Ordering Dynamics with Moving Plane Boundary between Ordered and Disordered Phases

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(Received July 24, 1991)

The ordering dynamics with a moving plane boundary between ordered and disordered phases is discussed focusing on the instability of disordered material near the plane boundary. The ordered phase is extending steadily. The material is modeled on the infinite state Potts model. A dynamics suitable to the interfacial motion is introduced. The ordered phase may create many grains. Three typical grain morphologies are found by two dimensional numerical simulations, i.e., compact, columnar and huge ones, depending both on the extending speed of the ordered phase and system boundary condition.

§ 1. Introduction

When a disordered system is brought into a thermodynamically unstable state, the system may start to be ordered undergoing phase transition. There is an ordering process where the ordered phase extends spatially as time goes on. For instance, a crystal growth is an example. A crystalline phase is separated from a disordered phase such as vapor, melt or solute by a boundary surface, i.e., crystal surface, and the crystalline phase continues to grow when the system stays in the unstable state. Such an ordering process may be classified into two cases according to the stability of the boundary surface. The formation of the snowflake is a typical example of ordering process with an unstable boundary (crystal) surface, whereas the formation of an ingot is an example with a stable boundary surface. The stability of the boundary surface is determined by the condition of the heat flow accompanied with the ordering. The (plane) boundary surface is stable when the heat flow is much faster than the material diffusion, or otherwise when the direction of the heat flow is opposite to that of the extension of the ordered phase. Although many papers have been devoted to studies of the crystal growth focusing on the instabilities of crystal surfaces, our understanding of the ordering process with stable surfaces is still lacking. Here in this paper we shall present a simplified model for the ordering dynamics with a moving plane boundary between ordered and disordered phases. This model is suitable to the crystalization process with stable crystal surfaces especially in the case where the thermal diffusion is much faster than the material diffusion. The model is a simplified lattice gas model, and we intend to explain not detailed quantitative properties of real crystal growth but its qualitative aspects as an ordering process.

The scheme of the ordering process which we shall study is as follows. Let us prepare a stable disordered system, for instance such as a vapor, melt or solution. Then the system is partially quenched by bringing a part of the system into a thermodynamically unstable state. Let us assume that the quenched part starts to be ordered. Our task is to examine what we may observe when we steadily extend the
quenched part. When the interface between stable and unstable phase is steadily flat, the speed of the extension of the ordered phase would be only the significant control parameter (if the speed is measured in a suitable reduced unit).

We introduce the "quench boundary". The quench boundary is the boundary between the thermodynamically unstable phase and the thermodynamically stable one, and certainly exists for the partial quenching. To explain this let us consider a crystal growth gathering atoms from vapor. The assembly of atoms which arrive at the crystal surface is thermodynamically unstable. Such atoms on the crystal surface rearrange their positions to unite with the host crystal. The quench boundary is the boundary separating the unstable part from the stable vapor, and such a thing as the crystal surface is formed inside the quench boundary.

Our model is the Potts model with the infinite number of spin states. By the two dimensional numerical simulation we found the following three typical results depending on the quench boundary velocity and system boundary conditions.
1) A very large single-ordered grain may be created.
2) Many column grains are created: They have irregular interfaces.
3) Many compact grains are created: They coarsen with time.

In the next section we present details of our model. In § 3 we present results of numerical simulation. In § 4 discussions and some remarks are presented.

§ 2. Model

A) System We use a lattice gas model. Namely, the continuous system is modeled on the square lattice. At each lattice site an atom is placed and its attribute is represented by a spin variable \( \sigma \) with infinite number of spin states:

\[
\sigma = 1, 2, 3, \ldots.
\]

(2\cdot1)

The value of \( \sigma \) corresponds to the direction of a crystal axis. For an ordered phase all spin variables \( \sigma \) take the same value, whereas for a disordered phase each spin variable takes a random value. The interaction between atoms is simplified. Namely, there is no interaction between different spin states, but the interaction energy between atoms with the same spin state is negative. The hamiltonian of the system is thus

\[
\mathcal{H} = -J \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j},
\]

(2\cdot2)

where \( \langle ij \rangle \) indicates the summation over all neighboring pairs, and \( J \) is a coupling constant \( (J > 0) \). The model described by (2\cdot2) is equivalent to the infinite state Potts model.

B) Dynamics We introduce the following dynamics\(^9\) similar to the Glauber dynamics. The dynamics consists of four steps. First, one of lattice sites is chosen randomly. Let this site be the \( i \)-th site and the spin state of this site be \( \sigma_i \). We calculate the total energy of the system \( E(\sigma_1, \ldots, \sigma_i, \ldots) \). Second, a neighboring site of the first site is chosen randomly. Let this site be the \( j \)-th site and the spin state be \( \sigma_j \). Third, we change the spin state of the first site from \( \sigma_i \) to \( \sigma_j \), and calculate the total energy
$E(\sigma_1, \cdots, \sigma_i \rightarrow \sigma_i, \cdots)$. Fourth, let

$$\Delta E = E(\sigma_1, \cdots, \sigma_i \rightarrow \sigma_j, \cdots) - E(\sigma_1, \cdots, \sigma_i, \cdots).$$

(2·3)

If $\Delta E > 0$, then the spin state of the $i$-th site is fixed to be original one $\sigma_i$, whereas if $\Delta E \leq 0$, then it is fixed to be new one $\sigma_j$:

$$\sigma_i \rightarrow \sigma_i \text{ for } \Delta E > 0,$$

$$\sigma_i \rightarrow \sigma_j \text{ for } \Delta E \leq 0.$$  

(2·4)

Note that the present dynamical scheme is not the same as the one traditionally used for the Potts model. In the traditional method a new spin state is chosen randomly among available spin states (corresponding to the above second and third steps), and hence computation time increases as the number of the spin state increases. Any real system with continuous state variables undergoes phase transformation in a finite time. The present scheme is therefore more realistic than the other. We can show that for the homogeneous quenching the expected $t^{1/2}$ growth law of grain size can be really observed in the present dynamical scheme. Moreover, the present dynamical scheme is modeled on the grain boundary motion.

C) Interaction range. The interaction between spins is taken up to the next nearest neighbor sites with the same interaction parameter $J$. Therefore, our system has essentially eight neighboring sites. The interaction between next nearest neighbor sites is introduced in order to avoid the freezing of grain growth on square lattice. The triangular lattice is usually used to avoid such a freezing. If we switch-off one of diagonal sets of interactions in the present model, then the present model is equivalent to the model with the triangular lattice. We cannot here decide which model is more suitable, six or eight neighbor interaction. Both are models in any way. The only difference between two models significant to the present purpose is the microscopic time scales in units of Monte Carlo steps per spin. The time scale for the eight-neighbor interaction is longer than that for the six-neighbor interaction.

The microscopic time scale is the basis of the macroscopic time evolution. Therefore, if we scale the macroscopic time scale by the microscopic time scale, then macroscopic phenomena would be essentially the same for both the models: The microscopic time scale should be removed by a suitable scaling procedure.

D) Quench boundary The quench boundary is the boundary between stable random phase and unstable phase. In Fig. 1(a) a schematics of the quench boundary is shown. The shaded region is the region just quenched and is going to be ordered. Inside the quench boundary, say $y \leq y_t$, interactions among spins
are defined as above, but over the quench boundary and outside the quench boundary interactions between spins are switched-off (see Fig. 1(b)). Due to the steady supply of atoms from gas phase or gradually cooled molten material, the quench boundary shifts. The shift velocity is treated as a control parameter. The quench boundary is shifted once in each set of \( n \) Monte Carlo steps (MCS) per spin. Thus the shift velocity is
\[
v = \frac{1}{n} \quad \text{(lattice space/MCS)}.
\] (2.5)

Here we have set the lattice space to be unity. The noninteger number \( n \) is also used, which can be easily defined as the total Monte Carlo steps divided by the total spin number. The quench boundary is shifted in the direction of one of lattice axes, say \( y \)-direction. We have examined also the broad quench boundary, but the qualitative aspect is the same as that of the sharp quench boundary, and therefore we report here only the case of sharp quench boundary.

§ 3. Numerical simulation

We here present numerical results. Patterns of grain boundary for various values of quench boundary velocity \( v \) and for system boundary conditions are shown in Fig. 2. In all patterns the quench boundaries are shifted from the upper system edge to the lower system edge. In these patterns two different system boundary conditions are used. One is the boundary condition that the upper horizontal edge is disordered at initial and it is set free to evolve throughout the ordering process (upper figures). The other is that the upper edge is a single ordered phase, i.e., all spins at the upper horizontal edge take the same spin state and are fixed throughout the ordering process (lower figures). The periodic boundary condition is used for the vertical edges. A grain boundary pattern for \( v = \frac{1}{3} \) is also shown in Fig. 3. Here spins at the upper system edge are set randomly at initial and the boundary condition at this edge is free one.

Some quantitative analyses of the morphological change in grain shape are done. We examined two quantities. One is the relative size of the biggest grain to the system size. The other quantity is calculated as follows. We calculated first the numbers of pairs of boundary sites in horizontal and vertical directions, respectively, and then calculated the ratio of these two numbers. This quantity represents the deformation of the grain shape. For the value 1 the grain shape is isotropic, whereas for the value 0 grains are columns with straight boundaries. In Fig. 4 these quantities

Fig. 2. Patterns of grain boundary for several quench boundary velocities and two different system boundary conditions. Upper figures: ordering in contact with a disordered phase, which is set freely to evolve. Lower figures: ordering in contact with a single ordered phase, which is fixed temporally. Note that the quench boundary is the lower system edge in each figure and is shifting downward. The system size is 100 by 100.
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are shown. The system size is 200 \times 200 and the five different runs are averaged. Figure 4(a) shows the case of the free boundary at the upper edge, and (b) the case of the single-ordered-phase-boundary at the upper edge. We see that there are two critical shift velocities for quench boundary:

\[ v \approx 1/3 \quad \text{and} \quad 1/8. \]

For velocities larger than about \( v = 1/3 \) (lattice space/MCS) there are many compact grains in the system, whereas for velocities smaller than about \( v \approx 1/3 \) grains are elongated (see Fig. 3). As the shift velocity is decreased, the grain morphology again drastically changes at about \( v = 1/8 \) in the case of single phase boundary condition at the upper edge. For velocities smaller than about 1/8 the region swept out by the quench boundary is a single ordered phase. The growth rate of such a single phase is anomalously large: The size of the single phase is equal to that of a part swept out by the quench boundary and thus the area (volume in three dimensions) is proportional to time \( t \). We find that a large single ordered phase is created also for large quench boundary velocities with the same boundary condition. But the growth of such a single phase is done with shrinkings of neighboring smaller

(a)

(b)

Fig. 4. Quantitative investigation of morphological change. Upper figures represent the biggest grain size relative to the system size. Lower figures represent degrees of deformation of grains. The value 1 corresponds to the grain shape which is isotropic, whereas 0 corresponds to column grains with straight boundary. (a) The case where the upper edge is, at initial, a disordered phase. (b) The case where the upper edge is a fixed single ordered phase (the deformation of grain shape cannot be defined for single-ordered-grain for \( 1/v > 8 \)).
grains. Therefore the size of such a phase is proportional to $t^{1/2}$. It seems that the transition from compact to columnar grains and transition from columnar to large-single-ordered grains are not sharp. But in the latter transition there is an obvious critical value of the quench boundary velocity ($\approx 1/8$) below which the system is in a single-ordered-phase (Fig. 4b). We also note that the width of the columnar grain is almost independent both of the quench boundary velocity and the system size. For instance, the size of columnar grain relative to the system size corresponds to the grain width. The upper graph of Fig. 4(a) shows that the maximum width of the columnar grain is almost independent of quench boundary velocity. The biggest size of compact grain depends on the time passing after the quench and in this respect depends on the quench boundary velocity, but does not depend on the system size if grains are much smaller than the system size.

So far a sharp quench boundary has been used. To examine how created patterns depend on the shape of the quench boundary we also used broad quench boundaries. The broad quench boundary may appear, for instance, when the composition or the temperature near the boundary between the ordered and disordered phases gradually changes in space. We set the quench boundary by continuously changing the frequency of the Monte Carlo sampling in the region of the quench boundary. That is, the Monte Carlo try is more frequently done as approaching ordered phase, whereas it is less frequently done as approaching disordered phase. We found that critical boundary velocities at which grain morphologies change depend on the width of the quench boundary. Such changes are caused by the change in the microscopic time scale which is caused due to the change in the frequency of the Monte Carlo sampling. The relation between the critical velocity and the microscopic time scale will be discussed in § 4 in the case of the sharp quench boundary.

Before closing this section we present a numerical result for the homogeneous quench by the present model. The purpose of this simulation is to confirm the reliability of the model. It is known that the thermodynamic driving force for the grain growth or the crystal growth is the surface tension. This yields the well-known $t^{1/2}$ law for the grain growth. Figure 5 shows the temporal evolution of the average area of grain in two dimensions. The average grain area $A$ is defined by

$$A(t) \propto \frac{1}{N(t)},$$

(3·1)

where $N(t)$ is the number of the grain and $\langle \cdot \rangle$ indicates the average. The system size is $500 \times 500$. The number of the possible spin state is infinity. The periodic boundary condition is used. The average is taken over 12 different runs.
The maximum simulation time is 2000 MCS per spin. We find the $t^{1/2}$-law for the growth of the length scale $A^{1/2}$. To the author's knowledge the justification of the $t^{1/2}$-growth law by numerical simulation for the infinite state Potts model is first done by the present work.

§ 4. Discussion and remarks

The numerical simulation suggests the existence of two critical values for the quench boundary velocity, $v \approx 1/3$ and $\approx 1/8$ (Monte Carlo steps per spin). These critical velocities can be explained as follows. A single ordered phase can grow successfully when the spin state near the phase boundary always takes the same value as that of host phase. The Monte Carlo sampling to choose a new spin state is done so as to pick out one of the eight neighbouring spin states. Therefore, in each set of eight Monte Carlo steps, any desired spin state can be sampled out. Therefore, for the quench boundary velocities smaller than 1/8 the same spin state as that of the host phase is always chosen on the surface of the host phase. This gives a large single phase which grows with the same velocity as the quench boundary.

The larger critical velocity $v \approx 1/3$, which yields elongation of grain, may be explained as follows. Any spin which is in contact with grain boundary interacts with three spins on the grain boundary. In order for these spins to take the same values as that of the host phase it takes 8/3 MCS. If the same spin state continues to be in contact, it is possible for long grains to be created. Thus the critical quench boundary velocity for which grains become long is given by $3/8 \approx 1/3$ (lattice space/MCS).

As is already noted in § 2, these critical velocities depend on the microscopic time scale. For instance, we found larger critical velocity for the triangular lattice, and smaller critical velocities for broad quench boundaries, if we measure them by the Monte Carlo step per spin. Practically there are several ways of setting a microscopic time scale. For instance, one may make it from the measurement of the grain growth in the case of the homogeneous quench.

In a real system an anomalously large single crystal is observed when the crystal grows in contact with vapor. This is consistent with the present observation. The columnar pattern is often observed in a generated ingot. Interfaces of column grains in such a structure are irregular, just like that in our simulation. These facts suggest that the crystallization of the real material is often done by the inhomogeneous quench mechanism we explored in this paper.

The partial quench model we discussed here can be applied also to the phase separation of binary mixture where the "order parameter" is conserved. In that case we find three typical patterns, i.e., random, lamellar and columnar ones, depending on the quench boundary velocity.

References

1) For reviews see


