Transients due to Instabilities Hinder Kardar-Parisi-Zhang Scaling: A Unified Derivation for Surface Growth by Electrochemical and Chemical Vapor Deposition

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We propose a unified moving boundary problem for surface growth by electrochemical and chemical vapor deposition, which is derived from constitutive equations into which stochastic forces are incorporated. We compute the coefficient in the interface equation of motion as functions of phenomenological parameters. The equation features the Kardar-Parisi-Zhang (KPZ) nonlinearity and instabilities which, depending on surface kinetics, can hinder the asymptotic KPZ scaling. Our results account for the universality and the experimental scarcity of KPZ scaling in the growth processes considered.

The dynamics of rough surfaces [1] is a subject of high interest. This is due both to its implications for processes of technological relevance [2,3], and to the interesting instances that it offers of extended systems evolving in the presence of fluctuations [4]. A very successful framework for the study of rough interfaces has been the use of stochastic growth equations for the interface height. Among these, the one proposed by Kardar, Parisi, and Zhang (KPZ) [5] has played a prominent role, since in particular it has enabled connections to be made with other physical problems, such as directed polymers in disordered media or randomly stirred fluids [1]. On the basis of a coarse-grained description of surface growth and symmetry arguments, the KPZ equation was initially expected to describe the dynamics of surfaces growing, e.g., at the expense of a vapor phase, in the absence of conservation laws, and is thus expected to be relevant to such diverse physical growth systems as electrochemical deposition (ECD) [2] or chemical vapor deposition (CVD) [3]. The generality of KPZ scaling would be a consequence of the phenomenon of *universality* observed for the scaling properties of rough surfaces. However, to date very few experiments have been reported which are compatible with the predictions of the KPZ equation [6−8]. Moreover, mere symmetry arguments do *not* enable a detailed connection with phenomenological parameters describing specific experimental systems, while detailed *derivations* of the KPZ equation were achieved for discrete or continuous theoretical models [9], only indirectly related with experiments. These facts have led to invoking additional effects on the same coarse-grained level, such as specific noise statistics, nonlocal effects, etc. [1], in order to account for the difference between the observed and the predicted scaling behaviors of rough surfaces. However, a wide range of scaling exponents ensued, there being no theoretical argument that could identify the correct exponents for a specific growth experiment.

In this Letter we study two of the main techniques employed in experiments on nonconserved surface growth, namely ECD and CVD. These techniques have actually played a preeminent role in the study of pattern formation [10], but only recently have they been shown to provide experimental realizations of rough interfaces in the KPZ universality class [7,8]. The asymptotic behavior is in both systems preceded by exceedingly long unstable transients, extending in, e.g., the experiments in [8] for up to two days deposition time. This complex time behavior is thus far unaccounted for on general grounds by any coarse-grained continuum model. Here we start from the constitutive equations of ECD and CVD, into which we allow for stochastic forces, following a similar treatment to that employed in studies of solidification [11], step dynamics [12], or fluid imbibition [13]. We show that ECD and CVD can both be described within a unified framework, which provides a stronger statement on universality in nonconserved growth phenomena than that restricted to scaling behavior. Moreover, we compute the coefficient appearing in the ensuing stochastic interface equation of motion (IEOM) as functions of the phenomenological parameters characterizing the corresponding physical growth process. The IEOM features the expected KPZ nonlinearity, but also instabilities which can hinder asymptotic KPZ scaling. Specifically, for the case of noninstantaneous growth events at the surface, the IEOM is a stochastic generalization [12,14] of the Kuramoto-Sivashinsky equation [15], for which very long transients due to instabilities are known to occur [16] before scaling behavior can be observed. Thus, there is no need to invoke additional effects at a coarse-grained level in order to account for the difficulty in observing KPZ scaling, but rather they are due to the long unstable transients which will quite generically occur. Our approach also accounts for features of discrete growth models [17] and our conclusions are thus expected to apply rather generally for nonconserved growth systems.

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We first consider growth by CVD. A successful model of this type of growth was formulated and developed in [18]. A stagnant diffusion layer of infinite vertical extent is assumed to exist above the substrate upon which an aggregate will grow. Particles of an intermediate species [concentration $c(x, z, t) \equiv c(\mathbf{r}, t)$, where x is the coordinate along the initial one-dimensional substrate and z is the growth direction] diffuse through the stagnant layer. When they meet the surface they react in order to stick to the aggregate, this occurring with an efficiency measured by a kinetic mass-transfer coefficient k_D [19]. Additional curvature driven effects, such as surface diffusion and evaporation condensation, can influence the local growth velocity of the aggregate. Moreover, we will take into account local fluctuations in the vapor phase and surface diffusion currents, as well as in the deposition events, in order to account for the experimental relevance of fluctuations for the morphology of surfaces grown by CVD [8]. We thus propose the following stochastic generalization of the deterministic model of CVD [18]:

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \nabla \cdot \mathbf{q}, \qquad (1)$$

$$k_D(c - c_{eq}^0 - \Gamma\kappa + \chi) = (D\nabla c - \mathbf{q}) \cdot \mathbf{n}, \quad (2)$$

$$\mathbf{v} \cdot \mathbf{n} = \Omega(D\nabla c - \mathbf{q}) \cdot \mathbf{n} - B\nabla_s^2\kappa - \Omega\nabla \cdot \mathbf{p}, \quad (3)$$

$$c(x, z \to \infty, t) = c_a. \qquad (4)$$

In Eq. (1), D is the diffusion constant, and the conserved noise $\mathbf{q}(\mathbf{r}, t)$ represents fluctuations in the concentration associated with diffusion through the stagnant layer. Equations (2) and (3) hold at any point on the aggregate surface $\mathbf{r} = \mathbf{s}$, the symbol ∇_s^2 denoting the surface Laplacian operator and $\mathbf{n}$ the local unit normal vector. Equation (2) is a mixed boundary condition which relates the diffusion current arriving at the aggregate from the stagnant layer with the material which actually deposits, via the kinetic coefficient k_D. The noise term χ represents fluctuations in the deposition events [12], c_{eq}^0 is the equilibrium concentration for a flat interface, κ is the local mean curvature, and $\Gamma = \gamma c_{eq}^0 \Omega/(k_B T)$, with γ the surface tension—whose anisotropy will be neglected, i.e., we will consider an amorphous or polycrystalline aggregate—and T the temperature. In Eq. (3), $\mathbf{v}$ is the local aggregate velocity, Ω is the atomic volume of the depositing species, and the coefficient of the surface diffusion current [1] $B = D_s\nu_s\gamma\Omega^2/k_B T$, with D_s the surface diffusivity and ν_s the surface concentration of particles. Moreover, $\mathbf{p}$ is a noise term associated with the surface diffusion current. Finally, c_a in (4) is a constant value held fixed at the edge of the stagnant layer. Note that the deterministic model of CVD [18] is recovered by neglecting $\mathbf{q}$, $\mathbf{p}$, and χ in (1)–(4). We consider zero-mean, uncorrelated, and white noise terms. A local equilibrium hypothesis [11,12] then allows us to determine their variances to be [20]

$$\langle q^i(\mathbf{r}, t)q^j(\mathbf{r}', t')\rangle = 2Dc(\mathbf{r}, t)\delta_{ij}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t'), \qquad (5)$$

$$\langle p^i(\mathbf{s}, t)p^j(\mathbf{s}', t')\rangle = 2D_s\nu_s\delta_{ij}\delta(\mathbf{s} - \mathbf{s}')\delta(t - t'), \quad (6)$$

$$\langle \chi(\mathbf{s}, t)\chi(\mathbf{s}', t')\rangle = (2c(\mathbf{s}, t)/k_D)\delta(\mathbf{s} - \mathbf{s}')\delta(t - t'). \qquad (7)$$

Before studying the interface dynamics predicted by model (1)–(4), let us show that it also describes electrochemical deposition, under a proper interpretation of the fields and parameters appearing. For simplicity, we assume a rectangular thin cell in which the two electrodes are made of the same metal, the cell being filled with a *dilute* solution of a salt of this metal. In a growth experiment by ECD [2], an electric field is applied driving the motion of cations towards the cathode, whereupon they stick via a reduction reaction, leading to the growth of an aggregate. The constitutive equations, neglecting convection of the electrolyte, [21] describe diffusion of cations (concentration C) and of anions (concentration A), together with Poisson's equation for the electric field across the cell. This highly nontrivial system can be somewhat simplified under the electroneutrality condition [22] $z_a A = z_c C$, where ez_c and $-ez_a$ are the cationic and anionic charges, implying

$$\partial_t C = D\nabla^2 C, \qquad (8)$$

where $D = (\mu_c D_a + \mu_a D_c)/(\mu_a + \mu_c)$ is the ambipolar diffusion constant, with $\mu_{c,a}$ being the cationic and anionic mobilities. The electric field configuration and the anion dynamics are implicit in the definition of D and in the boundary conditions (BC), which we need to specify. The simplest BC are that the anion flux be zero both at the anode and at the cathode, where only cations contribute to the aggregate growth. The current density at the cathode surface is then [2]

$$\mathbf{J} \cdot \mathbf{n} = -[z_c D_c F/(1 - t_c)]\nabla C \cdot \mathbf{n}, \qquad (9)$$

where $t_c \equiv \mu_c/(\mu_a + \mu_c)$ and F is Faraday's constant. Moreover, charge transport at the cathode is an activated process, whose balance is described by the Butler-Volmer equation [2,23]

$$J = J_0[e^{(1-\beta)\eta z_c F/RT} - e^{-(\beta\eta + \eta_s)z_c F/RT}C/C_a], \quad (10)$$

where J_0 is the exchange current density in equilibrium, β is a coefficient between 0 and 1 describing the asymmetry of the energy barrier related to the cation reduction reaction, C_a is the initial cation concentration, R is the gas constant, and η is the overpotential, from which a surface curvature contribution η_s has been singled out. By defining the concentration field $c \equiv D_c C/[D(1 - t_c)]$ (c_a and c_{eq}^0 are defined accordingly) and performing an expansion of Eq. (10) for a small value of $\eta_s = \Omega^{ECD}\gamma^{ECD}R\kappa/(z_c F k_B)$ [2], Eqs. (1)–(4) provide the stochastic generalization of the ECD model (8)–(10) incorporating surface tension and surface diffusion effects at the aggregate surface. Note that Eqs. (9) and (10) together amount to a

mixed BC [24] on c of the type of Eq. (2), with a kinetic coefficient $k_D^{\mathrm{ECD}} \equiv J_0 e^{-\beta z_c F \eta/RT} D(1 - t_c)/(z_c F C_a D_c)$. For instance, the $\eta \to -\infty$ limit of completely efficient reduction at the cathode leads to an absorbing boundary condition there of the type $c = c_{\mathrm{eq}}^0 + \Gamma\kappa$.

We are now in a position to study the generic model (1)–(4) and draw conclusions for the two diverse growth systems considered. We follow a similar approach to that in [11–13], and references therein. Namely, we first note that in the zero noise limit Eqs. (1)–(4) support a flat solution $c(\mathbf{r}, t) = c(z, t)$, moving at a constant velocity $V = k_D[\Omega(c_a - c_{\mathrm{eq}}^0) - 1]$. By the use of the diffusion Green function, we project the moving boundary problem onto the aggregate surface. Finally, we perform a perturbation expansion and a long wavelength analysis in order to derive a stochastic differential equation for a local deviation $\zeta(x, t)$ (in the frame moving with velocity V) from the flat interface solution. Details will be reported elsewhere [20]. The results are conveniently classified by the value of the kinetic coefficient k_D [25].

Instantaneous surface kinetics ($k_D \to \infty$).—Denoting by $\zeta_k(t)$ the kth Fourier mode of $\zeta(x, t)$, in the case of infinitely fast reaction kinetics at the interface (absorbing boundary condition) the IEOM reads

$$\partial_t \zeta_k(t) = \omega(k)\zeta_k(t) + \frac{V}{2}\mathcal{F}_k[(\nabla\zeta)^2] + \beta_k^{\mathrm{absorb}}(t).$$

$$(11)$$

Here $\mathcal{F}_k[f(x)]$ denotes the kth Fourier mode of $f(x)$, the nonlinear term in (11) having the expected KPZ form, and $\beta_k^{\mathrm{absorb}}(t)$ is an *additive* noise term whose correlations depend on the dispersion relation $\omega(k)$ [26]. Note that, in principle, the system (1)–(4) has *multiplicative* noise. However, similarly to [12], to lowest nonlinear order in $\zeta(x, t)$ the IEOM features only *additive* noise terms. For Eq. (11) the dispersion relation reads $\omega(k) = V|k|(1 - d_0 l_D k^2)[1 - d_0/l_D + (d_0^2/4 - B/D)k^2]^{1/2} + D(d_0^2/2 - B/D)k^4 - 3d_0 D k^2/l_D$, where we have defined a capillarity length $d_0 = \Gamma\Omega$ and a diffusion length $l_D = D/V$. As we see, due to the shape of $\omega(k)$, the IEOM (11) is nonlocal in space. This is a reflection of the diffusional instabilities present in the system [10]. For instance, in the absence of surface diffusion currents ($B = 0$), and as long as $d_0 \ll l_D$, the dispersion relation of Eq. (11) is of the Mullins-Sekerka type [10], $\omega(k) \simeq V|k|(1 - d_0 l_D k^2)$. However, the IEOM does have additive noise and a KPZ nonlinear term with coefficient $V/2$, both facts as expected on general grounds [1]. Although the behavior of Eq. (11) at large scales is not completely known, both a scaling argument and preliminary numerical simulations indicate that KPZ scaling is not asymptotic under these growth conditions [27].

Noninstantaneous surface kinetics ($k_D < \infty$).—For the case of noninstantaneous deposition events at the surface, the dispersion relation $\omega(k)$ turns out to depend only on even powers of k, which allows to express the IEOM directly in configuration space, featuring only *local* terms [we omit the $\mathbf{r}$ and t dependencies of $\zeta(\mathbf{r}, t)$]:

$$\partial_t \zeta = -a_2 \nabla^2 \zeta - a_4 \nabla^4 \zeta + \frac{V}{2}(\nabla\zeta)^2 + \beta^{\mathrm{mixed}}(\mathbf{r}, t),$$

$$(12)$$

where $a_2 = k_D l_D \Delta$, $a_4 = k_D l_D^2 \Delta d_0/[1 - (d_0/l_D)^{1/2}] + B(1 + k_D/V)$, and $\Delta = 1 - d_0/l_D$. Again, $\beta^{\mathrm{mixed}}(\mathbf{r}, t)$ is an *additive* noise with $\omega(k)$-dependent correlations [26]. As in Eq. (11), the coefficient of the KPZ nonlinearity is $V/2$. However, while (11) always has a band of linearly unstable modes, this happens in Eq. (12) only if $\Delta > 0$, i.e., when surface tension is unable to counteract the diffusional instabilities ($d_0 < l_D$). In this unstable case, (12) is the stochastic Kuramoto-Sivashinsky (KS) equation, already encountered in other interface dynamics contexts, such as step dynamics [12], or surface erosion by ion-beam sputtering [14]. In the stochastic KS system, there is a linearly most unstable mode $k_m = (2l_D d_0)^{-1/2}$ (assuming $B = 0$), whose onset time is $\omega_m^{-1} = 2/(k_D l_D k_m^2)$. For asymptotic times, KPZ scaling is obtained, but only after an exceedingly long transient [16].

From the above analysis of Eqs. (11) and (12), KPZ scaling should be expected only for slow surface kinetics, and will, nevertheless, be affected by early time instabilities, unless the capillary length is larger than the typical diffusion length in the system. KPZ scaling corresponds to the *conformal growth* mode, which is most interesting for applications of CVD-grown films and can indeed be achieved under industrial conditions by tuning the relative values of k_D, l_D, and d_0 [3,8,18]. In the case of ECD, we can further verify the predictions from model (1)–(4) via Eqs. (11), (12) with both experimental [7,28] and Monte Carlo [17] studies. For instance, in the ECD experiment in [28] the diffusion length $l_D \approx 2$ cm is the largest length scale in the system, and a Mullins-Sekerka dispersion relation is reported; consequently, after a stable transient the diffusional instabilities that occur completely override any scaling behavior at long times. As a difference, in the experiments of [7] the growing aggregate undergoes an unstable transient, beyond which its surface stabilizes into the KPZ stationary state. This behavior is qualitatively compatible with that of the noisy KS equation: from the experimental value of the branch spacing one has $k_m \simeq 1.3 \times 10^3$ cm^{-1}. Using [7] $D \simeq 10^{-5}$ cm^2 s^{-1} and $V \simeq 2 \times 10^{-4}$ cm s^{-1}, one obtains a typical value $d_0 = 1/(2l_D k_m^2) \simeq 5 \times 10^{-6}$ cm, hence indeed $d_0 \ll l_D \simeq 0.05$ cm. Moreover, the instability occurs after $1/\omega_m \simeq 0.3 \times 10^3$ s, which allows one to estimate $k_D \simeq 8 \times 10^{-8}$ cm s$^{-1} \ll V$, hence conditions are in the slow kinetics regime.

Equations (1)–(4) also apply to the dynamics of discrete growth models such as the multiparticle biased diffusion limited aggregation (MBDLA) model [17], which is a generalization of the DLA model [1,10] to the case of a finite concentration of random walkers performing biased

random walks (bias parameter p), which stick to the growing aggregate with a finite sticking probability s. MBDLA reproduces ECD experiments for one-dimensional substrates *quantitatively* [17], and ECD experiments for two-dimensional substrates *qualitatively* [29]. Thus, the sticking probability s plays the role of a noise reduction parameter, in the sense that for small s values the system reaches faster its KPZ asymptotic scaling behavior; this role is played in our continuum model by the kinetic mass transfer coefficient k_D [19]. Furthermore, the bias p is proportional to the aggregate velocity V. As the characteristic branch spacing is, according to (12), approximately equal to $(l_D d_0)^{-1/2}$, the continuum model predicts a ramified-to-compact transition as p increases, such as is observed in MBDLA [17]. Moreover, since the coefficient of the KPZ term also increases, the corresponding scaling is expected to occur earlier as V (or p) increases, again as is observed in the discrete model.

In summary, our study of CVD and ECD leads us to expect diffusional instabilities to generically hinder KPZ scaling in nonconserved growth experiments. Our continuum approach from constitutive equations allows us to perform detailed comparison with phenomenological parameters in experiments, and also provides a physical interpretation for features of discrete models of kinetic roughening such as noise-reduction parameters [1], e.g., of the type of the sticking parameter in MBDLA [17]. More detailed predictions from model (1)−(4) would benefit from a computationally more efficient formulation. Work along these lines is currently under way [20].

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