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Chemically induced diffusion-limited interface growth

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Employing a lattice-gas model, we study the Monte Carlo kinetics of heterogeneous reaction resulting in the growth of a new phase on the top of the solid in the case when the process is limited by reactant diffusion via the film. For the simplest set of particle-particle interactions and Metropolis diffusion dynamics, the model proposed predicts the power-law growth of the film thickness, $h \propto t^{\alpha}$, with $\alpha \simeq 0.3$. Such low values of the growth exponent are usually attributed to the reactions involving grain-boundary diffusion. We have however shown that the growth slowdown might result from the formation of a thin dense layer just on the bottom of the newly formed phase. The model introduced is rather flexible. Choosing other types of the particle-particle interactions or diffusion dynamics, one can easily get diverse regimes of the growth.

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Surface growth under nonequilibrium conditions has attracted attention already for several decades. Nowdays, this interdisciplinary field enjoys rapid progress, especially in such subfields as crystal growth, molecular-beam epitaxy, vapor deposition, and surface biology [1–3]. In other subfields, the development is slower. In particular, the understanding of the formation of a new interface phase during heterogeneous reactions (e.g., oxidation, hydride formation, etc.) is still rather limited. Such reactions have long been recognized to be often limited by reactant diffusion via a newly formed film [4,5]. If the distribution of the reaction product in a new phase is uniform, the diffusion flux calculated in the steady-state approximation is inversely proportional to the film thickness h, i.e.,

$$dh/dt \propto D/h, \tag{1}$$

where D is the diffusion coefficient. Integrating Eq. (1) yields the conventional parabolic growth law,

$$h \propto (Dt)^{1/2}. \tag{2}$$

In real systems, the newly formed phase is often inhomogeneous as a consequence of grain growth, cracking, etc. In such cases, the film growth kinetics are usually represented in the power-law form,

$$h \propto t^{\alpha}, \tag{3}$$

where α is the exponent dependent on the type of processes occurring in the film. For the growth accompanied by formation of grains, one has $\alpha < 1/2$. On the other hand, cracking of the film may result in $\alpha \simeq 1$.

Rationalization of the power-law kinetics of the chemically induced formation of a new phase is usually based on the mean-field (MF) kinetic equations [5–7]. The MF treatments are conceptually simple but often not self-consistent. For example, the effect of the grain formation on the film growth is customarily described by using Eq. (1) and assuming that D depends on the average drain size R, which is in turn assumed to satisfy the Allen-Cahn law, $R \propto t^{1/2}$. There is, however, no guarantee that the latter law is applicable under the reaction conditions. Self-consistent Monte Carlo (MC) treatments of the chemically induced growth of a new phase on the interface are lacking. Our goal is to fill this gap (at least partly).

Our treatment of the 1+1 interface growth is based on the lattice-gas model. Substrate atoms, M, gas-phase particles, A, and reaction products, B, are assumed to occupy sites on the $L_x \times L_y$ square lattice (L_x and L_y are the lattice sizes) with periodic boundary conditions along the X axis. Immobile M atoms are considered to form initially (at $t=0$) the close-packed $L_x \times L_y^0$ slab ($L_y^0 < L_y$). A particles, located at $t=0$ at random at sites with $L_y^0 + 1 \leqslant y \leqslant L_y$ above the slab, are assumed to diffuse by jumping to nearest-neighbor (nn) and next-nearest-neighbor (nnn) vacant sites. The concentration of A particles above the substrate, $p_A \ll 1$, is maintained constant. The model reaction,

$$A + M \rightarrow B, \tag{4}$$

occurs between nn A particles and M atoms. B particles are considered to diffuse by jumping to nn sites.

Structure of the new phase depends on the B-B interactions. We assume that the nn and nnn B-B interactions are repulsive and attractive, $\epsilon_{BB}^1 > 0$ and $\epsilon_{BB}^2 < 0$, respectively. To be specific, we set $\epsilon_{BB}^2 = -\epsilon_{BB}^1$. In this case, B particles are known [8] to form a $c(2\times 2)$ structure at $T < T_c \simeq 1.2\epsilon_{BB}^1$ (we use $k_B = 1$). The density of B particles in this phase is half as high as the density of M atoms in the substrate. Thus, the reaction under consideration is accompanied by considerable expansion of the solid.

The B-M interaction is for simplicity assumed to be the same as the B-B one, i.e., $\epsilon_{BM}^1 = \epsilon_{BB}^1$ and $\epsilon_{BM}^2 = \epsilon_{BB}^2$. To describe A diffusion in the B phase, we take into account the nn A-B interaction, ϵ_{AB}^1, which is considered to be repulsive. The A-A interaction is neglected because the concentration of A particles inside the B phase is low. The A-M interaction is neglected as well in order to reduce the number of model parameters.

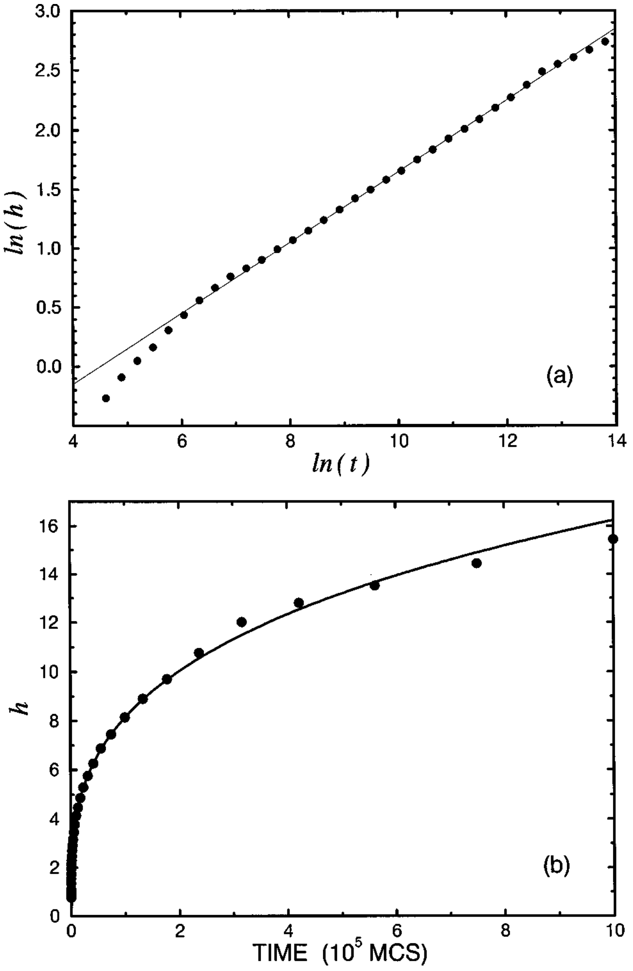

FIG. 1. Film thickness as a function of time in (a) logarithmic and (b) normal coordinates. Circles show the MC data. Solid lines correspond to the power-law growth (3) with $\alpha=0.3$. The time unit is (a) 1 and (b) 10^5 MCS, respectively.

The interactions introduced above correspond to nonactivated particles. In general, *A* and *B* diffusion in the *B* phase and reaction (4) depend also on the interactions in the activated state [9]. Taking into account that at present the type of the latter interactions for reactions in the solid is not well established, we use the simplest Metropolis (MP) dynamics for *A* and *B* diffusion, i.e., the normalized dimensionless probability of jumps is considered to be $W=1$ for $\Delta\mathcal{E}\leqslant 0$, and $W=\exp(-\Delta\mathcal{E}/T)$ for $\Delta\mathcal{E}\geqslant 0$, where $\Delta\mathcal{E}$ is the energy difference of the final and initial states. The $A+M$ reaction probability is assumed to be independent of the arrangement of particles in sites adjacent to the *A*-*M* pair.

The algorithm of our MC simulations is as follows.

(1) A site on the lattice is chosen at random. If the site is occupied by *A*, the *A* diffusion or reaction trials are realized as described in item (2) below. If the site is occupied by *B*, the *B* diffusion attempt is performed as outlined in item (3). If the site is vacant or occupied by *M*, the trial ends.

(2) For *A* diffusion or reaction, one of the nn and nnn sites is selected at random. If the latter site is vacant, the *A* particle jumps to it with the probability prescribed by the MP rule. If the site selected is nn and if it is occupied by *M*, the $A+M$ reaction is executed with the unit probability (i.e., the *A* particle participating in the reaction is removed from the lattice and the *M* atom is replaced by *B*). In other cases, the trial ends.

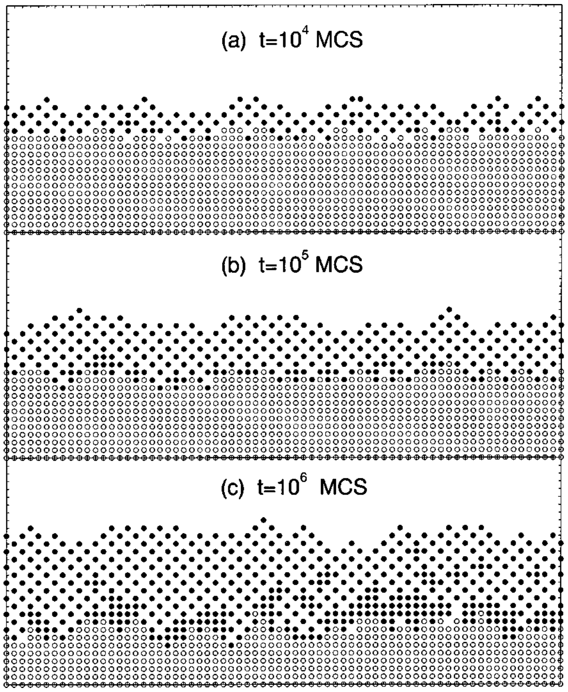

FIG. 2. A 70×30 fragment of the 400×30 lattice at different stages of the growth. Open and filled circles exhibit *M* atoms and *B* particles, respectively. *A* particles are not shown.

(3) For *B* diffusion, one of the nn sites is chosen at random. In the latter site is vacant, the *B* particle is replaced into this site with the probability $p_B W$ (*W* is the MP probability) provided that in the final state it has at least two nn or nnn *B* particles (this constraint prevents evaporation of *B* particles). The factor $p_B<1$ is introduced to take into account that *B* diffusion is slower compared to *A* diffusion.

Initially, *A* particles are distributed above the substrate at random. To maintain the *A* concentration above the *B* phase, $p_A=\text{const}\ll 1$, we keep for the top lattice row (with $y=N_y$) the grand canonical distribution of *A* particles with the desirable concentration. Taking into account that the ratio of the *A* concentrations inside the *B* phase and above the substrate is low [$\leqslant\exp(-4\epsilon_{AB}/T)$], we conclude that the *A* diffusion flux inside the *B* phase is fairly weak and accordingly the gradients in the *A* concentration above the *B* phase are negligible.

To measure time, we use MC steps. One MCS is defined as $L_x\times L_y$ MC trials described above. To calculate *h*, we divide the total number of *B* particles by $0.5N_x$. The factor 0.5 is introduced because the density (per site) of *B* particles in the $c(2\times 2)$ phase is 0.5.

The reaction kinetics have been simulated on a 400×30 lattice with $L_y^0=15$ for $p_A=0.1$, $p_B=0.1$, $\epsilon_{BB}^2/T=-\epsilon_{BB}^1/T=1.5$ (in this case, $T\simeq 0.56T_c$), and $\epsilon_{AB}^1/T=1$ up to $t=10^6$ MCS. For these parameters, the dependence of the film thickness on time is found (Fig. 1) to be described by Eq. (3) with $\alpha\simeq 0.3$. Typical snapshots of the interface are shown in Fig. 2. The *B* phase is seen to be well ordered. Just above the *M* phase, the concentration of the *B* particles is however much higher compared to that corresponding to the $c(2\times 2)$ structure. This thin region in fact limits the access of *A* particles to the *M* phase.

In summary, we have formulated a lattice-gas model for describing chemically induced diffusion-limited interface growth. For the simplest set of particle-particle interactions, the model predicts the power-law growth with $\alpha \simeq 0.3$. Such low values of the growth exponent are usually attributed to the reactions involving grain-boundary diffusion. We have, however, shown that the growth slowdown might result from the formation of a thin dense layer just on the bottom of the newly formed phase. Finally, we may note that the model introduced is rather flexible. Choosing other types of the particle-particle interactions or diffusion and reaction dynamics, one can easily get diverse regimes of the growth.

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