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Abstract

We study a model of corrosion and passivation of a metallic surface in contact with a solution using scaling arguments and simulation. The passive layer is porous, so the metal surface is in contact with the solution. The volume excess of the products may suppress the access of the solution to the metal surface, but it is then restored by a diffusion mechanism. A metallic site in contact with the solution or with the porous layer can be passivated with rate p and the volume excess diffuses with rate D. At small times, the corrosion front grows linearly in time, but the growth velocity shows a $t^{-1/2}$ decrease after a crossover time of order $t_c \sim D/p^2$, where the average front height is of order $h_c \sim D/p$. A universal scaling relation between h/h_c and t/t_c is proposed and confirmed by simulation for $0.000\,05 \leqslant p \leqslant 0.5$ in square lattices. The roughness of the corrosion front shows a crossover from Kardar–Parisi–Zhang (KPZ) scaling to Laplacian growth (diffusion-limited erosion—DLE) at t_c. The amplitudes of roughness scaling are obtained by the same kind of arguments as previously applied to the other competitive growth models. The simulation results confirm their validity. Since the proposed model captures the essential ingredients of different corrosion processes, we also expect these universal features to appear in real systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The corrosion of metallic surfaces is a subject of increasing interest due to the widespread use of corrodible materials with all the economical and environmental implications [1, 2]. When the metal is in contact with an aggressive solution, the formation of a passive layer containing the metal oxide is observed after the corrosion of the topmost layer of the surface. As this layer grows, it more efficiently protects the surface from the attack of the solution, leading to
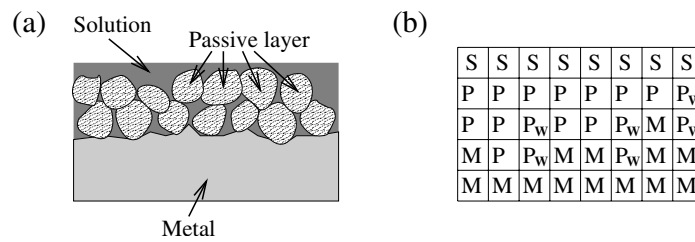
Figure 1. (a) Scheme of the metal and the porous passive layer in contact with the solution. (b) Lattice model after some steps of the corrosion process.

the slowdown of the corrosion rate. For instance, according to the Cabrera and Mott [3] law, the corrosion front is expected to move as $t^{1/2}$ (growth rate decreasing as $t^{-1/2}$), which is in agreement with experimental findings.

The changes in the corrosion rate are certainly accompanied by changes in the roughness of the front separating the metal and the passive layer. In the beginning of the process, all the surface is uniformly exposed to the corrosive solution, but after the formation of the passive layer there appear points of easier or more difficult access to the solution. It is particularly important to investigate the scaling properties of the roughness because they are intimately connected to the main dynamical processes during the interface evolution [4, 5]. From the theoretical point of view, additional motivation comes from the renewed interest in systems whose competitive dynamics leads to crossover in roughness scaling [6–12].

Here we will analyse the crossover in the front evolution and in the roughness scaling of a recently introduced model for the corrosion of a metallic surface by a solution [13–15]. The basic mechanisms of the model are the corrosion of the metallic surface exposed to the solution and the formation of the passive layer with the oxides. The layer is assumed to be porous, but the larger molar volumes of the products may block the pores and, consequently, diffusive relaxation of the volume excess is necessary for new corrosion events. This model was not devised to represent a particular real process [13], but to contain essential ingredients of a large variety of corrosion processes, allowing the investigation of universal features.

Previous numerical work on this model has shown significant differences in the corrosion fronts for small and large values of the local corrosion rate of the metal in contact with the solution [13]. However, besides these qualitative features, only universal laws for the global growth rates in limiting cases were already derived [15]. In the present paper, we advance the quantitative study of the model, focusing on the properties of the corrosion front which separates the metal and the passive layer. We show the emergence of a crossover in the global growth rate accompanied by a crossover in surface roughness scaling, from a short-time KPZ behaviour to long-time Laplacian growth (or diffusion-limited erosion—DLE) [16, 17]. A scaling picture of the process is derived, along the same lines of those developed for related systems [12], and the results are confirmed by numerical simulation.

The rest of this paper is organized as follows. In section 2 we present the model for corrosion and passivation. In section 3, we present a scaling theory for the front growth and numerical results that confirm it. In section 4, we discuss the crossover KPZ–DLE of the surface roughness. In section 5 we summarize our results and present our conclusions.

2. The model of corrosion and passivation

The model represents a system with the structure shown in figure 1(a). While the metal is corroded, a porous passive layer grows, with some products filling their pores. These products
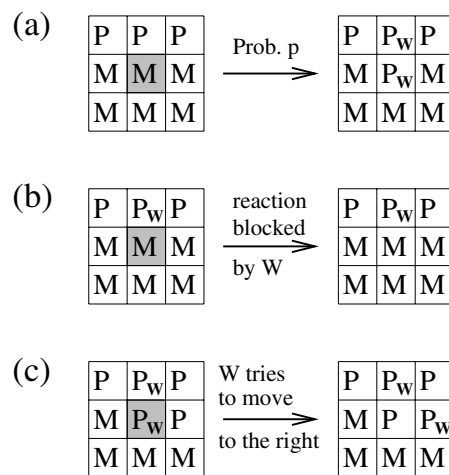
Figure 2. (a) Corrosion of the central M site, which is passivated (reaction M → P) with the creation of two new W particles. (b) Example of an M site (central site) whose passivation is not possible due to the blockage (by a W particle) of the only neighbouring P (above the M site). (c) Example of movement of a W particle, initially at the central P site.

block the access of the solution to the surface, but they may diffuse and leave the surface of the metal exposed again.

For simplicity, the model is defined in a lattice, where the sites may have three different states: M (metal), S (solution) or P (passive). A lattice site represents the dominant chemical species inside one mesoscopic region. Due to computational limitations of memory and time, a square lattice will be considered in our numerical work. In order to represent the effect of the porosity of the passive layer, we assume that a site M can be corroded (passivated) even when it is in contact only with P sites, thus avoiding the complication of representing the porous structure of the passive layer. The excess of products will be represented by particles W, which can only lie at P sites and may diffuse through the P matrix. At most one W particle is allowed at each P site. A region of the lattice is illustrated in figure 1(b).

In the beginning of the process, all sites above a certain row of the lattice (height $h = 0$) are labelled S, and all sites below or at that row are labelled M. An M site is said to be in contact with the solution if it has at least one neighbour S or one neighbour P without a W particle over it. At each time unit, each M satisfying this condition may be changed into P with probability p (reaction M → P). This corresponds to the reduction of a chemical species in the solution by the metal and the formation of an insoluble film. A reaction M → P is illustrated for the central site in figure 2(a). On the other hand, figure 2(b) shows a case where this reaction is not possible for the central M site due to the blocking effect of the W particle.

We assume that the molar volume of the oxide products is larger than that of the metal (Pilling and Bedworth factor larger than one [18]), and we represent this excess by the creation of W particles after the reaction M → P. Two W particles are produced immediately after each reaction: the first one lies at the newly created P site and the second one lies at a neighbouring P or S site. The creation of the new W particles is also illustrated in figure 2(a). Some differences between models with creation of one or two W particles per reaction were discussed in [13–15].

The W particles may also diffuse through the P layer. This represents some type of stress relaxation which leads to the redistribution of the excess of corrosion products [15]. At each time unit, each W attempts to execute D random displacements to neighbouring sites. The
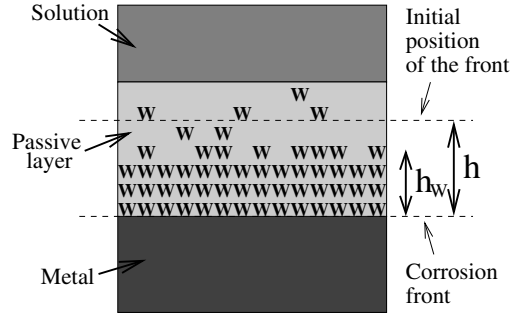
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Figure 3. Scheme of the lattice model after a long time, when a large number of W particles are accumulated above the corrosion front, which separates the metal and the passive layer. For simplicity, flat interfaces between metal, passive layer and solution were drawn.

movement is possible only if the target site is P or S and if it does not contain a W particle; otherwise the attempt is rejected. An acceptable movement is illustrated in figure 2(c), but an attempt to move the same W particle to any other direction would be rejected in that case.

When a W particle attempts to move to an S site, or when the W particle is created over an S site (top of the passive layer), this S site is converted into P. This condition is reasonable to represent the expansion of the passive layer towards the solution side. However, it does not have a significant influence on the corrosion front, which separates the metal and the passive layer, and which is the main interest of the present study.

3. Scaling of the height of the corrosion front

Here we focus on the case of small corrosion rates p and of not very small values of D.

First we consider the short-time behaviour of the system. In one time unit, the number of corroded sites is small compared to the total number of sites in the front, but all W particles attempt to move during the same time interval. The diffusion of W particles removes the restrictions for the corrosion and the situation in figure 2(b) is rare: the W particle at the neighbouring P site will move away long before a successful corrosion attempt occurs at the central site. Consequently, we expect that all M sites at the interface are available for corrosion with equal probabilities. The distance of the corrosion front from the initial level, hereafter called the height of the corrosion front, increases as

$$h_{\text{ini}} \sim pt \tag{1}$$

(h_{ini} is being measured in lattice units). In this regime, the model is equivalent to an inverse of the Eden model [4, 21], in which a new particle is added to a randomly chosen neighbour of the aggregate surface at each time step. This regime also resembles the erosion model of [30].

Now consider the system at long times. Since W particles move diffusively, their upwards displacement away from the corrosion front increases as $(Dt)^{1/2}$; thus their velocity in the upwards direction evolves as $\frac{\text{d}}{\text{d}t}[(Dt)^{1/2}] \sim (D/t)^{1/2}$. This decreasing velocity leads to the accumulation of W particles near the surface, which block new corrosion events. This is schematically illustrated in figure 3, where a sea of W particles is shown at the bottom of the passive layer.

The crossover from the initial regime to the long-time one takes place at a characteristic time t_c in which the height of the sea of W particles covers a finite fraction of the passive layer.

The height of that sea increases as

$$h_W \sim (Dt)^{1/2} \tag{2}$$

because it is determined by the diffusion of W particles produced at short times. On the other hand, the height of the passive layer increases as equation (1) before the crossover. Matching these heights we obtain the crossover time

$$t_c \sim D/p^2. \tag{3}$$

The height of the corrosion front at the crossover, measured in lattice units, is

$$h_c \sim D/p. \tag{4}$$

After the crossover, a corrosion event is possible only when an M site has an empty neighbour P, which requires the migration of voids (holes) through the sea of W particles and their arrival at the corrosion front. When the M site is corroded (reaction M → P), the hole of the W sea disappears because it is occupied by one of the new W particles. Since these holes move diffusively from the top of the W sea to that front (similarly to the W particles), we conclude that the corrosion front will also move diffusively, with displacement increasing as $t^{1/2}$ and velocity decreasing as $t^{-1/2}$.

The time evolution of the height h of the corrosion front is expected to follow a scaling relation that involves h_c and t_c:

$$h/h_c = f(t/t_c), \tag{5}$$

where f is a scaling function. Indeed, with $f(x) \sim x$ for small times, we regain equation (1), and with $f(x) \sim x^{1/2}$ for long times we obtain $h \sim (Dt)^{1/2}$, in agreement with the above discussion.

In order to test the scaling relation (5), we use simulation data for several values of p, ranging from $p = 5 \times 10^{-5}$ to $p = 0.5$, and $D = 1$. These data were obtained in lattices with lateral length $L = 10\,000$ and periodic boundary conditions. In figure 4 we show a scaling plot of hp versus tp^2, which are respectively proportional to h/h_c and t/t_c. The excellent data collapse of the results for consecutive values of p shows that there is a universal relation between those quantities. Lines with slopes 1 and 1/2 are also included in the plot in order to highlight the crossover from the $h \sim t$ growth to the $h \sim t^{1/2}$ growth.

In previous numerical works with small and large p [14, 15], this universal behaviour was not observed because, for a single value of p, it is difficult to span a time interval long enough to show both scaling regimes. Numerical studies in three dimensions would certainly be more difficult. However, the scaling picture will be the same in three dimensions because it is derived from diffusion properties and the same stochastic rules for the model.

4. Scaling of surface roughness

For small times, the equivalence to the Eden model (section 3) indicates that the corrosion model is in the KPZ class of growth [4, 19], i.e. in the continuous limit it is represented by the KPZ equation

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2}(\nabla h)^2 + \eta(\vec{x}, t). \tag{6}$$

Here, h is the height at the position $\vec{x}$ in a d-dimensional substrate at time t, ν and λ are constants and η is a Gaussian noise [4, 19]. In the growth regime, the lateral correlation length is much smaller than the lattice length and the roughness increases as $W \sim At^\beta$, where β is called the growth exponent ($\beta = 1/3$ in $d = 1$ [19], $\beta \approx 0.23$ in $d = 2$ [20]) and A is an amplitude related to the coefficients of the KPZ equation.
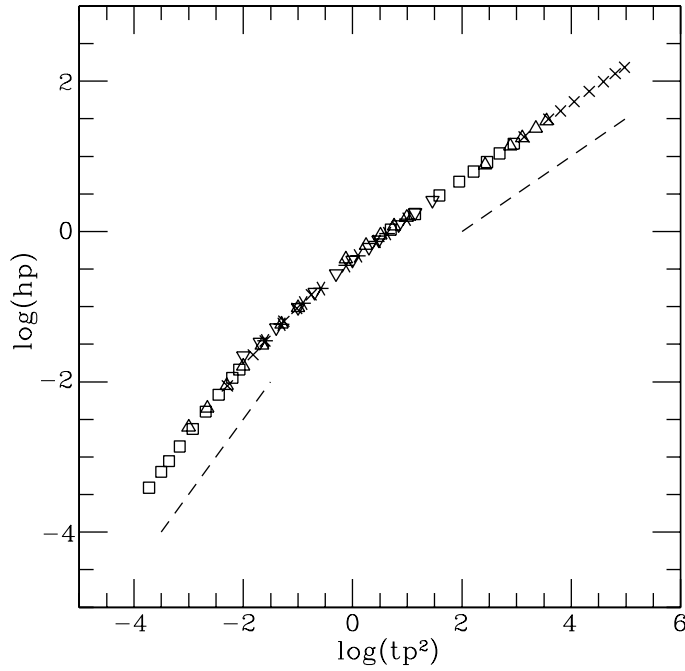
Figure 4. Scaling plot of $h/h_c \sim hp$ versus $t/t_c \sim tp^2$ with data for $D = 1$ and $p = 0.5$ (crosses, right side), $p = 0.1$ (up triangles, right side), $p = 0.05$ (squares, right side), $p = 0.01$ (down triangles), $p = 0.005$ (asterisks), $p = 0.001$ (up triangles, left side), $p = 0.0005$ (crosses, left side), $p = 0.00005$ (squares, left side). The dashed lines have slopes 1 (left) and 1/2 (right).

In the original Eden model, each site of the front can grow with probability 1 at each time unit [4, 21]. However, the corrosion of an M site in our model takes place with probability p per time unit. Thus, for small times we expect that

$$W_{KPZ} \approx A_{Eden}(pt)^{\beta}, \tag{7}$$

where A_{Eden} is a constant related to Eden growth properties. In figure 5 we show a log–log plot of the small-time roughness as a function of pt, for small p, confirming the validity of equation (7). The average slope of this plot is significantly below the asymptotic KPZ value $\beta = 1/3$, but these short-time deviations are expected in the Eden model [22, 23] as well as in related KPZ models [24, 30].

At long times, a corrosion event takes place when a void of the W sea arrives at the metal surface, after performing a random walk which begins at a distant point. Consequently, surface peaks will be more easily subject to corrosion than the valleys of the surface, which favours the production of surfaces with low roughness, as observed in previous numerical works for high values of p [13, 14]. These features indicate that the long-time regime is equivalent to that of the DLE model [16]. In DLE, eroding particles are randomly left at points very distant from the solid surface, they are allowed to diffuse and, when they reach the surface, they are annihilated together with the particle of the solid. In our model, the eroding particles of DLE are represented by the holes of the W sea.

In the continuous description of DLE, the stable interface is driven by the gradient of a Laplacian field [17]. A logarithmic scaling of the squared roughness is predicted in $1 + 1$
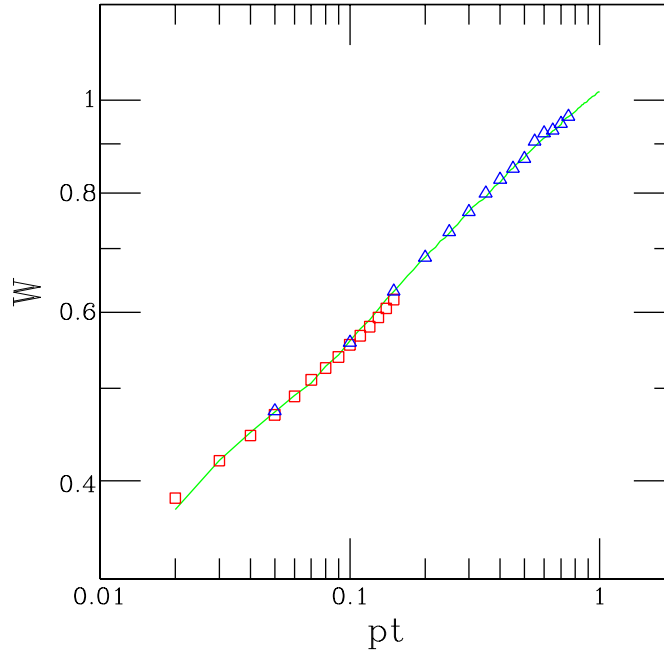
Figure 5. Short-time evolution of the surface roughness, with time scaling accounting only for the local corrosion rate p. Data for $p = 0.001$ (solid line), $p = 0.01$ (squares) and $p = 0.000\,05$ (triangles) are shown.

dimensions:

$$W^2_{\text{Laplacian}} \approx \frac{\Delta}{2\pi v} \ln (4\pi vt/a), \tag{8}$$

where v is the growth velocity, t is the time, a is the lattice parameter and $\Delta = va_r^d$, where a_r is a lengthscale associated with the noise [17].

Our model is equivalent to a DLE with a probability p of the incident particle to remove a particle of the solid. Moreover, changes in the timescale are also expected because the growth rate of our model decreases in time, while it is constant in the original DLE [16, 17]. Thus, for a connection of the DLE roughness in equation (8) and that of our model, we use $h = vt$ as the height of the corrosion front and $a = 1$. This gives

$$W^2_{\text{DLE}} \approx B \ln (4\pi h), \tag{9}$$

where h is measured in lattice units and B is a time-independent constant associated with the noise (p and D).

The time scaling of the surface roughness, implicitly given in its relation with the height h in equation (9), is tested in figure 6, where we plot $y = W^2/\ln (4\pi h)$ as a function of tp^2. Large values of tp^2 were chosen in order to ensure that only data in the long-time regime were considered ($tp^2 > 1$—see figure 4), but simulations for extremely long times are feasible only for large p. We notice that, for a given value of p, y oscillates around some constant value, which provides the estimate of the constant B in equation (9).

The crossover from KPZ to DLE scaling is expected to take place at a time of order t_c because the changes in the growth rate and in the roughness scaling are caused by the same mechanisms. In other models with crossover between different growth dynamics, it is observed that matching the scaling relations for the roughness of both dynamics leads to correct
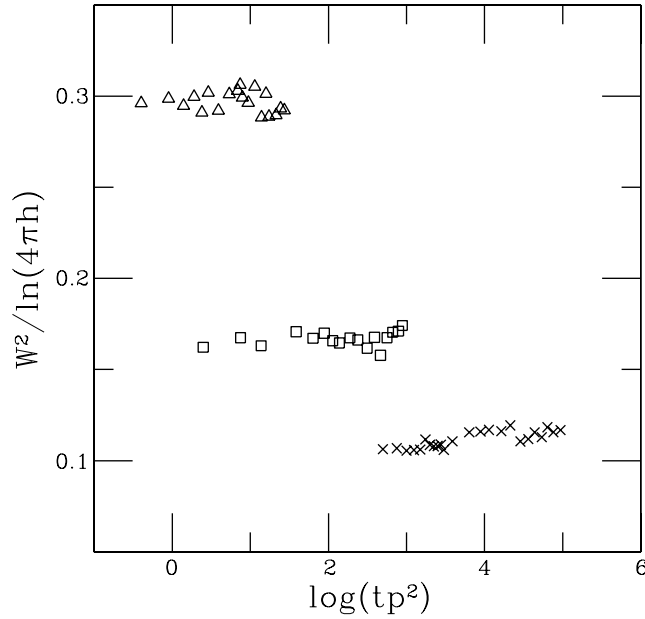
Figure 6. Scaling plot of the roughness in the DLE regime (long times): $p = 0.5$ (crosses), $p = 0.05$ (squares) and $p = 0.01$ (triangles).

predictions of t_c [9, 12]. Following this reasoning, the W values in equations (7) and (9) must be the same at time $t_c \sim 1/p^2$ and for a height $h_c \sim 1/p$. This gives

$$B \sim p^{-2/3}/\left(C_1 - C_2 \ln p\right), \tag{10}$$

where C_1 and C_2 are constants. In order to test relation (10), we plot $p^{-2/3}/B$ as a function of $\ln p$ in figure 7. We obtain a reasonable linear fit of the data for three orders of magnitude of p, which suggests the validity of our approach.

The crossover of surface roughness is slightly different in $2 + 1$ dimensions because the exponent β of the KPZ class is changed [20] and the roughness of DLE saturates at a finite value [17]. However, the model rules indicate that the short-time and long-time dynamics are also KPZ and Laplacian growth, respectively.

5. Summary and conclusion

We studied the crossover from Kardar–Parisi–Zhang growth to Laplacian front growth in a model for corrosion and passivation of a metallic surface. At small times, a regime of constant growth of the corrosion front is observed, with the roughness obeying KPZ scaling. At long times, a large fraction of the layer is blocked, leading to a global corrosion rate that decreases as $t^{-1/2}$. The roughness shows logarithmic scaling, with amplitudes depending on the corrosion probability p. Scaling arguments show that the crossover between these different dynamics takes place at $t_c \sim 1/p^2$, and that the height of the corrosion front at that time is $h_c \sim 1/p$. Universal scaling relations between the height of the corrosion front h and the time t are obtained, as well as relations for the surface roughness. All results are confirmed by numerical simulations in square lattices, although the scaling arguments are also valid in three dimensions.

As far as we know, the crossover from KPZ to DLE scaling in statistical growth models was not predicted before. The inverse situation, i.e. the crossover from DLE (short times) to KPZ
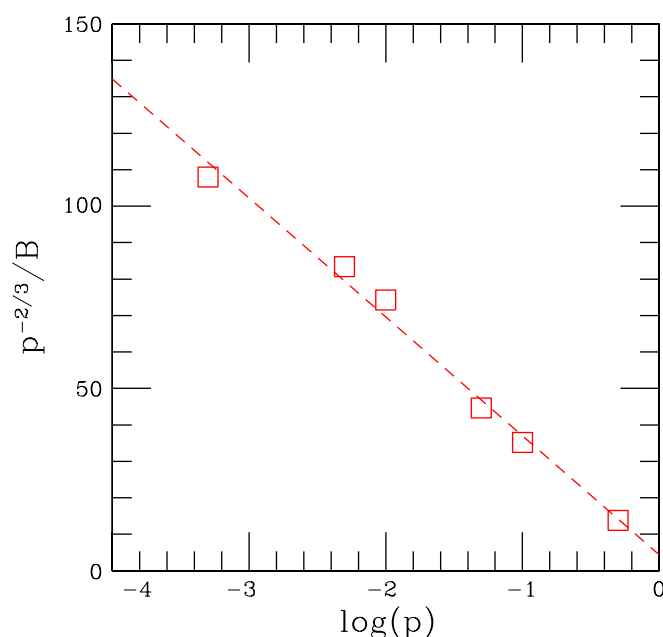
Figure 7. Ratio $p^{-2/3}/B$ as a function of $\log p$, obtained from long-time data for values of p ranging from 0.5 to 0.0005.

(long times) was suggested to appear in an extension of the DLE model where the movement of the eroding particles is biased towards the surface [17]. However, recent simulation results suggest a crossover to Edwards–Wilkinson scaling instead of KPZ [25]. We also recall that the crossover of our model must not be confused with the widely studied crossover from KPZ to diffusion-limited aggregation (DLA)—see, e.g. [26–29]. Indeed, surface roughness scaling is very different in DLE and DLA.

The universal behaviour discussed here may be observed in real systems where the basic features illustrated in figure 1 are expected. Such tests are certainly possible with the modern techniques of microscopy, that allow the determination of surface roughness with good accuracy. One of the interesting points for comparison is the time behaviour of the roughness, which evolves from a rapid growth, typical of KPZ scaling, to a very slow growth, typical of the logarithmic scaling in Laplacian front growth. Moreover, it would also be interesting to confirm the association of the changes in the growth rate with the changes in roughness scaling.

Acknowledgments

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