{\partial \tilde{v}_{\tilde{x}}}{\partial \tilde{t}} + \tilde{v}_{\tilde{x}} \frac{\partial \tilde{v}_{\tilde{x}}}{\partial \tilde{x}} + \tilde{v}_{\tilde{y}} \frac{\partial \tilde{v}_{\tilde{x}}}{\partial \tilde{y}} = -\frac{\partial \tilde{p}}{\partial \tilde{x}} + Pr \left( \frac{\partial^2 \tilde{v}_{\tilde{x}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{v}_{\tilde{x}}}{\partial \tilde{y}^2} \right)$$

$$\frac{\partial \tilde{v}_{\tilde{y}}}{\partial \tilde{t}} + \tilde{v}_{\tilde{x}} \frac{\partial \tilde{v}_{\tilde{y}}}{\partial \tilde{x}} + \tilde{v}_{\tilde{y}} \frac{\partial \tilde{v}_{\tilde{y}}}{\partial \tilde{y}} = -\frac{\partial \tilde{p}}{\partial \tilde{y}} + Pr \left( \frac{\partial^2 \tilde{v}_{\tilde{y}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{v}_{\tilde{y}}}{\partial \tilde{y}^2} \right) + Ra \cdot Pr \tilde{T}$$

$$\frac{\partial \tilde{T}}{\partial \tilde{t}} + \tilde{v}_{\tilde{x}} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{v}_{\tilde{y}} \frac{\partial \tilde{T}}{\partial \tilde{y}} = \left( \frac{\partial^2 \tilde{T}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{T}}{\partial \tilde{y}^2} \right)$$

where $Ra$ and $Pr$ stand for Rayleigh number and Prandtl number, respectively.

Boundary and initial conditions are as follows.

**Boundary conditions:**

- Left-hand plate ($\tilde{x}=0$): non-slip ($\tilde{v}_x=\tilde{v}_y=0$) and fixed temperature ($\tilde{T}=T^*$).
- Right-hand plate ($\tilde{x}=1$): non-slip ($\tilde{v}_x=\tilde{v}_y=0$) and fixed temperature ($\tilde{T}=T^{**}$).
- Top and bottom plates ($\tilde{x}=0, 1$): non-slip ($\tilde{v}_x=\tilde{v}_y=0$) and adiabatic condition ($\frac{\partial \tilde{T}}{\partial \tilde{y}}=0$).

**Initial conditions:**

Temperature of liquid is $T^*=0.0$ and liquid is quiescent.

Using two-dimensional Cartesian coordinates (See Fig. 1), governing equations are discretized by the finite difference method and solved by the HSMAC method\(^{(14)}\) with an UP-WIND scheme.

2. Microscale

In most studies only the effect of diffusion on a microscopic scale is included. However, in many cases one would expect that the influence of the flow on the solute distribution is important. In the present model, the precipitation proceeds by accumulation of solute and the amount absorbed determines the microscopic growth probability. Since we wish to consider the effect of the fluid movement on growth by the aggregation, this solute is modeled using a ballistic model with the effect of the macroscopic environment. This model contains some of the essential features of the process of solution growth. The present model can be extended to the ballistic model or other model, in a fairly straightforward way. In the ballistic model, the precipitates grow by the accumulating particles that move purely straight and the direction of ballistic particles is determined by the flow of the solution obtained by hydrodynamics. By calculating the distribution of solute particles in the fluid, we can model the growth which accumulate this solute. By varying the macroscale system, we can examine the effect of the ag-

![Fig. 2 Two dimensional mesh for the hybrid model used in the present simulation. The system used in the present study is divided into 20 x 20 meshes, where each one includes 300 x 300 microscopic meshes.](image-url)
gregation process from the hydrodynamics simulation to the ballistic model. In the present simulation, when the particle makes contact with the surface, it sticks permanently, because we ignored the surface reaction. (the sticking probability between the particle and the crystal is 1).

The basic concept of the present model is shown in Fig. 2. The substrate is initialized with a "seed" located on the right-hand plate of the lattice. The right-hand plate, "the substrate", is positioned at x=1. We divide the entire system into 20×20 meshes to calculate the hydrodynamics simulation, and each macroscopic mesh includes 300×300 microscopic meshes to calculate the ballistic model.

III. Results and Discussion

In Fig. 3, aggregating precipitates are shown resulting from a simulation condition in which $\Delta \tilde{T}$ the value 2.0 and where a purely ballistic model is used for the atomistic model. A "seed" located on the right-hand plate, and the precipitates are grown from this seed. Figures 4, 5 show the temperature and the velocity distributions of the solution corresponding to Fig. 3, respectively. Figure 5 reveals that natural convection is generated by temperature differences and the velocity of this fluid is affected by the aggregating precipitates. In aggregating precipitates region, the velocity is low, and, this change of flow during the growth process affects the later morphologies of the precipitates and mass and heat transport phenomenon. Figures 3(b), 4(b), and 5(b) are the results of later steps than 3(a), 4(a), and 5(a). We can suppose that the convection is affected strongly by the change of mass and heat transport, therefore, the morphologies of precipitates change rapidly.

If convection effects are dominant, the particles follow essentially linear trajectories and the resulting clusters...

Fig. 3 A typical growth morphology obtained by the hybrid model using hydrodynamics simulation and a purely ballistic model as outlined in the text. The branches of the aggregate develop towards the origin of the flow; (a) precipitate after 300 steps and (b) precipitate after 500 steps.

Fig. 4 Temperature contour lines ($\Delta T^* = 0.12$) in solution; (a) after 300 steps and (b) after 500 steps.
have a uniform structure on the whole. On the other hand, if diffusion effects are dominant, the particles move at random, and this model is the so-called Diffusion-Limited Aggregation (DLA)\textsuperscript{15,16} and leads to the growth of a beautiful branching pattern with fractal dimension of 1.67 on a two-dimensional square lattice. For intermediate cases, convection and diffusion effects are small, and the resulting morphologies have structure similar to, but not as uniform as, clusters grown with the DLA model.

In the purely ballistic model, the mean free path of the particle is infinite, and the fractal dimension is the same as the Euclidean dimension of the space\textsuperscript{17}. In the present simulation, we modify the ballistic model to include the effect of diffusion of solute in solution. Namely, the effect of flow is simulated by the ballistic nature and the effect of diffusion is simulated by the DLA model. At each Monte Carlo step, we chose either the DLA model or the ballistic model with some ratio so as to combine both models. Figures 3, 4, and 5 are the results obtained by 100% ballistic model as an atomistic model. In this case, the obtained morphologies are similar to the ballistic model.

Figures 6(a), (b) and (c) show precipitates grown with the use of a 1%, 3% and 5% ballistic model, respectively. These structures are becoming more open than those with a ballistic morphology and density fluctuations are beginning to extend to a longer range. Increasing the ratio of ballistic model to DLA model, the tendency of the branches of the aggregating precipitates is to grow towards the origin of the flow. This effect becomes stronger as the flow becomes more important, which is similar to the other previous simulations\textsuperscript{19}. Moreover, as the effects of convection are higher and higher, the DLA structure extend to longer and longer length scales.

**IV. Conclusions**

We applied a hybrid model to solution growth to examine the effect of the multiscale phenomena, which are the convection of liquid and the sticking process on surface. In Fig. 3, it is demonstrated that the influence of hydrodynamics on the solution concentration occurs at various conditions. In case convection effects are dominant, morphologies of the precipitates are affected by convection, because the transfer of solute depends on convection. In case diffusion effects are dominant, the morphologies of the precipitates are open. Although we have used a very simple growth model, our results show that branches in the direction of the flow develop when the influence of hydrodynamics becomes more dominant.
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