Molecular Dynamic Simulation of Directional Crystal Growth

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Abstract. We use molecular dynamic to simulate the directional growth of binary mixtures. Our results compare very well with analytical and experimental results. This opens up the possibility to probe growth situations which are difficult to reach experimentally, being an important tool for further experimental and theoretical developments in the area of crystal growth.

1 Introduction

The rapid expansion of the use of high quality crystalline materials in optical and electronic devices has strongly stimulated research, both theoretical and experimental, on dynamics of crystalization. Computer simulation has played an important role on the development and understanding of crystal growth. During growth the solid-fluid interface can display several interesting phenomena like segregation, dynamical instabilities and pattern formation [1].

A crystal can grow from the adjacent fluid by different mechanisms, depending on the structure of the interface (rough or smooth), material purity, growth rates, temperature gradients and so on. For a crystal to grow atoms or molecules must be transported from the fluid towards the interface with a non-zero sticking probability. Besides that, the latent heat generated at the interface as well as the solute excess segregated must be carried away. These requirements can be met in a controlled way by putting the sample in an appropriate furnace submitted to a temperature gradient and pulling it with constant speed toward the colder region. Results of such experiments have been compared with results of two dimensional models. Nijmeijr and Landau [2] reported molecular dynamic (MD) simulation on laser heated pedestal growth of fibers. Previous simulations consisted of kinetic models using Monte Carlo techniques and numerical solution of transport equations [3].

2 Simulation

In this work we use MD to simulate the solidification of a two component system of a solvent (particles of type a) and solute (particles of type b) interacting via a Lennard-Jones (LJ) potential. By tuning the LJ parameters
we set the struture of the interface (rough or smooth) and the segregation coefficient. We also simulate morphological instabilities, the planar interface becoming cellular and eventually dendritic (Mullins-seckerka instability). The simulation is carried out with all particles interacting through the LJ potential

$$\phi_{i,j}(r_{i,j}) = \epsilon_{i,j} \left[ \left( \frac{\sigma_{i,j}}{r_{i,j}} \right)^{12} - \left( \frac{\sigma_{i,j}}{r_{i,j}} \right)^6 \right].$$

(1)

The indexes $i$ and $j$ stands for particles in the positions $r_i$ and $r_j$ respectively and $r_{i,j} = |r_i - r_j|$. There are three types of interactions, solvent-solvent, solvent-solute and solute-solute. In each case the LJ parameters are labeled as $(a,a)$, $(a,b)$ and $(b,b)$. distance $r$, time $t$ and temperature $T$ are measured in units of $\sigma_{a,a}$, $\sigma_{a,b}$, $m_a/\epsilon_{a,a}$ and $k_B/\epsilon_{a,a}$. initially we distribute $N = n_x \times n_z$ particles over the two dimensional volume $L_x \times L_z$. We assume periodic boundary conditions in the $x$ direction. In the $z$ direction we divide the system in to two distinct regions, a solid and a fluid one. In the solid region particles stand initially in their equilibrium position in a total of $n_x \times n_{0z}$ particles. on the fluid region we distribute the rest of the particles with the density chosen to be $\rho = 0.5 \sigma_{a,b}^2$, randomly distributed in a triangular lattice and slightly dislocated from their equilibrium position. We impose a temperature gradient along the $z$ direction using a velocity renormalization approach. The system is divided in two regions, one cold which is set to $T = 0$ and the other to $T = T_h$ higher than the melting temperature $T_m$ which is $T_m = 0.4$ in our units, we let the system evolve in time for $N_e$ time steps of size $\delta t$ until it reaches equilibrium. Once the equilibrium is reached we start pulling the system in the $+z$ direction, at a pulling velocity $V_p$. The $-z_{max}$ layer works as a particle source, maintaining a constant flow to the material. The basic experimental set up is shown in Fig. 1.

In Fig. 2 we show an example of solute segregation during directional growth of the binary mixture: caprolactane as solvent and methyl-blue as solute. In the top part of Fig. 2 is shown an image of the crystal (left side) and melt (right side), with maximum concentration of methyl-blue at the melt side of the interface. From the gray level of the image we obtain the methyl-blue concentration profile across the sample, which in the melt, decays exponentially as a function of the distance from the interface (bottom part of Fig. 2). Fig. 3 shows the simulation results done in a system initially with $27 \times 30$ particles, solute concentration of 5%, pulling velocity $V_p = 0.004$, and LJ parameters given by : $\epsilon_{a,b} = 0.5$, $\epsilon_{b,b} = 0.1$, $\sigma_{a,b} = 1.0$, $\sigma_{b,b} = 1.0$ and $m_b = 1.0$.

After averaging over many runs to improve statistics one obtains the steady-state solute concentration profile represented as data points with error bars.
Fig. 1. Basic experimental set up for directional growth. The interface motion is visualized using an optical microscope. $T_m$ is the melting temperature of the mixture and $V_p$ is the pulling velocity.

Fig. 2. Directional solidification of a binary mixture showing the solute segregation at the interface. The experimental result is for the mixture caprolactane (solvent) and methyl-blue (solute).
Fig. 3. Our simulation results using the Lennard-Jones potential describes in detail the experiment.

It is shown in Fig. 3 a theoretical result obtained from the diffusion equation for the solute concentration in the fluid phase

$$\frac{\partial c_f}{\partial t} = D \frac{\partial^2 c_f}{\partial z^2} + V_f \frac{\partial c_f}{\partial z}$$ (2)

where $D$ is the solute diffusion coefficient in the fluid phase and $V_f$ is the velocity of the system of reference. The diffusion equation is supplemented with the boundary conditions:

$$c_f = c_0 \quad \text{at} \quad z \to \infty,$$ (3a)

$$(1 - K) V_f c_f = - D \frac{dc_f}{dz} \quad \text{at} \quad z = 0.$$ (3b)

The second condition is just the mass conservation at the interface and $K$ is the ratio between the solute and solvent concentrations.

3 Cellular Instability

With the LJ parameters chosen above the morphological instabilities were inhibited during the cellular growth. We can stimulate instabilities by tuning
the LJ parameters, particularly by slightly varying the equilibrium position between particles $a$ and $b$, i.e., changing $\sigma_{a,b}$. Fig. 4 show the effect of varying this parameter.

![Graph showing concentration profile](image)

**Fig. 4.** The figure shows the concentration profile found in our simulation. It is to be compared to Fig. 2.

For $\sigma_{a,b} = 1$ the interface is rough, becoming cellular and dendritic for $\sigma_{a,b} > 1$. As should be expected a lower $\sigma_{a,b}$ sets the interface smoother than larger values indicating that the system is very sensitive to geometric factors. We have also simulated some experiments fixing the value of $\sigma_{a,b}$ and varying $\epsilon_{a,b}$ and $\epsilon_{b,b}$, the results did not show any qualitative change in their behavior. Raising $\sigma_{a,b}$ breaks the hexagonal structure of the solid. The energy involved in such distortion is so large that the interface segregate solute particles, bonds $(a,a)$ and $(b,b)$ are preferable than $(a,b)$. Once particles of the type $b$ concentrate at the interface its melting point is lowered and channels of $b$ particles are formed inside the crystal. Fig. 5 shows this effect.

We are now studying the stability of those interfaces. We start with a smooth interface then, we introduce a perturbation at the interface. It has been shown that near the bifurcation from planar to cellular the time evolution of the most instable Fourier mode of the perturbation can be described by a third order Landau-amplitude equation. This however is the subject of a new research and will be soon published elsewhere.
Fig. 5. Cellular instability originated by varying $\sigma_{a,b}$. From left to right $\sigma_{a,b} = 1.05, 1.10$ and $1.20$.

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