Scaling Behavior of Cyclical Surface Growth

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The scaling behavior of cyclical surface growth (e.g., deposition/desorption), with the number of cycles, n, is investigated. The roughness of surfaces grown by two linear primary processes follows a scaling behavior with asymptotic exponents inherited from the dominant process while the effective amplitudes are determined by both. Relevant nonlinear effects in the primary processes may remain so or be rendered irrelevant. Numerical simulations for several pairs of generic primary processes confirm these conclusions. Experimental results for the surface roughness during cyclical electrodeposition/dissolution of silver show a power-law dependence on n, consistent with the scaling description.

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Much interest has been devoted in recent years to scaling phenomena in kinetic growth of self-affine surfaces. They are observed in a variety of phenomena such as crystal growth, vapor deposition, molecular-beam epitaxy, electrochemical processes, bacterial growth, burning fronts, etc. [1–4]. Similar rough surfaces may also be generated by reciprocal processes of surface withdrawal caused by desorption, corrosion, evaporation, dissolution, and the like [5]. In many natural and artificial systems of interest, however, surfaces are not formed by a single process of growth or a sole process of recession. Rather, they are the product of a combination of both. We investigate here the fundamental scaling properties of surfaces formed by cyclical growth processes. We focus on surfaces formed by two alternating primary processes. Growth/recession cycles (excluding the trivial cases in which the primary processes are time-reversed images of each other) are our main interest but cycles of two different growth (growth/growth) processes will be addressed as well. Cyclical behavior, prevailing in all natural phenomena, may be found in many of the systems cited above. Typical examples include weather and light affected processes in organic (as the expansion/curtailment of a grass lawn or a bacterial colony according to the availability of water or nutrient) or nonorganic (such as alternating underwater erosion/sedimentation whether or not the water is flowing) systems. They are also widespread in technological applications (such as rechargeable batteries for which short circuit by the metal accumulated on the electrodes is one of the failure mechanisms). Understanding the cyclical scaling properties may lead to accelerated testing, and performance improvement, of such systems.

Our main challenge is to generalize the scaling approach in order to make it applicable to cyclical growth processes. The analytical, numerical, and experimental investigations, summarized below, lead us to the conclusion that this is indeed possible, provided that *the number of cycles n substitutes for the time variable, t, in the scaling relations.* We explore this generalized scaling behavior in several cyclical processes and reach some general conclusions on their behavior and their relations to the scaling relations of the primary processes, of which they are composed.

In the primary processes, the surface width $W(L,t)$, where L is the lateral size of the system, is defined as $W(L,t) = \langle [h(\vec{r},t) - h(t)]^2 \rangle^{1/2}$. In this definition, $h(r,t)$ is the surface height and $h(t) = \langle h(t) \rangle = vt$ is the average height, with v being the average growth velocity. $W(L,t)$ obeys the following scaling form [1,6]:

$$W(L,t) \sim L^{\alpha} g\big(L/\xi(t)\big), \tag{1}$$

$\xi(t) \sim t^{1/z}$ is the lateral correlation length. For large time $t \gg L^z$: $W \sim L^{\alpha}$; while for $t \ll L^z$: $W \sim t^{\beta}$, where $\beta = \alpha/z$ is the growth exponent. A related relation holds for the mean square height difference $\langle [h(\vec{r} + \vec{x},t) - h(\vec{x},t)]^2 \rangle = 2[C(0,t) - C(r,t)]$, where $C(\vec{r},t)$ is the (equal-time) height-height correlation function.

The growth processes fall into different universality classes [2]. All processes within one class share the same exponents and their asymptotic continuum stochastic equations differ at most by irrelevant terms [in the renormalization group (RG) sense]. Using the symbolic index $i = 1, 2, \ldots$ to denote different processes, the ones we consider here follow growth equations of the form

$$\frac{\partial h(\vec{r},t)}{\partial t} = A_i\{h\} + \eta_i(\vec{r},t) + v_i\,, \tag{2}$$

where $A_i\{h\}$ is a local functional depending on the spatial derivatives of $h(\vec{r},t)$ and $\langle \eta_i(\vec{r},t)\eta_i(\vec{r}',t') \rangle = 2D_i\delta(\vec{r} - \vec{r}')\delta(t - t')$.

We recall the simplest generic growth processes of this type: (i) random deposition (RD) for which $A_{\mathrm{RD}} = 0$ and $\beta = 1/2$ (α and z are not defined); (ii) the Edwards-Wilkinson (EW) model [7] of preferred growth at local minima has $A_{\mathrm{EW}} = \nu\nabla^2 h$ and $\alpha = \frac{3-d}{2}$, $\beta = \frac{3-d}{4}$, $z = 2$; (iii) the Kardar-Parisi-Zhang (KPZ) [8] model which accounts for the growth being locally normal to the surface has $A_{\mathrm{KPZ}} = \nu\nabla^2 h + \frac{\lambda}{2}(\vec{\nabla}h)^2$ and $\alpha = 1/2$, $\beta = 1/3$, and $z = 3/2$ in 2D, while $\alpha \simeq 0.39$, $\beta \simeq 0.24$, and

$z \simeq 1.61$ in 3D; (iv) the Das Sarma–Tamborenea (DT) [9] (see also [10]) for molecular beam epitaxy deposition or growth on kink sites has $A_{\rm DT} = \nu_4 \nabla^4 h$ with $\alpha = \frac{5-d}{2}$, $\beta = \frac{5-d}{8}$, and $z = 4$.

We investigate theoretically and experimentally the hypothesis that in cyclical processes the scaling law in Eq. (1) should be replaced with

$$W_c(L,n) \sim L^{\alpha} g_c\big(L/\xi_c(n)\big), \tag{3}$$

with $\xi_c(n) \sim n^{1/z}$.

We begin with the study of cyclical processes composed of two primary linear processes, namely, those for which $A_i\{h\} = a_i(\vec{\nabla})h(\vec{r},t)$, where $a_i(\vec{\nabla})$ is a differential operator (e.g., the EW and DT models) and for which time-reversal symmetry holds if the height is defined with respect to the average height [i.e., for $h(\vec{r},t) - h(t)$]. The first process in the cycle ($i = 1$) is of duration $T_1 = pT$ and second process ($i = 2$) lasts $T_2 = (1-p)T$. The total duration of one cycle is $T = T_1 + T_2$.

We also define $f(t)$ as the fractional part of t/T. The growth equation thus becomes

$$\frac{\partial h}{\partial t} = [a_1 h + \eta_1 + \upsilon_1]\Theta\big(p - f(t)\big) + [a_2 h + \eta_2 + \upsilon_2]\Theta\big(f(t) - p\big), \tag{4}$$

where $\Theta(x)$ is the unit step function.

For such linear processes, the full scaling behavior may be retrieved by looking at $h(\vec{q},t)$, the Fourier transform (FT) of $h(\vec{r},t)$. The first observation we make is that, in these time-reversible processes, only the averaged height $h(t) = h(\vec{q} = 0, t)$ is sensitive to the difference between growth ($\upsilon_i > 0$) and recession ($\upsilon_i < 0$), and grows as $nT\upsilon_c$, where $\upsilon_c = p\upsilon_1 + (1-p)\upsilon_2$ is the average velocity. The roughness, on the other hand, will not discern between a growth/growth and a growth/recession cyclical process (as long as a_i and D_i are not altered).

In Fourier space, the growth equations for the modes with $\vec{q} \neq 0$ may be integrated. The $h(\vec{q},t)$ after n [respectively, $(n+p)$] cycles are assigned as the initial conditions for the $(n+1)$th application of the first (respectively, second) process. The structure factor $S(q,t) = \langle h(q,t)h(-q,t)\rangle$ [FT of $C(r,t)$; for simplicity we assume spatial isotropy in the basal plane] is then derived by averaging over the noise. We define $\bar{a}_i = a_i(q)T_i$ and $\bar{a}_c = [a_1 p + a_2(1-p)]T$, in terms of which we find $S_c(q,n) \equiv S(q,nT)$ after exactly n cycles to be

$$S_c(q,n) = \exp\{-2\bar{a}_c n\}S(q,0) + \{\tfrac{D_1}{a_1}\exp(-2\bar{a}_2)[1 - \exp(-2\bar{a}_1)] + \tfrac{D_2}{a_2}[1 - \exp(-2\bar{a}_1)]\}[\tfrac{1-\exp(-2\bar{a}_c n)}{1-\exp(-2\bar{a}_c)}]. \tag{5}$$

A similar expression may be obtained for $S_c(q, n+p)$ and straightforwardly extended to any time $t = (n+f)T$.

For small q, such that $\bar{a}_c(q) \ll 1$, $S_c(q,n)$ takes the form

$$S_c(q,n) \sim \frac{D_c}{a_c(q)}[1 - \exp\{-2[a_c(q)Tn]\}], \tag{6}$$

where we introduce the *effective* parameters of the cyclical growth process: $D_c = pD_1 + (1-p)D_2$, and $a_c(q) = pa_1(q) + (1-p)a_2(q) = \bar{a}_c/T$. The same conclusion may be reached from coarse graining Eq. (4) and eliminating all modes with frequencies larger than $2\pi/T$ [11] [this also yields the corresponding propagator $G_c(q,n)$ on time scales larger than T]. In terms of these effective parameters, $S_c(q,n)[G_c(q,n)]$, with large $n = t/T$, of the cyclical process are equivalent to $S(q,t)[G(q,t)]$ of a primary linear process. Hence, the scaling behavior, presumed for the former in Eq. (3), indeed substitutes for that of Eq. (1) which holds for the latter [2].

In the $n \to \infty$ limit, the asymptotic large-scale roughness is determined by the small q divergence of $S_c(q,n)$. Since $a_i(q) \sim |q|^{z_i}$, it is the process with the smaller z_i which dominates the large L cyclical roughness: $W_c(L,\infty) = AL^{\alpha}$, with $\alpha = \min(\alpha_1,\alpha_2) = \min(z_1,z_2) - (d-1)$ (the *amplitude* A is proportional to D_c and is determined by *both* primary processes). The larger α_i appears as a correction to scaling exponent.

As for the dynamic exponent z of the cyclical process, since n appears always multiplied by $\bar{a}_c(q)$, the slower of the two primary processes dictates the cyclical dynamics: $z = \min(z_1,z_2)$. The correlation length increases with n as $\xi_c = n^{1/z}$ with an amplitude proportional to $[T_i]^{1/z}$, with T_i of the dominating process. For the initial cycles ($nT \ll L^z$), the roughness grows as n^{β}, with $\beta = \alpha/z = [z - (d-1)]/z$.

For processes described by stochastic nonlinear equations, the asymptotic behavior is explored by the RG approach [2,8]. An approximate RG procedure for cyclical processes may consist in first coarse graining the free cyclical propagator (obtained from the two primary free propagators as explained above) until it becomes that of an effective linear, noncyclical process. Using this effective linear process as the "free" part, all the nonlinear terms of the primary processes, with bare couplings multiplied by p or $(1-p)$, are added as "interactions." The RG flows may then be derived following the usual steps [11]. In this approximation, the initial flow of the couplings is replaced by a simplified one. It is implicitly assumed that simplifying the initial flow will not alter the ultimate fixed point for each of the renormalized couplings. Although this seems very plausible, it might not always hold.

Assuming it does, some conclusions may be reached. We begin with only one of the primary processes possessing a relevant nonlinear term. Its importance for the cyclical growth will depend on its relevance with respect to the coarse grained linear approximation of the cyclic propagator. We may conclude that, if the linear dominant term originates from the same primary process as the

nonlinearity, the latter will remain relevant. If, however, the nonlinear process yields the nondominant part of the free propagator, the nonlinearity may be rendered irrelevant, in which case the cyclical behavior will be that of the other (linear) process.

If both primary processes have a nonlinear term, a simple behavior is reached if one of them is rendered irrelevant. Then the other one will bequeath its scaling exponents to the cyclical descendant. Theoretically, nonlinear contributions from both processes may be relevant with various potential outcomes [12].

To examine these general conclusions, we performed numerical simulations on specific lattice atomistic models [2] in 2D (preliminary simulations in 3D show a similar behavior). The system size in the simulations was changed between 128 to 4096 lattice spacings. A typical cycle consisted of a deposition of 5–20 layers (average number of particle deposited per site) and desorption of between 10% to 100% of the deposited amount. The maximum number of cycles, n, varied between 500–10 000, averaged over 50–5000 independent runs, depending on the pairs of primary processes and the system size. The growth exponent β was extracted for different system size L. The value quoted is from the largest L (once β became size independent). From $W(L,\infty)$, the saturation width dependence on L, the roughness exponent α was derived. In most cases, we checked independently the value of α from the scale dependence of the rms height difference.

For linear primary processes, we looked at the pairwise combinations of RD/EW, its reverse EW/RD, and DT/EW, using the standard absorption/desorption algorithms for EW [13], DT [9,14] (see also [2]), and RD [15]. They all showed asymptotic cyclical scaling with EW exponents. This confirms the above conclusions for primary linear processes, since EW is the dominating one when paired with RD or DT. We also run the respective adsorption/adsorption cycles using the same pairs. The roughness behavior was identical, while their growth velocities were naturally different.

To simulate nonlinear processes, we included two lattice realizations which belong to the KPZ universality class: ballistic deposition (BD) [6,15,16] and the restricted solid-on-solid algorithm of Kim and Kosterlitz (KK) [17]. We have generalized both of these algorithms to desorption as well [11]. Both realizations yielded equivalent behaviors when combined with other processes (as they do in simple noncyclical adsorption or desorption), and we quote the ones obtained using the BD (ballistic deposition or desorption) algorithm. If we combine the nonlinear BD (or KK) algorithm with the EW (or DT) linear process to form a cyclical process, the above considerations lead us to expect KPZ exponents. Indeed, the KPZ free propagator is equivalent to the EW (and dominating over the DT) one. The exponents obtained are $\beta = 0.311(5)$, $\alpha = 0.51(1)$ for EW/BD, and $\beta = 0.322(5)$, $\alpha = 0.50(1)$ for BD/EW. These asymptotic exponents are consistent with the KPZ $\beta = 1/3$ (and, of course, with $\alpha = 1/2$, which is the common value of EW and KPZ). However, while for BD/EW these values were obtained for all sizes, for EW/BD the exponent β increased slowly with the system size and the effective β reached its asymptotic value only for the largest system size ($L = 4096$). Growth/growth cycles yielded results very similar to the growth/recession cycles.

To look at primary processes with different values of α, a DT ($\alpha_1 = 1.5$) deposition with ballistic desorption ($\alpha_2 = 0.5$) were performed. In Fig. 1 we show the logarithmic dependence of W (*roughness*) on $\ln(n)$, for different system sizes L, for this DT/BD process. The inset depicts the logarithmic dependence of W_m (the maximal roughness) vs $\ln L$. From the graphs, we obtain the asymptotic values of the exponents for DT/KPZ: $\beta = 0.311(15)$ and $\alpha = 0.48(2)$, both consistent with the KPZ values.

The solid line in Fig. 1 is the full time dependence of the roughness within the initial cycles. It shows that it is its average (or its envelope) which scales asymptotically. Within every cycle, only modulations around this average are observed. To understand the emergence of the scaling behavior, the full cycle has to be viewed as the basic unit of a more complex process, with T as the unit of time. The scaling behavior unfolds as the cumulative effect of many repetitions of the unit process (with exponents determined by the relevant among all the features it inherited from the primary processes). Finally, simulations of KK/KK gave surfaces with KPZ scaling for $T_1 \neq T_2$. For $T_1 = T_2$, however, EW behavior was found. This follows from the nonlinear KPZ terms in the primary processes having the same magnitude but opposite signs.

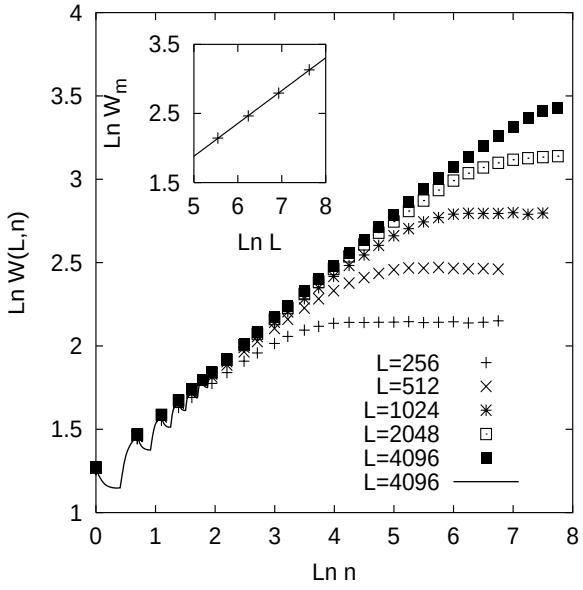

FIG. 1. $\ln W$ (roughness) of the simulated cyclical DT/BD process vs $\ln n$ (number of cycles) for different system sizes L. The solid line is its time dependence during the initial cycles. [inset: $\ln W_m$ (maximal roughness) vs $\ln L$].

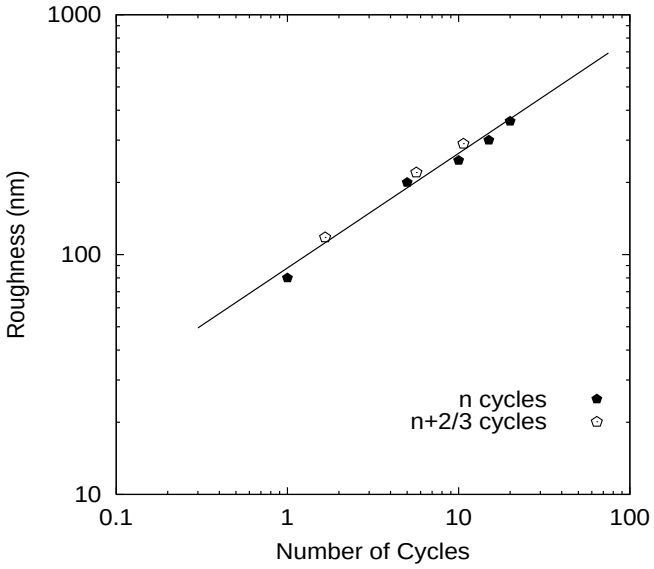

FIG. 2. The roughness vs number of cycles n in the electrochemical cyclical growth of silver (log-log plot).

Experiments of cyclical growth were performed by metal electrodeposition/dissolution of silver. Electrodeposition has been used in recent years to study the scaling behavior of surface growth (see [18–20] and references therein). To explore cyclical growth, multiple electrodeposition/dissolution cycles were carried out on initially vapor-deposited silver substrates, ranging from 1 to 20 cycles. The plating solution contained $0.092M$ AgBr (silver bromide), $0.23M$ $(NH_4)_2S_2O_3$ (ammonium thiosulfate), and $0.17M$ $(NH_4)_2SO_3$ (ammonium sulfite). Each cycle consisted of plating for 5 min followed by 2.5 min of electrodissolution with a current density of 0.8 mA/cm^2. Up to 20 cycles have been performed and the roughness was examined by atomic force microscopy after n full cycles and after the deposition part of the cycles (namely, after $n + p$ cycles with $p = 2/3$) [21]. Figure 2 shows a log-log plot of the rms roughness versus the cycle number. The data are consistent with a power-law scaling and the fit yields $\beta = 0.48(5)$. For comparison, $\beta = 0.71$ for electrodeposition only under the same conditions [21]. Future experimental measurements (on the cyclical as well as on the primary processes) will allow more detailed scaling analysis and quantitative comparison of the scaling relations with theoretical predictions.

In summary, the results of complementary studies of cyclical growth processes were presented, and show them to be amenable to scaling analysis. The scaling description holds, provided the time variable is replaced by the number of cycles. This conclusion is supported by the initial experimental findings. We have derived the cyclical behavior of two alternating linear processes and outlined how the RG approach may be applied in the presence of nonlinear effects in the primary processes. In all systems we have studied analytically or numerically, the related exponents are unaffected by the cycle period T or the relative durations (p and $1 - p$) of the two processes. One crucial question is how this behavior might be affected if the duration of the deposition (and/or desorption) phases are not uniform. We plan to address irregular intermittent growth/recession processes in the future [11].

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