Delocalization transition of a rough adsorption-reaction interface

Hüseyin Kaya,[1,2,*] Alkan Kabakçıoğlu[1,3,†] and Ayşe Erzan[1,2]
[1]*Gürsey Institute, P.O. Box 6, Çengelköy 81220, Istanbul, Turkey*
[2]*Department of Physics, Faculty of Sciences and Letters, Istanbul Technical University, Maslak 80626, Istanbul, Turkey*
[3]*Department of Physics and Center for Material Sciences and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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We introduce a kinetic interface model suitable for simulating adsorption-reaction processes which take place preferentially at surface defects such as steps and vacancies. As the average interface velocity is taken to zero, the self-affine interface with Kardar-Parisi-Zhang-like scaling behavior undergoes a delocalization transition with critical exponents that fall into a different universality class. As the critical point is approached, the interface becomes a multivalued, multiply connected self-similar fractal set. The scaling behavior and critical exponents of the relevant correlation functions are determined from Monte Carlo simulations and scaling arguments.

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Kinetically roughened interfaces display a rich phenomenology, have deep connections with fields as diverse as self-organized criticality, spin-glasses, and complex pattern formation, and lend themselves to modeling various systems with practical applications, ranging from heterogenous catalysis to geomorphology [1–4]. The huge amount of numerical and analytical effort that has recently been invested in them has revealed that they obey universal scaling relations, which fall into one of a few universality classes. In this paper we would like to present a kinetic interface model which exhibits an anisotropic to isotropic phase transition with different scaling behavior at the delocalization critical point.

Reaction fronts formed by $A+B\rightarrow\varnothing$ reactions in heterogeneous systems where the reaction takes place on a two-dimensional substrate [5] are often confined to a narrow ''reactive zone'' especially if the reactants are either initially segregated or become segregated due to reaction kinetics [6–9]. Our present model is motivated by recent findings [10,11] of high reaction rates and strong bonding at surface defects like steps and vacancies in studies of heterogeneous catalysis, a burgeoning field in surface science.

We consider an idealized surface with only one step, terminating a terrace made up of A particles (Fig. 1). The surface is exposed to two kinds of incoming particles, A and B, which are allowed to adsorb at first contact, and only on sites adjacent to the step, which we will call ''interface sites.'' The adsorption of A particles makes the interface advance. The adsorbing B particles, on the other hand, immediately react with an A neighbor to form a product which leaves the surface. This eats into the step, making the interface recede. We investigate the effect of changing the rate of injection [12] of the two reactants. We do not allow any reactions to take place with the substrate atoms. We assume, for simplicity, that the temperature is low enough so that no surface restructuring occurs; the bonding to the interface sites is sufficiently strong [13] for diffusion along the interface to be prohibited. The kinetics is, therefore, driven by the adsorption and reaction steps and not by the transport of the reactants.

The model is defined on an infinite strip of width L, on which we impose periodic boundary conditions. The interface is initially a perfectly straight line located at $h=0$. The system is driven weakly so that at any instant only one particle of either the A or B type, with probabilities p_A or $p_B=1-p_A$, impinges on the interface. As the interface moves with a mean velocity equal to $\epsilon\equiv p_A-0.5$, it roughens, and becomes multiply connected, shedding ''islands'' or ''lakes'' in its wake. As $|\epsilon|\rightarrow 0$, the growth direction is completely delocalized, the width of the interfacial region keeps on growing indefinitely, and the interface breaks up into an isotropic fractal (see Fig. 2). For finite L, there may exist more than one spanning string of interface sites at $\epsilon=0$; this phenomenon is similar to the formation of Liesegang bands [14]). It is the purpose of this paper to understand the nature of this delocalization transition, to describe the crossover behavior and to characterize the self-similar reactive region formed as $|\epsilon|\rightarrow 0$.

For many interface problems with a well-defined growth direction, such as the Eden [15] model, or the Edwards-Wilkinson model [16], where the interface can be described

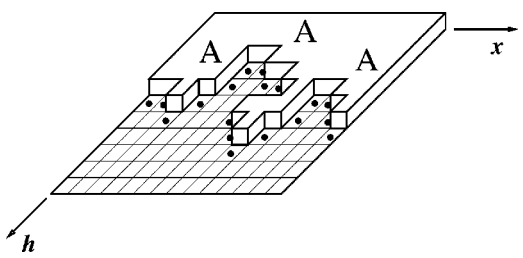

FIG. 1. A terrace of A particles, with the interface sites, indicated by dots, neighboring the step.

*Present address: Department of Biochemistry, Medicine Faculty, University of Toronto, 1 King's College Circle, Toronto, Ontario Canada M5S 1A8.

†Present address: Department of Physics of Complex Systems, The Weizmann Institute of Science, Rehovot 76100, Israel.

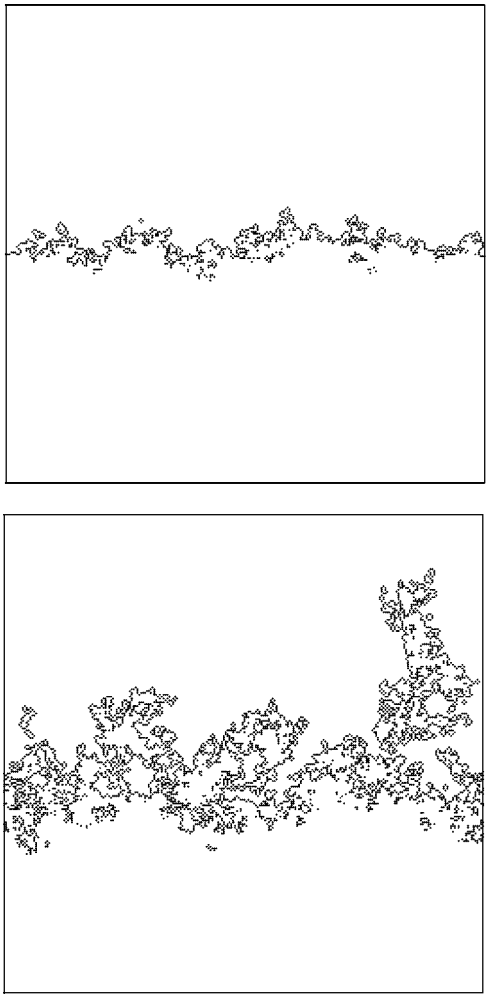

FIG. 2. The interface at $\epsilon=0$, for early and later stages of growth. The configurations for early times resemble the surface at larger values of ϵ.

with a single-valued, self-affine curve. The scaling behavior of the interface width may be conveniently summarized by the scaling form [17]

$$w \sim t^{\beta} g(\ell/t^{1/z}), \tag{1}$$

where $g(u)\sim$const for $u<1$ and $\sim u^{\chi}$ for $u\gg 1$; z is the dynamical critical exponent, and $\beta=\chi/z$. Kardar, Parisi, and Zhang (KPZ) [18] have found the values $z=3/2$, $\chi=1/2$, and $\beta=1/3$ for the stochastic differential equations describing Eden growth in $d=1+1$. This set of critical exponents characterizes a wide range of anisotropic growth phenomena with annealed noise [1], and where the local velocity of the interface increases with the slope. In the limit that the velocity goes to zero or is independent of the slope [3], one gets the Edwards-Wilkinson model [16], which is exactly solvable in $d=1+1$ dimensions and falls into another universality class, characterized by $z=2$, $\chi=1/2$, and $\beta=1/4$.

Since our interface is typically multivalued we define the width function within an interval of size ℓ as,

$$w(\ell)^2=\left\langle \frac{1}{N(\ell)} \sum_{i}^{N(\ell)} [h_i-\overline{h(\ell)}]^2 \right\rangle, \tag{2}$$

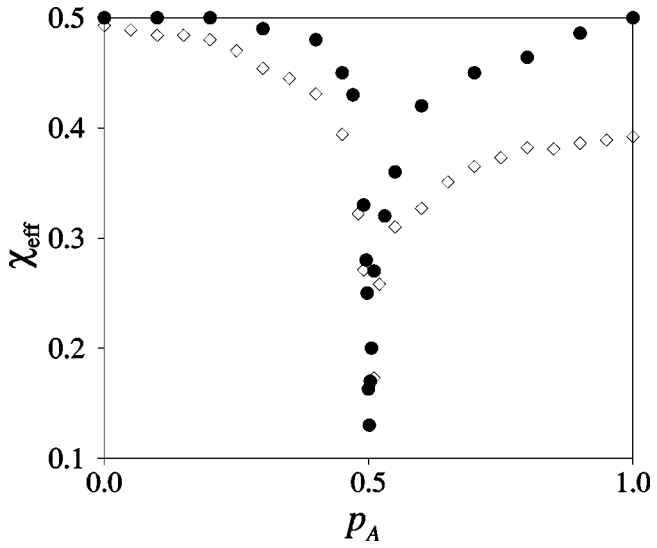

FIG. 3. The effective roughness exponent $\chi_{\rm eff}$, for disconnected parts of the interface included in ($\diamond$) and excluded from ($\bullet$) the analysis; $L\leqslant 1024$. The error bars are comparable to the size of the symbols.

where h_i is the height of the ith interfacial site, $i=1,\ldots,N(\ell)$, and $\overline{h(\ell)}$ is the mean position of the interface. We find $\beta=1/3$ for early times. In the limit of $p_A=0$ or $p_B=0$, i.e., for $|\epsilon|\to 0.5$, our model is equivalent to Eden [15] growth, and indeed, along the singly connected part of the interface $\chi=1/2$ in the steady state. However, effective roughness exponent ($\chi_{\rm eff}$) goes continuously to zero as $|\epsilon|\to 0$ as shown in Fig. 3.

The reason for this is that as we decrease $|\epsilon|$, the surface becomes highly convoluted, with islands (or lakes) of all sizes, and, therefore, increasingly multivalued. A competing length scale emerges in the system, the ''thickness'' of the interface, which we can measure by the variance of the height,

$$y(i)=\left(\frac{1}{n_i} \sum_{j=1}^{n_i} (h_{ij}-\overline{h_i})^2 \right)^{1/2},$$

with n_i being the number of interfacial sites $\{h_{ij}\}$, above any point i along the horizontal axis. The thickness obeys [19] a skewed-Gaussian distribution. The average $y_L\equiv\langle y\rangle_L$ and the second moment of this distribution both diverge as $|\epsilon|\to 0$ with a critical exponent $\nu=0.55\pm 0.05\simeq 1/2$, as $\sim|\epsilon|^{-\nu}$. The scaling form for y_L is

$$y_L \sim t^{\tilde{\beta}} G(|\epsilon|^{-\nu}/t^{1/\zeta}), \tag{3}$$

where $G(v)\sim v$ for $v<1$ while for $v>1$, $G(v)\sim$const with $\tilde{\beta}=1/2$ and the (longitudinal) dynamical critical exponent ζ obeys $\zeta=1/\tilde{\beta}$. The thickness of just the singly connected part does not diverge as $|\epsilon|\to 0$, so that the disconnected parts make up almost all of the interfacial region at the delocalization transition [19].

Normalizing $w(\ell)$ in Eq. (2) by $y_L^{1.1}$ yields a collapse of the data for all ϵ as can be seen from Fig. 4. We believe that the small deviation of the power of y_L from unity is due to

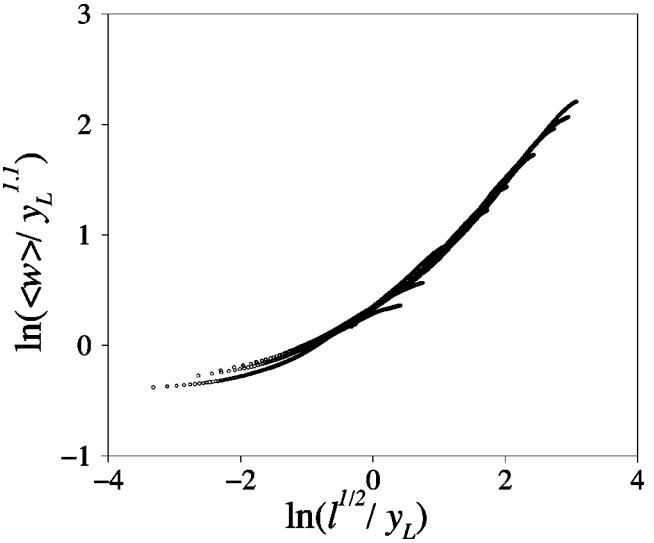

FIG. 4. The width normalized by a power of the thickness y_L very near unity, displays KPZ behavior for $\ell^{1/2}/y_L>1$. The different curves correspond to data taken at ϵ=0.001,0.003,0.005,0.01, 0.05,0.1,0.2,0.3,0.4,0.5. The deviations from the smooth collapse are due to ℓ becoming comparable to the system size $L=1024$.

insufficient statistics for y_L which converges extremely slowly as $|\epsilon|\to 0$ and may safely be neglected, and we conclude

$$w(\ell)\sim y_L\times\begin{cases}\ell^{1/2}/y_L & \ell^{1/2}\gg y_L\\ \text{const} & \ell^{1/2}\ll y_L\,.\end{cases} \tag{4}$$

Thus, χ_{eff} goes to zero as the self-affine excursions of the interface are blurred by the thickness of the interface as y_L becomes greater than $\ell^{1/2}$.

If one considers coarse-grained width functions, either by taking the average height at any given point or the maximum [20] height for $\epsilon>0$ (minimum for $\epsilon<0$), one finds that they obey the scaling form (1) with KPZ exponents for $\ell\ll L$.

To get the local scaling picture, we focus on a single spanning string in the interface and consider

$$C_x(l)=\langle[x(r+l)-x(r)]^2\rangle^{1/2}, \tag{5}$$

$$C_h(l)=\langle[h(r+l)-h(r)]^2\rangle^{1/2}. \tag{6}$$

where both r and l are the (''chemical'') length measured along the string, and x and h are Cartesian coordinates of the interface site. The scaling relations we have found from Fig. 5 for these quantities are given below. In the transient regime ($l\gg t^{1/2}$),

$$C_x\sim\begin{cases}l & y_L\ll l^{1/2}\\ l/t^{\psi} & y_L\gg l^{1/2}\end{cases} \tag{7}$$

and

$$C_h\sim t^{\beta}, \tag{8}$$

where $\psi=1/6$.

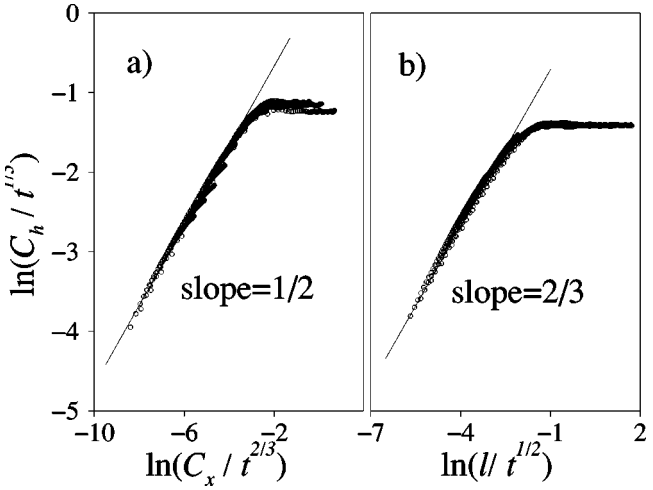

FIG. 5. (a) C_h and C_x for $\epsilon=0.5$ for $l=2,\ldots,L/2$, and different times. (b) C_h in the isotropic region, $\epsilon=10^{-4}$.

Note the horizontal projection of a segment of fixed ''chemical length'' decreases with t as the surface crumples with time in the critical ($|\epsilon|\to 0$) region. In the steady state, ($l\ll t^{1/2}$),

$$C_x\sim\begin{cases}l & (y_L\ll l^{1/2}),\\ l^{\chi_{\text{isot}}} & (y_L\gg l^{1/2}),\end{cases} \tag{9}$$

and

$$C_h\sim\begin{cases}l^{1/2} & (y_L\ll l^{1/2}),\\ l^{\chi_{\text{isot}}} & (y_L\gg l^{1/2}).\end{cases} \tag{10}$$

We see that for $y_L\gg l^{1/2}$, the interfacial region becomes isotropic, with $C_x\sim C_h$. This regime is characterized by an ''isotropic'' roughness exponent $\chi_{\text{isot}}=2/3$. In the opposite limit, $C_h\sim C_x^{1/2}$, as expected for the self-affine Eden surface. This crossover is clearly seen in Fig. 6. In accordance with

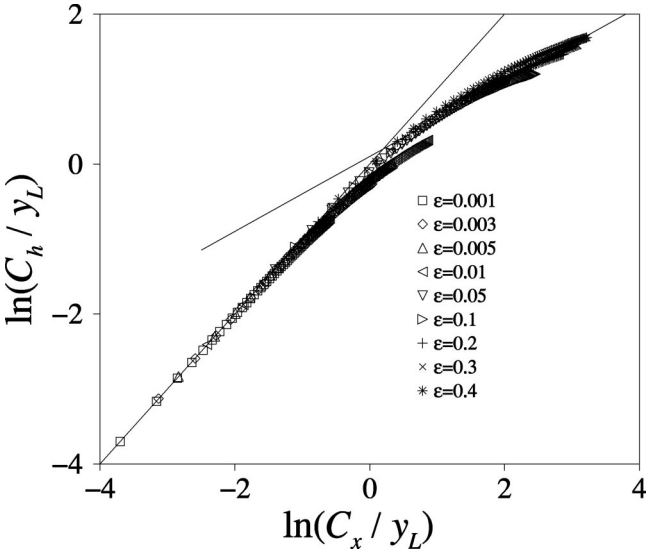

FIG. 6. The vertical projection C_h of sections of the singly connected part, plotted as a function of the horizontal projection C_x.

the above observations we propose the following scaling functions for the whole range of ϵ. Defining $u=l/t^{1/z}$ and $s=y_L/l^{\chi}$, we have

$$C_h \sim \alpha_h(\epsilon) t^{\beta} f(u,s), \qquad C_x \sim \alpha_x(\epsilon) t^{1/z} g(u,s), \tag{11}$$

where

$$f(u,s) \sim \begin{cases} \text{const}, & u \gg 1 \\ u^{\chi}, & u \ll 1,\ s \ll 1 \\ u s^{1/z}, & u \ll 1,\ s \gg 1, \end{cases} \tag{12}$$

and

$$g(u,s) \sim \begin{cases} u, & s \ll 1 \\ u^{\chi}/s, & u \gg 1,\ s \gg 1 \\ s^{-1/\tilde{\beta}z}, & u \ll 1,\ s \gg 1. \end{cases} \tag{13}$$

where χ, z, and β have their KPZ values. The amplitudes are defined as $\alpha_x(\epsilon)=(a+|\epsilon|^{1/6})$ and $\alpha_h=1/(a^{-1}+|\epsilon|^{1/6})$, where a is some constant.

From these scaling forms and Eq. (3) we see that the new critical exponents obey the relationships

$$\psi=\tilde{\beta}-\frac{1}{z^{\mathrm{KPZ}}}+\frac{\chi^{\mathrm{KPZ}}}{z^{\mathrm{KPZ}}} \tag{14}$$

and

$$\chi^{\mathrm{isot}}=\zeta\chi^{\mathrm{KPZ}}/z^{\mathrm{KPZ}}, \tag{15}$$

which yields

$$\chi^{\mathrm{isot}}=\beta^{\mathrm{KPZ}}/\tilde{\beta}. \tag{16}$$

From Eqs. (9) and (10) we see that the graph dimension of a singly connected part in the isotropic regime is $D_g=1/\chi^{\mathrm{isot}}$. Since in two dimensions, D_g is related to the roughness exponent via $D_g=2-\chi$, for $\chi=1/2$ we get $\chi^{\mathrm{isot}}=2/3$. The scaling relation (16) yields $\tilde{\beta}=1/2$, from Eqs. (14) and (15) it follows that $\psi=1/6$ and $\zeta=2$. The fractal dimension of the self-similar set of interface sites [19] within a band of width $y_L \sim |\epsilon|^{-\nu}$ is found, from boxcounting, to be $D_I=1.85\pm0.05$ for length scales $\ell < y_L^2$.

In conclusion, we have presented an absorption-reaction model where the interface undergoes a delocalization transition at the point where the mean velocity of the interface goes to zero. Although it might be conjectured [1] that as the velocity of the interface vanishes, the scaling behavior should cross over to the Edwards-Wilkinson universality class, this is not the case here. It has previously been observed [20,21], that the presence of overhangs, islands and inclusions may cause the small-scale structure of the interface to crossover from being self-affine to self-similar while the large-scale behavior remains self-affine. In the present model, this crossover is driven by a competing length scale, the thickness of the interface, which diverges at the critical point as $|\epsilon|^{-\nu}$ with $\nu=1/2$. In the critical region, the interface is characterized by a set of exponents $\chi^{\mathrm{isot}}=2/3$, $\tilde{\beta}=1/2$, $\zeta=2$, $\psi=1/6$, and the fractal dimension $D_I=1.85$. Except for ν and D_I, these exponents may be obtained from the KPZ exponents via scaling relations.

It should finally be mentioned that the reaction region can be described by stochastic differential equations of the multiplicative noise type with a single component field, since in our model interface sites cannot be created spontaneously either in the bulk or the vacant region. A field-theoretic renormalization-group computation similar to that by Tu, Grinstein, and Muñoz [22] is presently under way to obtain the values of the critical exponents.

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