

STOCHASTIC DIFFERENTIAL EQUATION FOR SURFACE GROWTH FROM A VAPOR PHASE: A MOVING BOUNDARY PROBLEM WITH FLUCTUATIONS

Rodolfo Cuerno* and Mario Castro†

*Departamento de Matemáticas & Grupo Interdisciplinar de Sistemas Complejos (GISC)
Universidad Carlos III de Madrid
Avenida de la Universidad 30, E-28911 Leganes (Madrid), Spain
e-mail: cuerno@math.uc3m.es, web page: <http://gisc.uc3m.es/~cuerno>

† GISC & Escuela Técnica Superior de Ingeniería (ICAI)
Universidad Pontificia Comillas
E-28008 Madrid, Spain
e-mails: marioc@upco.es

Key words: Moving boundary problems, fluctuations, Electrochemical Deposition, Chemical Vapor Deposition, diffusional instabilities, surface/aggregate growth

Abstract. *We report on the derivation of an stochastic differential equation that describes the growth dynamics of solid surfaces growing from a vapor phase, such as the surfaces of aggregates grown by Electrochemical Deposition (ECD), or of those produced by Chemical Vapor Deposition (CVD). We formulate an unified moving boundary problem that is relevant both to ECD and CVD experiments, into which we allow for fluctuations in the various processes leading to growth: surface diffusion, attachment/detachment events, and surface kinetics. By means of perturbative techniques we are able to derive a closed stochastic nonlinear differential equation for the surface profile. The equation has the form of the stochastic Kuramoto-Sivashinsky equation and generalizations thereof. As a function of surface kinetics, the dispersion relation is modified, in such a way that the interface properties (roughness, etc.) change. Moreover, our results allow to interpret the lack of universal properties for the surface fluctuations found in many experiments as originated in the (diffusive) instabilities existing in the system prior to achieving its asymptotic state.*

1 INTRODUCTION

Many processes of industrial and technological relevance involve growth of a solid aggregate at the expense of a rarified (vapor, solution, etc.) phase. Paradigmatic examples are electrochemical deposition (ECD) or chemical vapor deposition (CVD). In ECD processes, a solid deposit grows onto the cathode of an electrochemical cell containing a salt solution (generally of Cu, Ag or Zn), when a potential difference is set between two metallic electrodes across the cell. ECD is widely employed for deposition of pure metals and alloys for applications in microelectronics, magnetic media in recording devices, as well as for micromachine fabrication [1]. CVD is a technique in which, rather, solid thin films are produced onto an initial substrate through the incorporation to the latter of reacting species being supplied from a vapor phase [2]. This production technique is massively employed in the microelectronic industry for e.g. production of coatings. These two methods for production of thin films are conceptually similar, in that the main processes leading to growth can be simplified to incorporation of a reactant which aggregates when it reaches the growing deposit, after *diffusive* transport through the vapor or solution phase. In typical applications of ECD or CVD, device quality and performance is usually associated with a low roughness for the interface of the deposit or film grown. Therefore, it is important to develop analytical tools that can assess conditions under which the interface roughness is small. This becomes ever more critical since in both processes generic parameter conditions are associated with occurrence of *morphological instabilities* [3, 4], that can lead to macroscopic roughness for the growing aggregate surface. As the current trend for miniaturization is pursued, detailed understanding is also required, on the other hand, on the effect of *fluctuations* on the morphological properties of the aggregate surface. Such fluctuations originate in the stochastic nature of the processes determining film properties, such as mass transport by diffusion, chemical reactions at the interface leading to species attachment, etc. From the recent literature in Statistical Mechanics [5, 6], it is known that fluctuations in growth processes are associated with the emergence of *universal* behavior of the surface morphology, such as scaling behavior of the surface roughness for long time and length scales. In this communication, we report on the derivation of a continuum model that generically describes the aggregate surface from the constitutive equations of ECD and CVD under proper interpretation of the parameters and the fields appearing. The model takes the form of a moving boundary problem into which fluctuations are allowed for, under a local equilibrium approximation. As a result, a unified picture emerges on the growth process taking place in two diverse growth techniques, that provides understanding on the similarities among aggregate morphologies produced by both methods. Perturbative techniques allow us to derive a closed stochastic differential equation for the aggregate surface height. The study of this equation allows to assess [7] the origin for the unexpected lack of universality in growth experiments by ECD or CVD, and leads to considering a new equation [8], thus far unexplored in the context of rough interface growth dynamics.

2 MODEL FORMULATION

We recall briefly the classic constitutive equations of CVD [9, 10, 11], and then rephrase the constitutive of ECD in a way that matched exactly with those of CVD. To the thus unidified model of non-conserved surface growth we then incorporate the effect of fluctuations associated with to the various relaxation and transport mechanisms apperaring.

2.1 Chemical vapor deposition

A stagnant diffusion layer of infinite vertical extent is assumed to exist above the substrate upon which an aggregate will grow. This approach implies that the length of the stagnant layer is much larger than the typical width of the deposit. Particles within the vapor diffuse randomly until they arrive at the surface, react and aggregate to it. The concentration of these particles, $c(x, z, t) \equiv c(\mathbf{r}, t)$, follows the diffusion equation,

$$\partial_t c = D \nabla^2 c, \quad (1)$$

with boundary condition at the top of the stagnant layer $c(x, z \rightarrow \infty, t) = c(x, z, 0) = c_a$. Mass conservation at the aggregate surface implies that the growth velocity along the local normal direction is given by

$$V_n = \Omega \nabla c \cdot \mathbf{n} - \Omega \nabla_s \cdot \mathbf{J}_s, \quad (2)$$

where Ω is the molar volume of the substrate and \mathbf{J}_s is a flux of particles diffusing on top of the aggregate surface [12]. The particle concentration, c , and its gradient at the surface are finally related through the boundary condition:

$$k_D(c - c_{eq}^0 + \Gamma \kappa)|_{\zeta(x,t)} = D \nabla c \cdot \mathbf{n}|_{\zeta(x,t)}, \quad (3)$$

where c_{eq}^0 is the local concentration of equilibrium of a flat interface with its vapor, $\zeta(x, t)$ is the local deviation of the surface height with respect to its spatial average, κ is the surface mean curvature, and $\Gamma = \frac{\gamma c_{eq}^0 \Omega}{k_B T}$, with γ being the surface tension. The mixed boundary condition (3) appears in problems of diffusion where the particles only have a sticking probability, s , for irreversible aggregation (*i.e.*, the attachment is not deterministic). In such a case, the kinetic coefficient k_D equals [13]

$$k_D = \frac{s}{2-s} D L_{\text{mfp}}^{-1}, \quad (4)$$

where L_{mfp} is the particle mean free path. Assuming that L_{mfp} is sufficiently small, there are two limits associated with Eq. (4): if the sticking probability vanishes ($s = 0$; *reflecting boundary condition*), then $\nabla c = 0$ at the boundary, so the aggregate does not grow. On the contrary, if the sticking probability is close to unity (provided L_{mfp} is small enough), then k_D takes very large values and then equation (3) reduces to the Gibbs-Thompson relation [10] (*absorbing boundary condition*), which incorporates into the equations the fact that particle evaporation/condensation at the surface is different in regions with different mean curvature.

2.2 Electrochemical deposition

We now sketch the relationship between CVD and ECD. In this second case, the system involves two kind of species: cations and anions. Moreover, transport of mass is not only due to diffusion in the solution, but also due to electromigration and convection. Let C and A be the concentration of cations and anions, respectively; then, by neglecting the dynamics due to the supporting electrolyte (for a more complete treatment, see e.g. [14]):

$$\partial_t C = -\nabla \cdot \mathbf{J}_c, \quad (5)$$

$$\partial_t A = -\nabla \cdot \mathbf{J}_a, \quad (6)$$

$$\mathbf{J}_c = -D_c \nabla C + \mu_c \mathbf{E} C + \mathbf{v} C, \quad (7)$$

$$\mathbf{J}_a = -D_a \nabla A - \mu_a \mathbf{E} A + \mathbf{v} A, \quad (8)$$

where $D_{c,a}$ are respectively the cationic and anionic diffusion coefficients; $\mu_{c,a}$ their mobilities; and \mathbf{E} the electric field through the cell, which obeys the Poisson equation:

$$\nabla \cdot \mathbf{E} = -\nabla^2 \phi = e(z_c C - z_a A)/\varepsilon, \quad (9)$$

ez_c and $-ez_a$ being the cationic and anionic charge, respectively; ϕ the electric potential, and ε the fluid permittivity. The velocity \mathbf{v} of the fluid obeys the Navier-Stokes equations, although we will assume this velocity to vanish in very thin cells [15]. An important experimental variable is the electric current density, $J = F(z_c \mu_c C + z_a \mu_a A)E$, which experimentally is held fixed in the so-called galvanostatic conditions, that we will be considering here. Here F denotes Faraday's constant. We further simplify the set of equations (5)-(8) following [16, 17]. Assuming the deposit moves with a constant velocity V , and at distances from the surface larger than the typical diffusion length, $l_D = D/V$, the net charge is zero, so $z_a A = z_c C$. Hence, the transport of mass reduces to a one-variable diffusion equation, e.g.

$$\partial_t C = D \nabla^2 C, \quad (10)$$

where we have used the ambipolar diffusion coefficient, $D = (\mu_c D_a + \mu_a D_c)/(\mu_a + \mu_c)$, and the mean interface velocity equals the anion migration velocity, that is, $V = \mu_a E_\infty$, where E_∞ is the electric field very far from the cathode [16, 17],

$$\frac{J}{F} = z_c \mathbf{J}_c - z_a \mathbf{J}_a = -\frac{VFz_c C_a}{1 - t_c}, \quad \text{where } t_c = \frac{\mu_c}{\mu_a + \mu_c}. \quad (11)$$

The equation for the cation attachment is provided by the relation between the charge transport through the interface and its local properties, provided by the Butler-Volmer equation [18, 19, 20]:

$$J = J_0 \left[e^{\frac{(1-\beta)\eta z_c F}{RT}} - e^{\frac{-(\beta\eta + \eta_s) z_c F}{RT}} C/C_a \right], \quad (12)$$

where J_0 is the exchange current density in equilibrium; β is a coefficient which ranges from 0 to 1, and gives an idea about the asymmetry of the energy barrier related to the cation reduction reaction; $\eta = \Delta\phi - \Delta\phi_{eq}$ is the overpotential, from which a surface curvature contribution η_s has been singled out, of the form $\frac{z_c F \eta_s}{RT} = \frac{\Omega \gamma}{k_B T} \kappa$. Since the flux of anions through the cathode is zero (because they neither react nor aggregate) the electric current density at the aggregate surface is only due to the cations, so the charge current is proportional to the cation current. Hence [18, 21]:

$$J = -\frac{z_c D_c F V}{1 - t_c} \nabla C \cdot \mathbf{n}|_\zeta. \quad (13)$$

This equation, combined with Eq. (12), provides a mixed boundary condition for the cation concentration at the aggregate surface. Finally, we complete the system with an equation for mass conservation at the boundary. Note that the local velocity of the aggregate surface is proportional to the flux of particles arriving to it, therefore

$$V_n = -\Omega \mathbf{J}_c \cdot \mathbf{n} = -\frac{\Omega}{z_c F} J, \quad (14)$$

where Ω is the molar volume, defined as the ratio of the metal molar mass, M , and the aggregate mean density, ρ . For a flat front, $V_n = V$, so comparing this equation with Eq. (13) we have [21]:

$$\frac{M}{\rho} = \frac{1 - t_c}{C_a}, \quad (15)$$

which has been experimentally proved [15].

In order to make connection with the CVD system, we redefine variables and fields as follows:

$$c = CD_c / [D(1 - t_c)], \quad (16)$$

$$k_D = J_0(1 - t_c) D e^{-bz_c F \eta / RT} / (D_c z_c F C_a), \quad (17)$$

$$c_a = C_a D_c / [(1 - t_c) D], \quad (18)$$

$$c_{eq}^0 = C_a D_c e^{z_c F \eta / RT} / [(1 - t_c) D]. \quad (19)$$

With these definitions, Eqs. (1)-(3) describe (under the assumptions made above) the evolution of both the CVD and ECD systems. Tables with the equivalence between parameters and their interpretations for both systems can be found in [7, 8].

2.3 Fluctuations

The moving boundary problem (1)-(3) describes simultaneously the time evolution of the interface position and of the mean concentration value of the attaching species in the ‘‘vapor’’ phase. However, it ignores thermal fluctuations related to the different transport or relaxation mechanisms that exist in the system. To account for these, we define zero

mean noise terms \mathbf{q} , \mathbf{p} , and χ , as describing local fluctuations in the flux of particles in the vapor ($-D\nabla c$), in the the surface particle current (\mathbf{J}_s), and in the equilibrium concentration at the interface, respectively. We take these noise terms to be spatially uncorrelated, namely,

$$\langle q_i(\mathbf{r}, t) q_j(\mathbf{r}', t') \rangle = Q \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (20)$$

$$\langle p_i(\mathbf{r}, t) p_j(\mathbf{r}', t') \rangle = P \delta_{ij} \frac{\delta(\mathbf{r} - \mathbf{r}') \delta(t - t')}{\sqrt{1 + (\partial_x \zeta)^2}}, \quad (21)$$

$$\langle \chi(\mathbf{r}, t) \chi(\mathbf{r}', t') \rangle = I \frac{\delta(\mathbf{r} - \mathbf{r}') \delta(t - t')}{\sqrt{1 + (\partial_x \zeta)^2}}, \quad (22)$$

where Q , P , and I will be determined below, and the factor $\sqrt{1 + (\partial_x \zeta)^2}$ in the second and third equations ensures that the noise intensity is independent of the surface orientation. Thus, our proposed moving boundary problem with fluctuations reads finally:

$$\partial_t c = -\nabla \cdot \mathbf{J} = D\nabla^2 c - \nabla \cdot \mathbf{q}, \quad (23)$$

$$D\partial_n c = k_D(c - c_{eq}^0 + \Gamma\kappa + \chi)|_\zeta + \mathbf{q} \cdot \mathbf{n}, \quad (24)$$

$$V_n = \Omega D\partial_n c - \Omega \mathbf{q} \cdot \mathbf{n} - B\nabla_s^2 \kappa - \Omega \nabla_s \cdot \mathbf{p}, \quad (25)$$

$$\lim_{z \rightarrow \infty} c(x, z; t) = c_a. \quad (26)$$

where we have employed the standard form for the surface diffusion current [12], in which $B = \frac{\Omega^2 \gamma \nu D_s}{RT}$, with D_s being the *surface diffusion* coefficient, and ν the areal density of diffusing particles.

In order to determine Q , P and I defined in equations (20)-(22), we follow [22] and use a local equilibrium hypothesis. As an example, we detail the calculation of Q . Details for P , I can be found in [7, 8]. Let us consider an ideal concentration c_a of randomly distributed particles. The probability of finding n particles in a given volume is given by a Poisson distribution. The mean and variance of this distribution are c_a so the concentration c satisfies

$$\langle (c(\mathbf{r}, t) - c_a)(c(\mathbf{r}', t') - c_a) \rangle = c_a \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (27)$$

This equation will allow us to determine Q . First, we write Eq. (23) as

$$\partial_t(c - c_a) = D\nabla^2(c - c_a) - \nabla \cdot \mathbf{q}, \quad (28)$$

Let $c_{\mathbf{k}\omega}$ and $\mathbf{q}_{\mathbf{k}\omega}$ be the Fourier transform of $[c(\mathbf{r}, t) - c_a]$ and \mathbf{q} respectively,

$$c_{\mathbf{k}\omega} = \frac{1}{(2\pi)^{3/2}} \int d\omega e^{i\omega t} \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} [c(\mathbf{r}, t) - c_a], \quad (29)$$

$$\mathbf{q}_{\mathbf{k}\omega} = \frac{1}{(2\pi)^{3/2}} \int d\omega e^{i\omega t} \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{q}(\mathbf{r}, t), \quad (30)$$

we get, from (28),

$$c_{\mathbf{k}\omega} = \frac{i\mathbf{k} \cdot \mathbf{q}_{\mathbf{k}\omega}}{i\omega - Dk^2}, \quad (31)$$

where $k = |\mathbf{k}|$. Thus, comparing this equation with the Fourier transform of Eq. (27), we find:

$$\langle c_{\mathbf{k}\omega} c_{\mathbf{k}'\omega'} \rangle = c_a \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega') = \frac{-Q \mathbf{k} \cdot \mathbf{k}' \delta(\mathbf{k} + \mathbf{k}') \delta(\omega + \omega')}{(i\omega - Dk^2)(i\omega' - Dk'^2)}. \quad (32)$$

Integrating the variables ω and ω' , we obtain $Q = 2Dc_a$.

Analogous considerations lead to the values of P and I in (21), (22), the main assumptions being that fluctuations due to different relaxation mechanisms (e.g. surface tension as compared with surface diffusion), and that the *equilibrium fluctuations* of the interface deviation around the average height, $\zeta(x, t)$ follow the Boltzmann distribution:

$$\mathcal{P}(\{\zeta\}) \sim \exp \left[-\frac{\gamma}{k_B T} \int_{-L_x/2}^{L_x/2} dx \left\{ \sqrt{1 + (\partial_x \zeta)^2} - 1 \right\} \right] \simeq \frac{\gamma}{2} \int_{-L_x/2}^{L_x/2} dx (\partial_x \zeta)^2, \quad (33)$$

γ being the surface tension, assumed isotropic. Linearizing Eqs. (23)-(26) for small values of $\zeta(x, t)$, we thus obtain

$$\begin{aligned} I &= \frac{2\Gamma k_B T}{\Omega k_D \gamma} = \frac{2c_{eq}^0}{k_D}, \\ P &= 2D_s \nu. \end{aligned} \quad (34)$$

Note both fluctuation amplitudes in *bulk* (Q) and *surface* (P) diffusion currents are two times the product of the corresponding diffusion coefficient by the corresponding density of mobile species.

3 LINEAR STABILITY ANALYSIS

Equations (23)-(26) provide a full description of the growth dynamics of solid interface. However, they constitute a formidable problem both from the analytical and from the numerical points of view. It is thus interesting to reformulate them in an integro-differential form, amenable to perturbative approximations. In the end, we will be left with a lowest order non-linear closed differential equation for the interface height fluctuations, $\zeta(x, t)$. To this end, we use a technique based on the use of Green's functions, as has been successfully done in similar diffusion problems [22], in the contexts e.g. of solidification from a melt, or dynamics of steps on surfaces vicinal to a singular crystal orientation, in surface growth by epitaxy. For brevity, we show here the main results, and refer the interested reader to our related publications [7, 8]. By employing the diffusion Green function $G(x, z, t)$, the complete system (23)-(26) describing the full dynamics in

the vapor phase, can be projected onto the aggregate surface, resulting into the integro-differential equation

$$\frac{c(\mathbf{r}, t)}{2} = c_a - \int_{-\infty}^t dt' \left[\int_{-\infty}^{\infty} dx' \left(V + \frac{\partial \zeta'}{\partial t'} \right) c' G - D \int_{\zeta'} ds' \left(c' \frac{\partial G}{\partial n'} - G \frac{\partial c'}{\partial n'} \right) \right]_{z'=\zeta'} - \sigma(\mathbf{r}, t). \quad (35)$$

which relates the concentration at the boundary with the surface height. Eq. (35) is highly nonlinear, and has also multiplicative noise through the noise term $\sigma(\mathbf{r}, t)$, itself a complicated function of the noise terms appearing in the original moving boundary problem, and of the concentration and height fields. Nevertheless, it allows us to perform a perturbation expansion in a simpler way than in the original formulation of the problem.

Consider those solutions of Eq. (35) of the form $c = c_0 + c_1$, where c_0 stands for the part associated with the flat front solution, and c_1 is a small perturbation of the same order as the height fluctuation $\zeta(x, t)$. Hence, to lowest order [7, 8]

$$c_0 = \frac{V c_a + k_D c_{eq}^0}{V + k_D}. \quad (36)$$

We now proceed with the next order of the expansion. This order is related to the evolution of the interface, and contains *additive noise* terms [7, 8],

$$\partial_t \zeta_k(t) = \omega(k) \zeta_k(t) + \eta_k(t), \quad (37)$$

whose solution is simply

$$\zeta_k(t) = \int_0^t ds e^{\omega(k)(t-s)} \eta_k(s). \quad (38)$$

Here, the dispersion relation $\omega(k)$ is a function of k yielding (as a function of its sign) the stability (instability) under perturbations of the interface profile by waves with wave vector k if $f(k)$ is positive (negative). Remarkably, the functional shape of the dispersion relation depends critically on the kinetic coefficient k_D .

3.1 Instantaneous surface kinetics ($k_D \rightarrow \infty$)

As remarked above, the $k_D \rightarrow \infty$ limit in the mixed boundary condition (24), leads actually to an *absorbing* boundary condition for the diffusion problem taking place in the vapor phase. This means growth is only diffusion limited. Under these conditions, we obtain [7, 8]

$$\omega_k = D \left(\frac{\Gamma^2 \Omega^2}{2} - \frac{B}{D} \right) k^4 - \frac{3\Gamma\Omega V k^2}{2} + |k|(V - \Gamma\Omega D k^2) \left[1 - \frac{\Gamma\Omega V}{D} + \left(\frac{\Gamma^2 \Omega^2}{4} - \frac{B}{D} \right) k^2 \right]^{1/2}. \quad (39)$$

This dispersion relation has several interesting limits. For instance, if we neglect surface tension and surface diffusion (that is, for $\Gamma = B = 0$), then $\omega_k = V|k|$, which is the

well-known relation of dispersion of the diffusion-limited-aggregation (DLA) model [4]. In this system perturbations grow unstably for any wave vector, leading to an aggregate made of wide branches plenty of smaller ramifications.

Neglecting only the surface diffusion term, and for values of $\Gamma\Omega \equiv d_0$ (capillarity length) much smaller than $D/V \equiv l_D$ (diffusion length), we obtain

$$\omega_k \simeq V|k|(1 - d_0 l_D k^2), \quad (40)$$

characteristic of the well-known Mullins-Sekerka (MS) instability in solidification [3]. Occurrence of such a dispersion relation is well documented in ECD experiments [23], and has been proposed before (theoretically) by Barkey *et al.* [24]. As is clear from (40), irreversible growth is an unstabilizing mechanism inducing positive values for ω_k , while surface tension is stabilizing. As a balance between these opposing tendencies, a characteristic length scale is selected in the morphology, corresponding to the fastest growing perturbations, $\lambda_m = 2\pi/k_m$, with k_m being the value for which ω_k is maximum.

Finally, there are conditions, as in low-pressure CVD [25], in which the vapor pressure is so low that the Gibbs-Thompson effect is negligible, the only non-negligible *stabilizing* relaxation mechanism term being surface diffusion. In this case,

$$\omega_k = V|k|\sqrt{1 - \frac{B}{D}k^2} - Bk^4 \simeq V|k|(1 - Bk^2/2D) - Bk^4. \quad (41)$$

Finally, when surface tension and surface diffusion are both non-negligible, and considering again $d_0 \ll l_D$, we get:

$$\omega_k = V|k|[1 - (d_0 l_D + B/2D)k^2] - Bk^4. \quad (42)$$

3.2 Non-instantaneous surface kinetics (finite k_D)

The kinetic coefficient k_D has dimensions of velocity, hence the ratio D/k_D can be considered as a *sticking length* a random walker can travel within the vapor between two successive attachment attempts. The $k_D \rightarrow \infty$ limit considered above corresponds physically to $D/k_D \ll D/V$. However, for $k_D \ll V$, kinetics at the interface takes place in time scales comparable to growth, the sticking length becoming non-negligible. In this case, in the large length scale limit ($k \rightarrow 0$) we find [7, 8]

$$\omega_k = a_2 k^2 - a_4 k^4, \quad (43)$$

where

$$a_2 = \frac{Dk_D}{V}\Delta, \quad a_4 = \frac{Dk_D\Delta l_D d_0}{V\left[1 - \sqrt{\frac{Vd_0}{D}}\right]}, \quad (44)$$

with $\Delta = 1 - d_0/l_D$. If $\Delta > 0$, then a_2 and a_4 are both positive and there is a band of long wavelength unstable modes for

$$0 \leq k \leq k^* = \sqrt{\frac{V}{Dd_0} \left(1 - \sqrt{\frac{Vd_0}{D}} \right)}. \quad (45)$$

On the contrary, if $\Delta < 0$, then $k = 0$ is the only zero of ω_k , thus a_2 being negative every mode is stable. If we include surface diffusion into the analysis, we just have to change a_4 to $a_4 + B(V + k_D)/V$, shifting k^* to zero and therefore shrinking the band of unstable modes.

In summary, as intuitively expected, changing the character of the growth problem from diffusion limited ($k_D \ll V$) to reaction limited ($k_D \gg V$) suppresses effects of unstable competitive growth (shadowing among branches). The terms in the dispersion relation change from non-local (as is the character of $|k|$) to local. This can be even taken to the limit of unconditionally stable growth as obtained in this section. Heuristically, if the sticking probability is small, particles arriving at the interface do not stick to it at first contact but they can, rather, explore other regions of the aggregate. Branch tips are less favored and growth can occur in deeper fiords, thus stabilizing the surface morphology.

4 NONLINEAR EVOLUTION EQUATION

We can go beyond the linear stability analysis and derive a lowest-order nonlinear closed equation for the aggregate surface profile $\zeta(x, t)$. Technically, non-linear terms to this order will come from evaluation of the the diffusion Green function at the boundary, thus

$$G(\mathbf{r} - \mathbf{r}', \tau) = \frac{\Theta(\tau)}{4\pi D\tau} \exp \left[-\frac{(x - x')^2}{4D\tau} - \frac{(\zeta - \zeta' + V\tau)^2}{4D\tau} \right], \quad (46)$$

where $\tau = t - t'$. Performing an expansion of (35) for gentle surface variations to lowest non-linear order, Eq. (37) generalizes into [7, 8]

$$\partial_t \zeta_k(t) = \omega(k) \zeta_k(t) + \frac{V}{2} N[\zeta]_k + \eta_k(t), \quad (47)$$

where $N[\zeta]_k$ is the Fourier transform of $(\partial_x \zeta)^2$, and the noise term is still additive. The nonlinear term quadratic in the slope is of a purely non-equilibrium nature [5], and is termed in the kinetic roughening literature after Kardar, Parisi and Zhang (KPZ) [26]. Making explicit the two different forms that the dispersion relation can take, and writing the corresponding equations in real space, we obtain, for $k_D \rightarrow \infty$,

$$\begin{aligned} \partial_t \zeta(x, t) &= -\frac{V}{2} H \left[\partial_{x'} \zeta(x', t) + (d_0 l_D + B/D) \partial_{x'}^3 \zeta(x', t) \right] \\ &- B \partial_x^4 \zeta(x, t) + \frac{V}{2} (\partial_x \zeta(x, t))^2 + \eta(x, t), \end{aligned} \quad (48)$$

where we have used the Hilbert transform

$$H(f(x')) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{f(x')}{x' - x} dx', \quad (49)$$

with P denoting Cauchy's principal value of the integral. This form makes explicit the non-local nature of the growth and surface tension contributions to the surface dynamics in the diffusion limited regime. On the other hand, for finite k_D , we find

$$\partial_t \zeta(x, t) = -\frac{Dk_D \Delta}{V} \partial_x^2 \zeta(x, t) - R \partial_x^4 \zeta(x, t) + \frac{V}{2} (\partial_x \zeta(x, t))^2 + \eta(x, t), \quad (50)$$

where

$$R = \frac{Dl_D d_0 k_D \Delta}{V \left[1 - \sqrt{\frac{V d_0}{D}} \right]} + \frac{B(k_D + V)}{V}. \quad (51)$$

In both cases considered for k_D , the noise correlations involve a polynomial in k^2 . Since the study below addressed long distance and long time properties, we can restrict ourselves to the more relevant lowest order contributions for such physical range, namely,

$$\langle \eta_k(t) \eta_{k'}(t') \rangle = (\Pi_0 + \Pi_2 k^2) \delta(k + k') \delta(t - t'), \quad (52)$$

where $\Pi_{0,2}$ are constants.

Eq. (50) is indeed local in space. As long as the diffusion length is larger than the capillary length (i.e. $\Delta > 0$), this equation is a *stochastic* generalization of the celebrated Kuramoto-Sivashinsky (KS) equation [27], previously introduced in the contexts of step dynamics on vicinal surfaces and surface erosion by ion-beam sputtering [28]. The behavior of the KS equation is well known [28]: initially all Fourier modes are uncoupled, and growth is noise driven. After this transient, the linear instability develops and the most unstable mode grows exponentially faster than the others leading to formation of a periodic pattern with wavelength λ_m . Once the local slopes become large enough, the nonlinear term stabilizes the surface morphology, and eventually the system reaches a stationary state whose large scale features display universal scaling properties of the KPZ universality class.

In what follows, we devote ourselves to a numerical study of the interface equation obtained in the diffusion limited regime, Eq. (48), to our knowledge unexplored thus far. In the deterministic case, a related equation [without the $\partial_{x'} \zeta(x', t)$ in the argument of the Hilbert transform] describes flow of a thin viscous fluid film falling down an inclined plane, subject to an electric field, see a recent study with references in [29]. Moreover, and beyond its application to ECD and CVD as discussed, Eq. (48) is possibly relevant to other rough interface production processes in which shadowing effects take place, such as plasma etching and reactive ion etching of surfaces [30].

4.1 NUMERICAL INTEGRATION

To some extent [especially in the case of Eq. (48)], the interface equations derived in the previous section are simpler in Fourier space, where they read, respectively,

$$\partial_t \zeta_k(t) = (\nu|k| - K|k|^3)\zeta_k + \frac{\lambda}{2}N[\zeta]_k + \eta_k(t), \quad (53)$$

$$\partial_t \zeta_k(t) = (\nu k^2 - Kk^4)\zeta_k + \frac{\lambda}{2}N[\zeta]_k + \eta_k(t). \quad (54)$$

for appropriate (positive) constants ν , K , and λ .¹ We have neglected surface diffusion terms in Eq. (53), that are inessential for the results that follow. The shape of these equations lends itself quite naturally to application of pseudospectral schemes [31] of the type frequently employed in Fluid Dynamics, rather than explicit real space discretization approaches, more standard in studies of stochastic differential equations [32]. Moreover, for related stochastic equations such as the KPZ equation, pseudospectral methods are being found to outperform direct schemes in a number of features [33].

Below, we summarize the main steps of the method we employ. Note Eqs. (53), (54) are both of the form

$$\partial_t \zeta_k = \omega(k)\zeta_k + \mathcal{N}[\zeta]_k + \eta_k, \quad (55)$$

where \mathcal{N} is a functional carrying the nonlinear part of the equation. In absence of the nonlinear term, Eq. (55) has a solution given by Eq. (38). This motivates the use of a change of variable prior to the time discretization. Besides, we have to deal separately with the linear and nonlinear parts. More specifically, each integration step involves the following calculations:

1. The linear part of the equation is integrated directly because all the Fourier modes, $\zeta_k(t)$, are uncoupled. The noise term is also included in the linear part. To this end, we employ a simple Euler method [34]:

$$\zeta_k(t + \Delta t) = e^{\omega_k \Delta t} \left(\zeta_k(t) + \Delta t \mathcal{N}[\zeta]_k + \sqrt{\Delta t} \eta_k \right). \quad (56)$$

2. The KPZ nonlinear term is calculated in real space by squaring the inverse Fourier transform of $-ik\zeta_k(t)$. At this point, antialiasing is required. We employ a standard zero padding method [31].
3. Direct Fourier transform is calculated for the nonlinear part obtained above, that is added to the linear part of the equation as in (56), completing one temporal integration step.

¹Since we will study *universal* scaling properties that do not depend on the numerical value of these constants, we omit their explicit definitions in terms of original parameters D , V , k_D , etc.

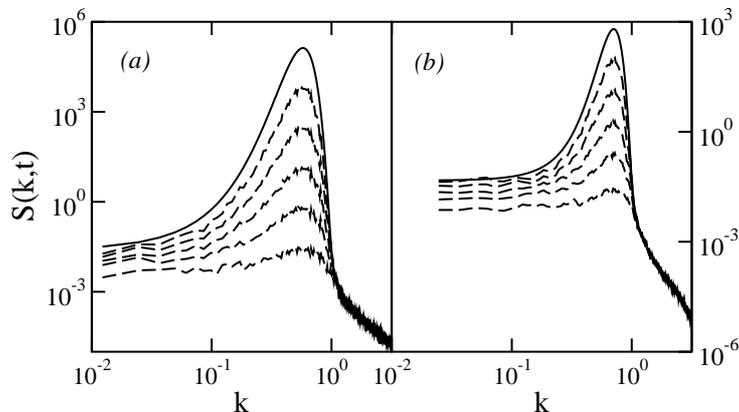


Figure 1: Power spectra, $S(k, t)$, for a $L = 512$ system with $\nu = K = \Pi_0 = 1$, and $\lambda = 0$ for: (a) Eq. (53) (dashed lines) at times $t = 4, 8, 12, 16$ and 20 ; (b) Eq. (54) (dashed lines) at times $t = 4, 8, 12, 16$ and 20 . Solid lines correspond to the exact solutions [Eq. (57)] at $t = 24$, for the corresponding dispersion relations.

4.1.1 Numerical results

As noted above, the stochastic KS equation, Eq. (54), has been extensively studied in the literature, so will concentrate in this section on Eq. (53) which, to our knowledge, has never been studied before. Its behavior will help us to understand dynamics of the interface in the diffusion limited regime, $k_D \rightarrow \infty$. In principle, one would expect dynamics to be quite similar to the KS system. Starting out from a flat initial condition,² at short times dynamics are essentially given by Eq. (37), and we find that both equations (53) and (54) feature similar interface power spectra $S(k, t)$, see Fig. 1, as can be easily understood by simple inspection of the corresponding exact results

$$S(k, t) \equiv \langle \zeta_k(t) \zeta_{-k}(t) \rangle = \Pi_0 \frac{e^{2\omega(k)} - 1}{2\omega(k)}. \quad (57)$$

Simple inspection of Fig. 57 could lead us to expect similar behavior for Eqs. (53) and (54) also in the nonlinear regime. In particular, this would imply KPZ behavior for Eq. (53) in the asymptotic regime. For a rough interface [5], the surface roughness of surface width (rms deviation of the height around its average value), $W(t) = \sum_k S(k, t)$, scales as $W(t) \sim t^\beta$ before the asymptotic state is reached, β being an universal exponent. However, Fig. 2 shows that at long times the growth exponent β is much larger than the expected $\beta = 1/3$ for the KPZ universality class. Actually, the rescaling $t \rightarrow b^z t$, $k \rightarrow b^{-1} k$, $\zeta_k \rightarrow b^{\alpha+1} \zeta_k$ —with b a constant factor, and z and α the dynamic and roughness critical exponents [5]—, transforms Eq. (53) into

$$\partial_t \zeta_k = b^{z-1} \nu |k| \zeta_k - b^{z-3} K |k|^3 \zeta_k + b^{\alpha+z-2} \frac{\lambda}{2} N[\zeta]_k + b^{z/2-\alpha-1/2} \eta_k. \quad (58)$$

²We employ periodic boundary conditions in the x coordinate, and a finite system size L .

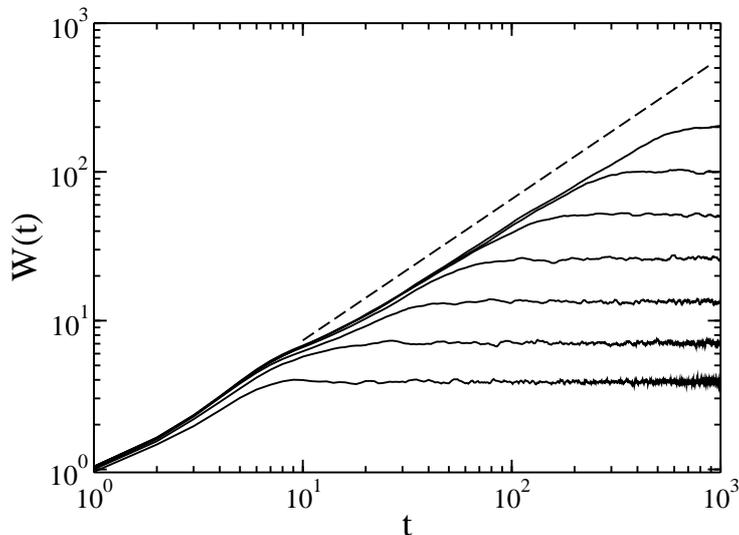


Figure 2: Interface width vs time for a system with $\nu = K = \lambda = \Pi_0 = 1$ obtained from Eq. (53), for different system sizes. From bottom to top: $L = 16, 32, 64, 128, 256, 512$ and 1024 respectively. As a reference, the dashed line has slope 1 indicating $\beta \simeq 1$ as the system size increases. Behavior for $t \leq 7$ is well described by the linear equation (37), $t \simeq 7$ marking the onset of nonlinear effects.

Using the KPZ exponents for a one-dimensional interface ($\alpha = 1/2$, $z = 3/2$) [26], it can be straightforwardly shown that in the hydrodynamic limit (that is, when $b \rightarrow \infty$) the most relevant term is the linear one $|k|\zeta_k$. Preliminary renormalization group (RG) calculations provide the same result [8]. Moreover, the fixed point (in the RG sense) associated with this term is characterized by $\alpha = \beta = z = 1$. These values are actually compatible with those obtained from numerical simulations of Eq. (53) displayed in Figs. 2 and 3, that are $\alpha = 1.0 \pm 0.02$, $\beta = 0.90 \pm 0.05$ and $z = 1.1 \pm 0.05$. In the inset of Fig. 3, we show the data collapse of the power spectrum using these exponent values, that are in good agreement with the theoretical ones.³ The discrepancies in the collapsed curves for large $kt^{1/z}$ values are due to the existence of a short scale scaling different from the asymptotic one. Note that these exponent values are compatible with the scaling relation $\alpha + z = 2$, associated with Galilean invariance, similarly to other non-local stochastic equations proposed for growth/etching processes with relevant shadowing effects [35].

5 SUMMARY AND CLOSING REMARKS

We have presented the derivation of a stochastic differential equation that describes the growth dynamics of solid surfaces growing from a vapor phase, such as the surfaces of aggregates grown by Electrochemical Deposition (ECD), or of those produced by Chemical Vapor Deposition (CVD). The equation has the form of the stochastic Kuramoto-

³In the stationary state, the structure factor of a rough d -dimensional interface scales as $S(k) \sim k^{-(2\alpha+d)}$, see [5].

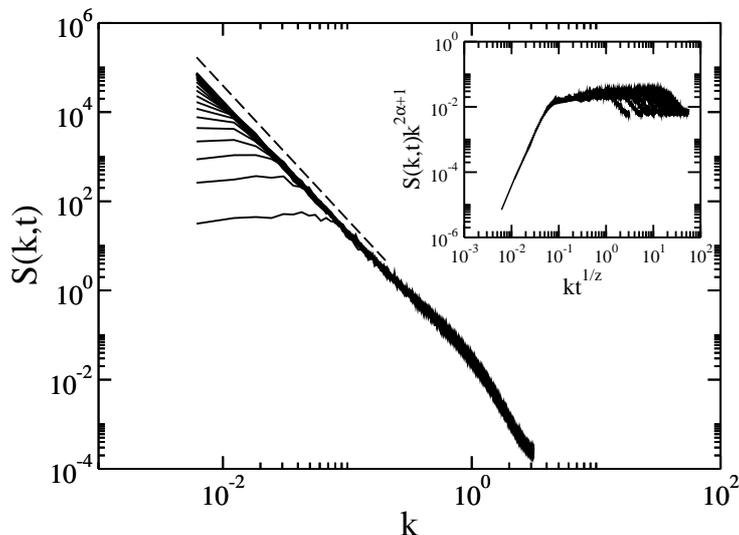


Figure 3: Power spectrum vs spatial frequency k with the same parameters as in Fig. 2 for $L = 1024$. Different curves correspond to different times, time increasing from bottom to top. Dashed line is a guide to the eye with slope -3 (that is, $\alpha = 1$). Inset: Collapse of $S(k, t)$ using $\alpha = 1.0$, $\beta = 0.90$ and $z = 1.1$.

Sivashinsky equation and generalizations thereof. As a function of surface kinetics, the dispersion relation is modified, in such a way that the interface properties (roughness, etc.) change. Our results allow to interpret the lack of universal properties for the surface fluctuations found in many experiments as originated in the (diffusive) instabilities existing in the system prior to achieving its asymptotic state [7]. Thus, in practical situations the crossover to asymptotic properties as exemplified in Fig. 2 can take times longer than those accesible experimentally. For such situations, the aggregate surface will unavoidably present large roughness and a disordered patterned morphology. The long wavelength approximation performed here has wider applicability than restricted to experiments in ECD and CVD, and thus similar equations are seen to be relevant in different experimental contexts. For the diffusion limited regime detailed here, such contexts correspond to surface growth or etching techniques in which shadowing effects among different surface features play a relevant role. The interface equation we have derived and studied in this diffusion limited regime combines the Mullins-Sekerka dispersion relation with the generic non-equilibrium Kardar-Parisi-Zhang non-linearity, and had remained unexplored thus far. We have seen that, similarly to the Kuramoto-Sivashinsky equation, in this system the nonlinear term is able to tame the linear instabilities, although, remarkably, does *not* dictate the scaling exponents characterizing the surface roughening in the asymptotic state.

Future improvements of our moving boundary model will require a computationally efficient implementation that allows assessment of possible shortcomings and limitations of our small slope approximations. Work along these lines is currently in progress [36].

Acknowledgments

Research presented here has been supported in part by grants from the Ministerio de Educación y Ciencia, Spain, Nos. BFM2003-07749-C05-01 (R.C.) and BFM2003-07749-C05-05 (M.C.).

REFERENCES

- [1] M. Paunovic and M. Schlesinger. *Fundamentals of Electrochemical Deposition*, John Wiley & Sons, 1998.
- [2] K. F. Jensen and W. Kern. Thermal Chemical Vapor Deposition. In *Thin Film Processes II*, edited by J. L. Vossen and W. Kern, Academic, 1991.
- [3] W. W. Mullins and R. F. Sekerka. Morphological stability of a particle growing by diffusion or heat flow. *J. Appl. Phys.* **34**, 323–329, 1963. Stability of a planar interface during solidification of a dilute binary alloy. *ibid.* **35**, 444–451, 1964.
- [4] Y. Saito. *Statistical Physics of crystal growth*, World Scientific, 1996.
- [5] A.-L. Barabási and H. E. Stanley. *Fractal concepts in surface growth*, Cambridge University Press, 1995.
- [6] R. Cuerno and L. Vázquez. Universality issues in surface kinetic roughening of thin solid films. In *Advances in Condensed Matter and Statistical Physics*, edited by E. Korutcheva and R. Cuerno, Nova Science Publishers, 2004.
- [7] R. Cuerno, and M. Castro. Transients due to instabilities hinder Kardar-Parisi-Zhang scaling: a unified derivation for surface growth by Electrochemical and Chemical Vapor Deposition. *Phys. Rev. Lett.* **87**, 236103-1–4, 2001. Possible origin for the experimental scarcity of KPZ scaling in non-conserved surface growth. *Physica A* **314**, 192–199, 2002.
- [8] M. Castro. Mecánica Estadística y aplicaciones de modelos de procesos de crecimiento. *Ph. D. thesis*, Universidad Complutense de Madrid, 2001 (in Spanish). <http://gisc.uc3m.es/~mario/tesis/>. M. Castro and R. Cuerno. Fluctuations in an unified moving boundary model for the dynamics of interfaces in diffusion-limited problems: electrochemical and chemical vapor deposition. Preprint, 2004.
- [9] C. H. J. Van den Breckel and A. K. Jansen. Morphological stability analysis in chemical vapour deposition processes I. *J. Crystal Growth* **43**, 364–370, 1978.
- [10] B. J. Palmer and R. J. Gordon. Local equilibrium model of morphological instabilities in chemical vapor deposition. *Thin Solid Films* **158**, 313–341, 1988.
- [11] G. S. Bales, A. C. Redfield, and A. Zangwill. Growth dynamics of chemical vapor deposition. *Phys. Rev. Lett.* **62**, 776–779, 1989.
- [12] W. W. Mullins. Theory of thermal grooving. *J. Appl. Phys.* **28**, 333–339, 1957.

- [13] K. R. Naqvi, K. J. Mork, and S. Waldenstrøm. Reduction of the Fokker-Planck equation with an absorbing or reflecting boundary to the diffusion equation and the radiation boundary condition. *Phys. Rev. Lett.* **49**, 304–307, 1982.
- [14] M. Haataja, D. J. Srolovitz, and A. B. Bocarsly, Morphological stability during electrodeposition. I: steady states and stability analysis. *J. Electrochem. Soc.* **150**, C699–C707, 2003.
- [15] V. Fleury, M. Rosso, J.-N. Chazalviel, and B. Sapoval. Experimental aspects of dense morphology in copper electrodeposition. *Phys. Rev. A* **44**, 6693–6705, 1991.
- [16] J.-N. Chazalviel, and V. Fleury. Comment on “Modeling of metal electrodeposits: Analytical solutions”. *Phys. Rev. E* **54**, 4480–4481, 1996.
- [17] C. Lèger, J. Elezgaray, and F. Argoul. Dynamical characterization of one-dimensional stationary growth regimes in diffusion-limited electrodeposition processes. *Phys. Rev. E* **58**, 7700–7709, 1998.
- [18] J. O’M. Bockris, and A. K. N. Reddy, *Modern electrochemistry* (Plenum/Rosetta, New York, 1970).
- [19] A. J. Bard, and L. R. Faulkner, *Electrochemical methods* (John Wiley and Sons, New York, 1980).
- [20] D. Kashchiev and A. Milchev. Kinetics of the initial stage of the electrolytic deposition of metals. I. General theory. *Thin Solid Films* **28**, 189–200, 1975.
- [21] C. Lèger, J. Elezgaray, and F. Argoul. Internal structure of dense electrodeposits. *Phys. Rev. E* **61**, 5452–5463 (2000).
- [22] A. Karma. Fluctuations in solidification. *Phys. Rev. E* **48**, 3441–3458, 1993. O. Pierre-Louis and C. Misbah. Dynamics and fluctuations during MBE on vicinal surfaces. I. Formalism and results of linear theory. *Phys. Rev. B* **58**, 2259–2275, 1998.
- [23] J. R. de Bruyn. Early stages of ramified growth in quasi-two-dimensional electrochemical deposition. *Phys. Rev. E* **53**, R5561–R5564 (1996). G. L. M. K. S. Kahanda, X.-q. Zhou, R. Farrell, and P.-z. Wong. Columnar growth and kinetic roughening in electrochemical deposition. *Phys. Rev. Lett.* **68**, 3741–3744 (1992). J. M. Pastor. Estudio experimental de fenómenos de crecimiento por electrodeposición galvanostática a baja corriente: rugosidad e inestabilidades morfológicas. *Ph. D. thesis*. Universidad Nacional de Educación a Distancia, 1997 (in Spanish).
- [24] D. P. Barkey, R. H. Muller, and C. W. Tobias. Roughness development in metal electrodeposition. 2. Stability theory. *J. Electrochem. Soc.* **136**, 2207–2214, 1989.

- [25] F. Ojeda, R. Cuerno, R. Salvarezza, and L. Vázquez. Dynamics of rough interfaces in chemical vapor deposition: experiments and a model for silica films. *Phys. Rev. Lett.* **84**, 3125–3128, 2000 F. Ojeda, R. Cuerno, R. Salvarezza, F. Agulló-Rueda, and L. Vázquez. Modeling heterogeneity and memory effects on the kinetic roughening of silica films grown by chemical vapor deposition. *Phys. Rev. B* **67**, 245416-1–13, 2003.
- [26] M. Kardar, G. Parisi, and Y.-P. Zhang. Dynamic scaling of growing interfaces. *Phys. Rev. Lett.* **56**, 889–892, 1986.
- [27] Y. Kuramoto and T. Tsuzuki. Persistent propagation of concentration waves in dissipative media far from thermal equilibrium. *Prog. Theor. Phys.* **55**, 356–369, 1976. G. I. Sivashinsky. Self-turbulization of a laminar flame. *Acta Astronaut.* **6**, 569–591, 1979.
- [28] A. Karma and C. Misbah. Competition between noise and determinism in step flow growth. *Phys. Rev. Lett.* **71**, 3810–3813, 1993; R. Cuerno and A.-L. Barabási. Dynamic scaling of ion-sputtered surfaces. *ibid.* **74**, 4746–4749, 1995.
- [29] J. Duan and V. J. Ervin. Dynamics of a nonlocal Kuramoto-Sivashinsky equation. *J. Diff. Eqs.* **143**, 243–266, 1998.
- [30] J. T. Drotar, Y.-P. Zhao, T.-M. Lu, and G.-C. Wang. Mechanisms for plasma and reactive ion etch-front roughening. *Phys. Rev. B* **61**, 3012–3021, 2000.
- [31] C. Canuto, M. Y. Hussaini, A. Quarteroni, and T. A. Zang. *Spectral methods in Fluid Dynamics*. Springer-Verlag, 1987.
- [32] J. García-Ojalvo and J. M. Sancho. *Noise in spatially extended systems*. Springer-Verlag, 1999.
- [33] L. Giada, A. Giacometti, and M. Rossi. Pseudospectral method for the Kardar-Parisi-Zhang equation. *Phys. Rev. E* **52**, 036134-1–11, 2002. *ibid* **66**, 019902-1, 2002.
- [34] R. Toral. *Pseudospectral methods for the practitioner*, preprint (2000).
- [35] A. K. Chattopadhyay. Thermal re-emission model. *Phys. Rev. B* **65**, R041405-1–4, 2002.
- [36] M. Nicoli and M. Castro, in preparation. 2004.