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On the Effect of Bulk Diffusion on the Initiation of the Discontinuous Precipitation Reaction: Phase-Field Simulations

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Abstract. Discontinuous precipitation is a solid-state transformation involving the decomposition of a supersaturated matrix into two phases arranged periodically as alternate lamellae or rods, which is accompanied by a grain boundary migration. The rate-limiting step of this process is supposed to be boundary diffusion of solute along grain boundaries. However, volume diffusion is generally present as well, and its influence on the occurrence of the discontinuous precipitation reaction is at present not well understood. We investigate this problem using a phase-field model in which the bulk diffusivity, surface diffusivity and grain boundary mobility can all be varied independently. The main results are that (i) when volume diffusion is the dominant mechanism, a close analogy is observed between the precipitate growth and the growth of a crystalline finger in a channel, and (ii) both the geometry of the precipitate's tip and the growth velocity are strongly influenced by the relative magnitudes of the bulk and surface diffusivities as well as by the grain boundary mobility. Steady-state growth is possible only for a finite range of precipitate spacings, which is limited for low spacings by a fold singularity and for large spacings by an oscillatory or a tip-splitting instability. The values of these limits are found to depend on the supersaturation as well as on the ratio of bulk and surface diffusivities.

Introduction

The discontinuous precipitation (DP) is a solid-state transformation involving two different cooperating mechanisms: i) the decomposition of a supersaturated matrix called the mother phase into two phases, arranged periodically as alternate lamellae or rods, consisting of a solute-rich β phase and a solute-depleted α phase, ii) a grain boundary (GB) migration systematically accompanying the decomposition. The initiation of the reaction takes place at grain boundaries where the clustering of solute atoms, due to some segregation effects, leads first to the formation of solute-rich precipitates which may or may not give rise to the formation of precipitation cells. Indeed, the course of the reaction depends on the system considered since it is not observed systematically in all binary alloys. The process usually results in the formation of precipitation cells which grow at a constant velocity, often assumed to be the GB growth rate.

It has been shown that phenomena associated to cellular reactions can be understood either by effects of driving force or mobility of the reaction front [1]. Indeed, cellular reactions such as DP or discontinuous coarsening (DC) are usually treated in terms of either GB mobility, due to the motion of the RF, or driving force which would be exerted on the RF. Moreover, beside DP and DC, GB motion is observed to be involved also in many other solid state reactions such as diffusion induced grain boundary motion (DIGM), diffusion induced recrystallisation (DIR), as well as grain growth [2]. Thus, all of the phenomena cited above exhibit, to some extent, a "common" motion of the GB and are related to the DP since they involve grain boundaries or incoherent boundaries as reaction fronts [1].

Hence, it has been agreed that the rate-limiting step of this process is supposed to be boundary diffusion of solute, which takes place mostly along grain boundaries. However, volume diffusion is generally present as well, and its contribution to some specific phenomena occurring during the DP, such as the jerky motion, is still under discussion [3]. Furthermore, the relative magnitude of its contribution when compared to boundary diffusion, remains imperfectly understood [3, 4]. In particular, the knowledge on the initiation mechanism has remained scarce since the early investigations on DP [2, 3]. Nevertheless, it has been globally agreed that the reaction initiation depends both on the capacity of nucleation of precipitates at the boundaries and on the ability of the latter to undergo concurrent migration [2, 5]. It has also been argued that the ability of the boundary to initiate and sustain non-conservative motion across a supersaturated matrix seems most crucial to initiate DP [5].

We have investigated this problem using a phase field model in which the bulk diffusivity, surface diffusivity and grain boundary mobility can all be varied independently. The present paper has been motivated by our previous findings on the DP reaction [6] and could be seen as a simple extension to them. However, it turns out that the contribution of volume diffusion is indispensable for the initiation of DP, at least in our simulations. Indeed, the simulations revealed that the growth of a pre-existing seed or nucleus in the GB could not take place if boundary diffusion was the only transport process. Instead, lateral growth of the nuclei along GBs was observed. Moreover, no GB migration and hence no precipitation cells formation could be obtained in the absence of bulk diffusion. Besides, we have investigated the effect of bulk diffusion on steady-state precipitate morphology and steady-state growth velocity.

Methodology

The phase field model. The details of the phase field model have been presented elsewhere [6]. The simulation box, representing our system, is illustrated in figure 1, where the three involved phases are displayed. The reaction front consists of the GB separating the depleted mother phases α and the supersaturated matrix α_0, as well as the interface between the latter and the rich solute β daughter phase. The volume fractions of the three involved phases ($p_{\alpha0}$, p_α, p_β), called the phase fields, are the non conserved fields on which the free energy functional of our system depends. The latter also depends on a conserved field, the solute concentration, such that.

$$F = F(p_{\alpha 0}, p_\alpha, p_\beta, c) = \int f dV \,, \tag{1}$$

where f is the free energy density which comprises different contributions: A gradient term and a triple-well potential create diffuse interfaces of a preset thickness W, and a third term couples the phase fields and the concentration field and provides the driving force for boundary motion.

The phase fields p_i, i= α_0,α,β obey the equation of motion

$$\frac{\partial p_i}{\partial t} = -\frac{1}{\tau}\frac{\delta F}{\delta p_i} \,, \tag{2}$$

where τ is the phase-field relaxation time, and the right-hand side denotes a functional derivative. The concentration field obeys the continuity equation:

$$\frac{\partial c}{\partial t} + \nabla . J = 0 \,, \tag{3}$$

where J, the solute concentration flux is given by:

$$J = -M(p)\nabla\mu = -M(p)\frac{\partial \mu}{\partial c}\nabla c = -M(p)\frac{\partial^2 f}{\partial c^2}\nabla c \,. \tag{4}$$

Here, μ is the chemical potential and $M(p)$, the mobility which is given by the expression:

$$M(p) = D_V + 4(D_S^{\alpha 0\beta} p_{\alpha 0} p_\beta + D_S^{\alpha\beta} p_\alpha p_\beta + D_S^{\alpha 0\alpha} p_{\alpha 0} p_\alpha) \,, \tag{5}$$

where D_V and D_S^i are the bulk and surface or boundary diffusivities, respectively.

In our model, we choose a simplified thermodynamics: the free energy densities are given by one parabola for the two mother phases and another one for the daughter phase β.

Thus, the term $\partial^2 f / \partial c^2$ is a constant which is the proportionality factor, called Darken factor, between the atomic mobility and the solute diffusion coefficient D according to the relation:

$$D = M_{at} f'' \quad (6)$$

This constant can be set to unity by a suitable non-dimensionalization [6]. The capillary length d_0 obeys the equation:

$$d_0 = \frac{\sigma_{ij}}{\lambda}, \quad (7)$$

where σ_{ij} is the surface tension between two phases and λ a coupling constant between the phase field and the concentration field [6].

It is worth mentioning that our model does not incorporate any solute drag effects, in the sense that the solute concentration profile across the GB is homogeneous (no concentration spike in the grain boundary).

Parameters and initial conditions. All of the theoretical and experimental investigations on the DP reaction focus on two key quantities:

(1) the steady state growth velocity V and

(2) the lamellar spacing L.

In experiments, the spacing is a quantity that results from the complex dynamics of large reaction fronts, and can thus freely be selected by the system. In contrast, in our phase-field simulations the spacing can be controlled by the simulation box size and the initial conditions. We mainly investigate here the dependence of V on:

(1) the lamellar spacing L by acting directly on the simulation box size and

(2) the scaled supersaturation $\Delta = (c_0 - c_\alpha)/(c_\beta - c_\alpha)$ (the global driving force)

Here, c_0 is the alloy nominal composition, whereas c_α and c_β are the equilibrium concentrations of α and β phases, respectively.

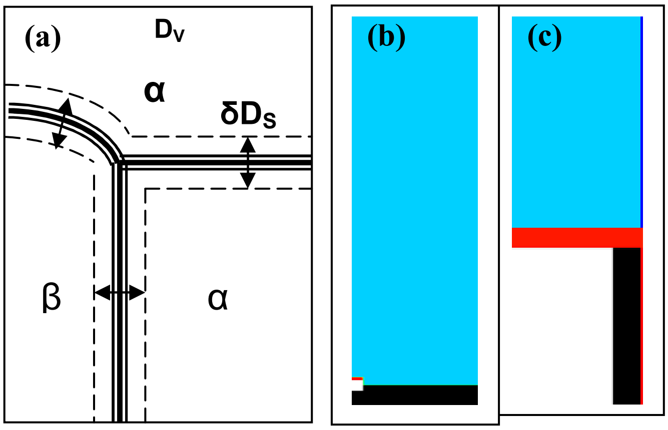

Figure 1: Schematic representations of: (a) simulation box; Initial conditions (b) a nucleus at the interface and (c) pre-existing lamellae.

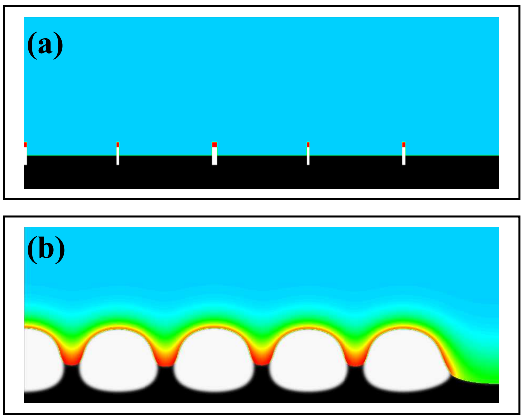

Figure 2. Rapid evolution and grain boundary migration for dominating bulk diffusivities: $D_V = 1$ and $D_S^i = 0$.

The phase-field model also depends on others parameters, some of which have been maintained fixed such as the surface tensions $\sigma_{\alpha0\alpha}, \sigma_{\alpha0\beta}, \sigma_{\alpha\beta}$ and the diffuse interface width W and some others have been varied such as boundary and bulk diffusivities. For more details on the choice of these quantities, see [6]. For simulations of bulk-diffusion limited growth, $D_V = 1$ and $D_S^i = 0$ was used, whereas surface- or boundary-diffusion limited growth was simulated with $D_V = 10^{-6}$, $D_S^{\alpha0\alpha} = D_S^{\alpha0\beta} = 1$ and $D_S^{\alpha\beta} = 10^{-3}$. Concerning the initial conditions, the simulations could either start from a seed (fig. 1. b) or from pre-existing lamellae (fig.1. c). Alternatively, the simulations could simply start from a steady state morphology obtained from a previous run, which generally reduced the convergence time of the simulations.

Results and Discussion

Initiation of the DP reaction and conditions of precipitation cells formation. Steady-state growth could only be observed for certain initial conditions for surface-diffusion limited growth. The simulations revealed that the growth of a pre-existing seed in the GB (fig.1. b), could not lead to steady-state growth if boundary diffusion was the only active transport process. Instead, lateral growth of the nuclei along GBs was observed to take place. Figure 3, illustrates such a growth, for a random distribution of seeds within the grain boundary, obtained with $D_V = 10^{-6}$, $D_S^{\alpha 0\alpha} = D_S^{\alpha 0\beta} = 1$ and $D_S^{\alpha\beta} = 10^{-3}$.

The numbers "n" mentioned on each picture indicate the time sequence during the run such that: t= n*ifreq*Δt, where Δt =0.02 (in units of the phase-field relaxation time), and ifreq denotes the frequency of picture "emission" and varies from one run to the other (ifreq=2.10^4 generally). Moreover, figures 3.d to 3.f, demonstrate that no GB migration and hence no precipitation cells formation could be obtained without the contribution of bulk diffusion. Thus, in our simulations, volume diffusion seems to be indispensable to obtain steady-state growth. The presence of bulk diffusion gives rise to a rapid evolution of the seeds, already at the first stages of the growth, even in the total absence of surface or boundary diffusion (fig. 2).

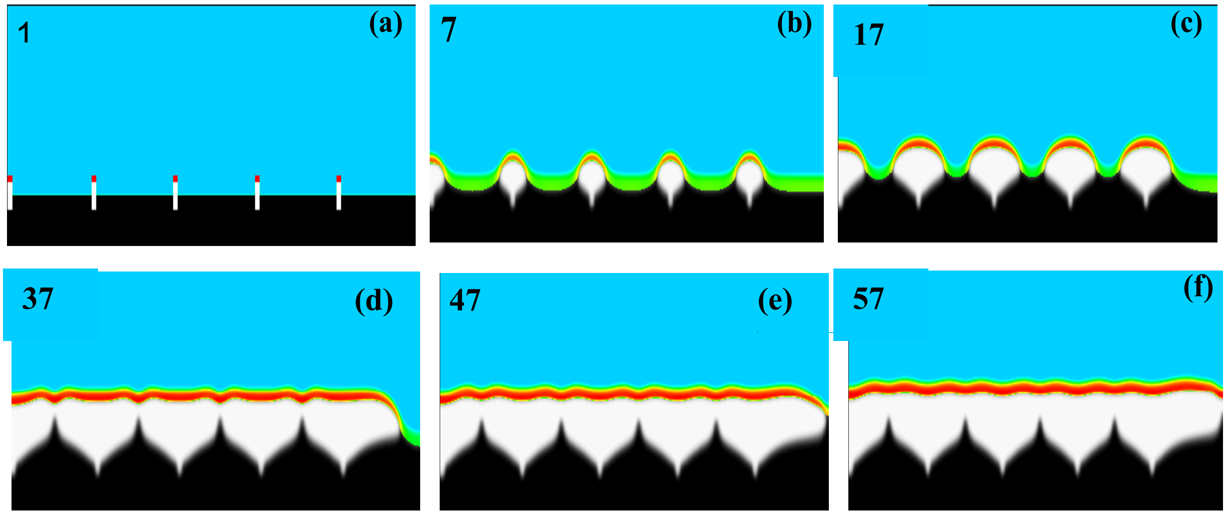

Figure 3. Lateral growth of β precipitates during DP reaction controlled by surface diffusion. $D_V = 10^{-6}$, $D_S^{\alpha 0\alpha} = D_S^{\alpha 0\beta} = 1$ and $D_S^{\alpha\beta} = 10^{-3}$.

Moreover, the development of the seeds into lamellae, the grain boundary migration as well as the bowing of the reaction front, which is an important characteristic of the DP reaction [7], are all observed to be reproduced by the phase-field model for DP reaction controlled by bulk diffusion (fig. 4). Figure 4 also illustrates the effect of bulk diffusion on the evolution of the diffusion field ahead of the reaction front. The colour scale indicates the bulk concentration field, and it can be seen that there clearly is a concentration gradient within the bulk, which is not observed for surface or boundary limited growth. It is known that bulk concentration gradients are necessary for the occurrence of morphological instabilities, which can lead to the initiation of the development of precipitation cells. In contrast, for the boundary-diffusion limited regime, steady state growth could be obtained only by starting the simulations with a whole lamella as shown in fig. 1. c.

Figure 4, displays as well the growth of the largest precipitates at the expense of the smaller ones which is one possible explanation for the curved shapes of the reaction front.

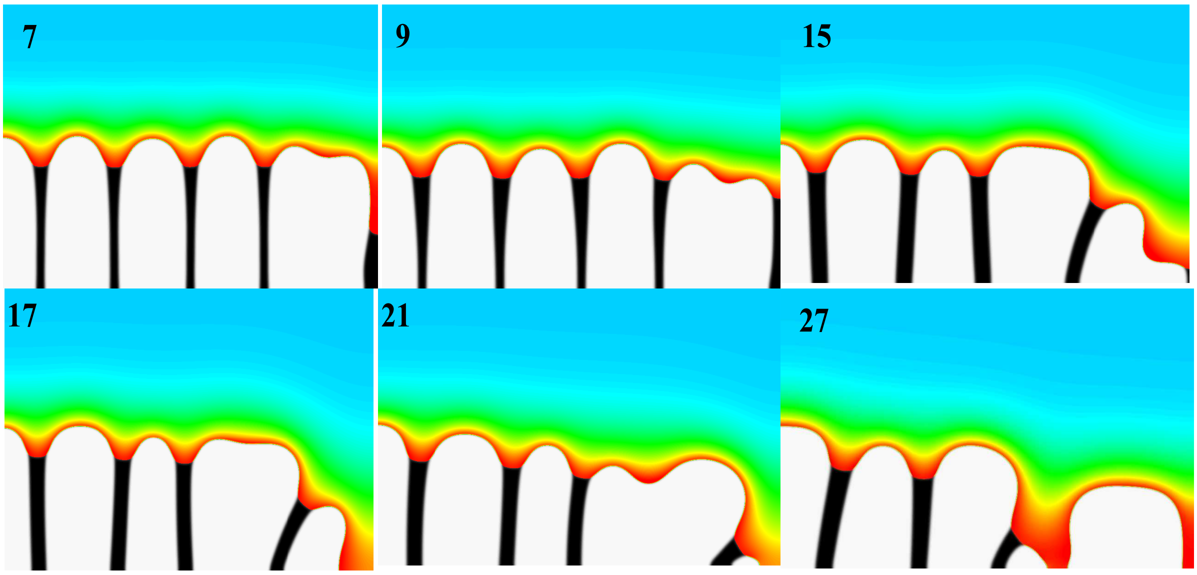

Figure 4: Lamellar precipitation cell formation, grain boundary motion and bowing of the reaction front, during DP reaction controlled by bulk diffusion. D_V =1 and D_S^i =0.

Effect of bulk diffusion on the precipitate morphology. Figure 5, reveals how a bulk diffusivity decrease affects the precipitate morphology and results in a drastic flattening of its tip. It should be noted that a notable decrease in the growth velocity has been observed to accompany such a flattening. Moreover, the latter was observed (fig.5.e) even after starting from a steady state morphology obtained from a previous run, with D_V = 1 and D_S=0 (fig.5.d), as initial condition.

Effect of bulk diffusion on the steady-state growth velocity. For dominating bulk diffusion and in the absence of surface or boundary diffusion, an analogy can be established between the precipitate's behaviour and a crystalline finger growing in a channel [8, 9]. Indeed, the tip region of the precipitate with the surrounding diffusion field as shown in Fig. 5. a is just like the tip of a crystalline finger; the only difference is the presence of the grain boundary, which is "attached" to the tail of the precipitate. Thus, it is not surprising to see that the curves of the steady-state growth velocity as a function of the spacing $V(\Lambda)$ (fig. 6. a) and the supersaturation $V(\Delta)$ (fig. 6. b), have the same shapes as for a crystalline finger [8, 9]: as a function of spacing, V first starts to increase for smaller spacings, then goes through a maximum, which seems to correspond to an optimum (for the spacing), and then decreases until the growth becomes unstable against oscillations or tip splitting. Besides, the precipitate's behaviour, in the vicinity of the fold singularity for the lower limit, is the same as the one reported by Brener and Temkin [8] for the growth of a finger, though their approach was completely different (they made use of Green's functions): the finger was observed to become fatter and fatter until filling the simulation box [8], due to the pileup of solute in front of the tip. Concerning the upper limit, it should be noted that both the oscillatory (jerky motion) and tip slitting instability could be observed in the course of DP experiments [3]. It should be noted also that both of the upper and the lower limits are found to depend on the supersaturation (fig.6. b). Finally, it was also found that D_V is not the only parameter that determines the growth velocity: as shown in Fig. 6. a, when V is scaled by D_V, different values are obtained for different values of D_V. This shows that our system is qualitatively different from a growing crystal finger. Indeed, the grain boundary mobility also comes into play: a change in this quantity changes the geometry of the grain boundary and thus the "drag force" exerted by the attached grain boundary on the precipitate.

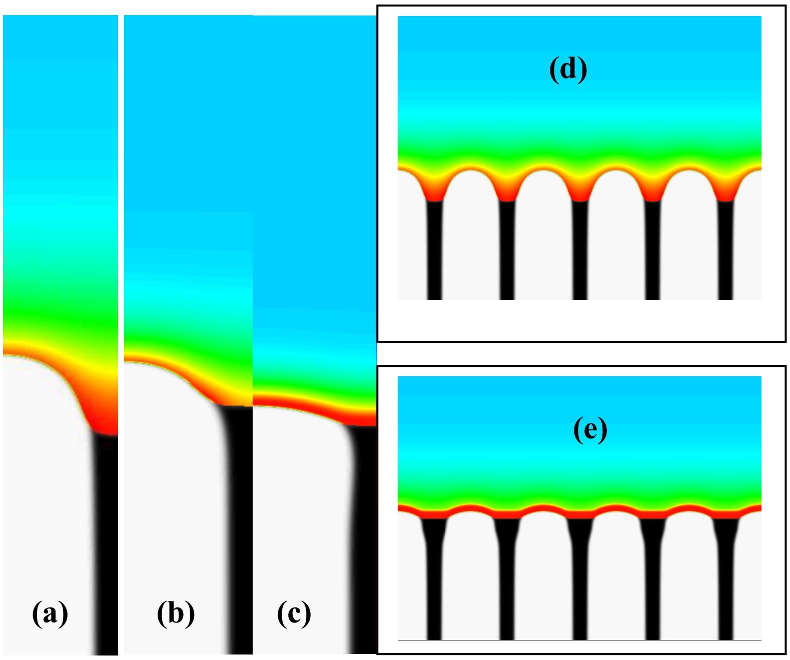

Figure 5. Effect of bulk diffusion on the precipitate morphology. (a) $D_V=1$ and $D_S = 0$; (b) $D_V = 0.1$ and $D_S=0$ and (c) $D_V = 0.01$ and $D_S=0$. $L/d_0= 50.91$, $\Delta= 0.8$. (d) Steady state shape of the RF, obtained with $D_V = 1$ and $D_S=0$, (e) RF recession observed with $D_V = 10^{-6}$.

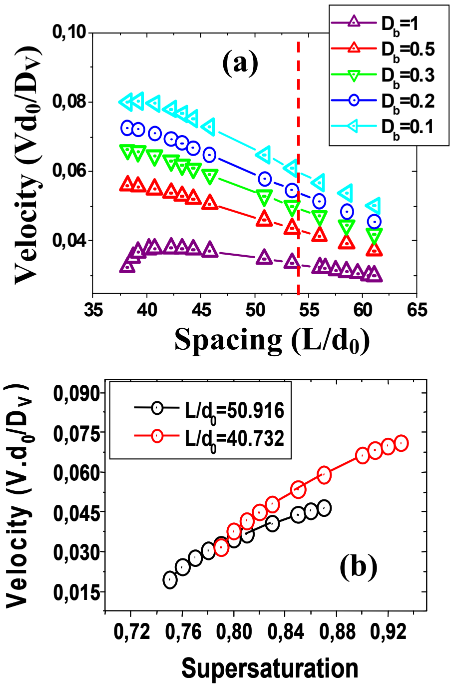

Figure 6. Growth velocity versus: (a) Spacing for $\Delta=0.8$ and different values of D_V; (b) Supersaturation for different spacings.

Summary and conclusions

The phase-field method has been applied to model the discontinuous precipitation reaction and the way it could be affected by the contribution of bulk diffusion. Many features of the DP reaction could be reproduced by the PF method, such as the formation of lamellar cells, the bowing of the RF as well as the migration of the latter. Our two main results are: (i) Bulk diffusion is important for the formation of precipitation cells and the initiation of the DP reaction and (ii) The steady-state growth rates depend generally on both bulk and surface diffusivities, as well as on the grain boundary mobility.

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