

Surfactant-Mediated Growth of Nonequilibrium Interfaces

Albert-László Barabási^(a)*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*

(Received 15 March 1993)

A number of recent experiments have shown that surfactants can modify the growth mode of an epitaxial film, suppressing islanding and promoting layer-by-layer growth. Here I introduce a set of coupled equations to describe the nonequilibrium roughening of an interface covered with a thin surfactant layer. The surfactant may drive the system into a novel phase, in which the surface roughness is negative, corresponding to a flat surface.

PACS numbers: 68.55.-a, 64.60.Ht, 68.35.Fx

There is much theoretical interest in the statistical properties of nonequilibrium surfaces. The growing interfaces naturally evolve into self-affine structures; the surface morphology and the dynamics of roughening exhibit simple scaling behavior despite the complicated nature of the growth process [1]. In particular, much attention has focused on different models to describe thin-film growth by molecular-beam epitaxy (MBE) [2–6].

Under ideal MBE conditions the primary relaxation mechanism is surface diffusion, which conserves the mass of the film. Experimentally both lattice strain and surface free energy determine whether the film undergoes layer-by-layer growth, islanding, or layer-by-layer growth followed by islanding. In experiments involving growth of Ge on a Si(100) surface layer-by-layer growth is limited to 3–4 monolayers (ML) due to the lattice mismatch between Si and Ge, and is followed by formation of unstrained Ge islands. It was shown recently that islanding in the Ge/Si system can be suppressed effectively by use of a surfactant monolayer, *changing the growth mode* from island growth to layer-by-layer growth [7]. Suitable surfactants such as As and Sb strongly reduce the surface free energy of both Si and Ge surfaces and segregate at the surface during growth. A number of subsequent experiments showed that surfactants can change the surface morphology in a wide variety of systems: Sb altered the growth behavior of Ag on Ag(111) [8], antimony was found to change the structure of islands in Ge/Si growth [9], and Te was used as a surfactant to sustain layer-by-layer growth of InAs on GaAs(001) [10].

Microscopically, arsenic placed on the surface of Si or Ge lowers the surface tension by eliminating the dangling bond states. But for ordinary surfactants reduced surface tension *enhances* roughness. The reduced adatom diffusion might change the growth mode, but so far most continuum models with or without surface diffusion predict rough interfaces [2–6,11]. While the microscopic mechanism of As and Ge/Si interaction is much investigated [12], understanding in the framework of continuum growth models is still lacking.

In this paper I study the generic problem of nonequilibrium roughening of an interface covered by a thin surfactant layer (see Fig. 1). Building on experimental results

and general symmetry principles, a set of nonequilibrium equations is proposed to describe the growth of an interface coupled to the fluctuations in the surfactant coverage. The analytic study of these equations indicates that the surfactant changes drastically the morphology of the interface in 2+1 dimensions. In particular, the coupled system supports the existence of a novel phase characterized by a negative roughness exponent, which can be identified with a morphologically flat surface.

As mentioned above, under ideal MBE conditions, relaxation proceeds via surface diffusion. In contrast to ideal MBE, there is experimental evidence that surfactant-mediated growth of Ge on Si proceeds by highly local Ge incorporation with minimum surface diffusion [13]. Ge atoms that adhere to the As-capped surface rapidly exchange sites with the As atoms and incorporate into subsurface sites. In the absence of surface diffusion, the growth equation may contain terms which violate mass conservation [14]. The simplest nonlinear growth equation with nonconserved dynamics was introduced by Kardar, Parisi, and Zhang (KPZ) [15]:

$$\partial_t h = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta. \quad (1)$$

Here $h(x, t)$ is the height of the interface in $d = d' + 1$

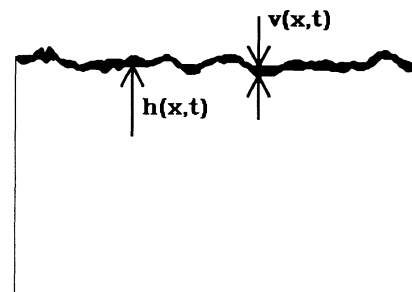


FIG. 1. Schematic illustration of the studied surfactant/surface system. The figure represents a cross section of the two dimensional surface of height $h(x, t)$ covered by a thin surfactant layer with thickness $v(x, t)$. A newly arriving atom penetrates the surfactant and is deposited on the top of the growing interface $h(x, t)$.

dimensions. The first term on the right-hand side describes relaxation of the surface by a surface tension ν . The second term is the lowest order nonlinear term that can appear in the interface growth equation, and is related to lateral growth. $\eta(x, t)$ is a stochastic noise driving the growth; it can describe thermal and beam intensity fluctuations. Additional terms in (1) will include the coupling to the surfactant fluctuations.

An efficient surfactant must fulfill two criteria: it must be sufficiently mobile to avoid incorporation, and it must surface segregate. Careful experimental studies showed for the Ge/Si system that the bulk As concentration is less than 1%; thus the effect of As on growth is a surface phenomenon [7]. Neglecting the desorption of the surfactant atoms, the equation governing the surfactant kinetics obeys mass conservation. This leads to the continuity equation $\partial_t v = -\nabla \cdot \mathbf{j} + \eta'$, where $v(x, t)$ is the *width of the surfactant layer* [16], η' is a conserved uncorrelated noise which incorporates the random local fluctuations of the surfactant, and \mathbf{j} is the particle-number current density. The simplest linear equation with conserved dynamics correctly incorporating the effect of surface diffusion is [2]

$$\partial_t v = -K\nabla^4 v + \eta'. \quad (2)$$

To account for the coupling between the growing surface and the surfactant it is necessary to introduce additional terms in Eqs. (1) and (2). There are two main criteria which restrict our choice: The coupling terms must satisfy the symmetry conditions characteristic of the interface and the obtained set of equations should be self-consistent; i.e., the resulting dynamics should not generate further nonlinear terms. In addition the coupling terms included in Eq. (2) must obey the required mass conservation for the surfactant.

The simplest set of equations that satisfies the above conditions is

$$\partial_t h = \nu \nabla^2 h + \lambda (\nabla h)^2 + \beta (\nabla v)^2 + \eta_0, \quad (3a)$$

$$\partial_t v = -K\nabla^4 v + \gamma \nabla^2 [(\nabla h) \cdot (\nabla v)] + \eta_1, \quad (3b)$$

where the noise terms η_0 and η_1 are assumed to be Gaussian distributed with zero mean and the following correlator:

$$\langle \eta_i(x, t) \eta_j(x', t') \rangle = \mathcal{D}_i \delta(x - x') \delta(t - t'). \quad (4)$$

Here

$$\mathcal{D}_0 = D_0 \quad (5)$$

and

$$\mathcal{D}_1 = -D_1 \nabla^2 + D_2 \nabla^4. \quad (6)$$

The D_2 term is generated by D_0 and D_1 as will be shown below.

The generic nonlinear term $(\nabla v)^2$ in (3a) can be derived using symmetry principles. In (3b) the $\nabla^2 [(\nabla h) \cdot (\nabla v)]$ term results from a current $\mathbf{j} = -\nabla [(\nabla h) \cdot (\nabla v)]$,

and obeys mass conservation. A geometrical interpretation [5] of this term suggests that a positive γ drives the surfactant to cover uniformly the irregularities of the surface, i.e., enhances the wetting properties [17]. A negative γ has the opposite effect, assigning a nonwetting character to the surfactant. Since in experiments there is no evidence of surfactant agglomeration (nonwetting character), but it is energetically favorable to terminate the Ge layer with As atoms, we assume that the surfactant wets the surface; thus $\gamma > 0$.

The quantity of main interest is the dynamic scaling of the fluctuations characterized by the width $w_0^2(t, L) = \langle [h(x, t) - \bar{h}(t)]^2 \rangle = L^{2\chi_0} f(t/L^{z_0})$, where χ_0 is the roughness exponent for the interface $h(x, t)$, and the dynamic exponent z_0 describes the scaling of the relaxation times with the system size L ; $\bar{h}(t)$ is the mean height of the interface at time t and $\langle \rangle$ denotes ensemble and space average. The scaling function f has the properties $f(u \rightarrow 0) \sim u^{2z_0/\chi_0}$ and $f(u \rightarrow \infty) \sim \text{const}$. In a similar way one can define χ_1 and z_1 to characterize the fluctuations in the surfactant coverage $v(x, t)$.

For $\beta = 0$, Eq. (3a) reduces to the KPZ equation (1). For the physically relevant dimension, $d = 2 + 1$, the scaling exponents are not known exactly. Extensive numerical simulations give $\chi_0 = 0.385 \pm 0.005$ and $z_0 \simeq 1.6$ [18]. Thus the interface is rough and the roughness increases with time as $w_0(t) \sim t^{\chi_0/z_0}$.

For $\gamma = 0$, Eq. (3b) is the fourth-order linear diffusion equation with conserved noise (2), which can be solved exactly, resulting in $z_1 = 4$ and $\chi_1 = 0$ [19].

Thus, neglecting the coupling terms, Eqs. (3a) and (3b) predict rather different values for z and the roughness exponents χ_i . To see how the couplings change this behavior, I have investigated Eq. (3) using a dynamical renormalization-group (DRG) scheme. During the DRG calculations only one dynamic exponent $z = z_0 = z_1$ was used, valid if the system does not decouple. The fast modes are integrated out in the momentum shell $e^{-1}\Lambda_0 \leq |k| \leq \Lambda_0$, and the variables are rescaled as $x \rightarrow e^l x$, $t \rightarrow e^{z_l} t$, $h \rightarrow e^{\chi_0 l} h$, and $v \rightarrow e^{\chi_1 l} v$. The calculations have been performed up to one-loop order.

The diagrams contributing to λ cancel each other, resulting in the scaling relation

$$z + \chi_0 = 2. \quad (7)$$

This relation is known to be the property of the KPZ equation and it is a consequence of Galilean invariance (GI). Since the DRG conserves the GI, this scaling law is expected to remain valid to all orders of the perturbation theory.

A second scaling relation can be obtained from the nonrenormalization of the diffusion coefficient D_1 :

$$z - 2\chi_1 - d' - 2 = 0. \quad (8)$$

The diagrams that contribute to D_1 have a prefactor proportional to \mathbf{k}^4 ; thus they are irrelevant (\mathbf{k} is the wave vector in the Fourier space). They in fact contribute to

D_2 , justifying its introduction in (6).

These two scaling relations already indicate that the coupled interface/surfactant system is qualitatively different from the uncoupled one. For a planar interface ($d' = 2$) (7) and (8) give

$$\chi_0 + 2\chi_1 = -2, \quad (9)$$

which means that at least one of the exponents has to be negative.

A third scaling relation unfortunately is not available, but insight can be obtained from numerical integration of the flow equations obtained from the DRG [20]. The integration showed the existence of two main regimes:

(i) In the first regime one or both of the coupling terms (β, γ) scale to zero. In this case the two equations become completely (both coupling terms vanish) or partially (only one coupling term vanishes) decoupled, and the two equations might support different dynamic exponents z . The DRG scheme used is not reliable in this regime.

(ii) The presence of a strong coupling fixed point is expected when both of the nonlinear terms diverge. The integration shows that this *coupled phase* exists only for $z \geq 8/3$ [21]. It is important to note that although there is no identifiable fixed point, in this phase the scaling relations (7) and (8) are exact. According to (7), for $z \geq 8/3$ the roughness exponent of the interface χ_0 is negative. With a negative roughness exponent, every noise-created irregularity is smoothed out by the growth dynamics and the resulting surface becomes flat. Thus the coupling of the surfactant to the growing interface results in the *suppression of the surface roughness*. This corresponds exactly to the experimentally observed behavior, i.e., the addition of the surfactant suppresses islanding, resulting in a morphological transition from a rough (without surfactant) to a flat (with surfactant) interface.

The roughness exponent of the surfactant from (8) is negative if $z < 4$, while for $z > 4$ it becomes positive. In the Ge/Si system, for example, the As has a saturation coverage of 1 ML, which is independent of the system size and is governed only by the microscopic bonding of the As to the Ge dangling bonds. One expects no relevant fluctuations in the thickness of the coverage; this requires a negative roughness exponent for the surfactant and thus limits the dynamic exponent to values smaller than four.

The DRG analysis fails to provide the exact value of the dynamic exponent z . As in the case of many other growth phenomena, simple discrete models might be very helpful in obtaining its value [22]. Summarizing the results of the direct integration of the DRG equations, for $z > 8/3$ the existence of a strong coupling fixed point is observed, in which the interface roughness exponent is negative, corresponding to a flat phase. There is no upper bound in z for the existence of this phase, but physical considerations suggest that $z < 4$, in order to allow the

uniform surfactant coverage observed experimentally.

It is important to note that introducing Eq. (3) I did not use directly the existence of the strain due to the lattice mismatch. Although an important problem [23], a continuum description of strain-induced roughening is still missing. The proposed model is expected to describe the coupled surfactant/interface system, but decoupling the surfactant does not necessarily result in an equation describing heteroepitaxial islanding. Further studies are necessary to understand the microscopic (perhaps strain induced) origin of the nonlinear coupling terms.

In Eq. (3) the desorption of the surfactant atoms is neglected by considering that (3b) obeys mass conservation. Lifting the conservation law, (3b) should be replaced by a nonconservative equation. Such a system has been recently studied [24,25], and it was found that in most cases the coupling does not change the KPZ scaling exponents. Enhancement of the exponents is possible *only* when the coupling is one way; i.e., one of the equations decoupled from the other one is acting as a source of correlated noise.

Further linear and/or nonlinear terms added to (3) might influence the dynamics of the system. The goal here was to derive the *simplest* set of equations predicting the experimentally observed morphological phase transition; the study of other possible nonlinear terms and their relevance is left for future work.

In conclusion, I have introduced a set of equations to describe the interaction of a growing surface with a surfactant. The main experimentally motivated requirements for (3) were (a) no surface diffusion of the newly landed adatoms and (b) conservative and diffusive surfactant dynamics, originating from neglecting incorporation and desorption of the surfactant during the growth process. The obtained equations indicate the existence of a coupled phase, in which two scaling relations between the three exponents are available. In this phase, the roughness exponent of the interface is negative, morphologically corresponding to a flat interface, as observed experimentally.

Moreover, Eq. (3) serves as a good starting point for future studies of an interface coupled to a local *conservative* field, a problem of major interest in the context of recent efforts to understand the general properties of nonequilibrium stochastic systems.

I wish to thank M. Gyure and E. Kaxiras for useful discussions and comments on the manuscript and H. E. Stanley for continuous encouragement and support. This research was partially funded by the Hungary-U.S. exchange program of the Hungarian Academy of Sciences and the National Science Foundation. The Center for Polymer Studies is supported by the National Science Foundation.

^(a) Electronic address: alb@buphy.bu.edu

[1] For recent reviews, see T. Vicsek, *Fractal Growth Phe-*

- nomena* (World Scientific, Singapore, 1992), 2nd ed.; D. E. Wolf, in *Kinetics of Ordering and Growth at Surfaces*, edited by M. Lagally (Plenum, New York, 1990); J. Krug and H. Spohn, in *Solids Far From Equilibrium: Growth, Morphology and Defects*, edited by C. Godrèche (Cambridge Univ. Press, Cambridge, England, 1991); F. Family and T. Vicsek, *Dynamics of Fractal Surfaces* (World Scientific, Singapore, 1991); *Surface Disorder: Growth, Roughening and Phase Transitions*, Proceedings of the Les Houches Workshop, 1992, edited by R. Jullien, J. Kertész, P. Meakin, and D.E. Wolf (Nova Science, Commack, NY, 1992).
- [2] D.E. Wolf and J. Villain, *Europhys. Lett.* **13**, 389 (1990).
 [3] J. Villain, *J. Phys. I (France)* **1**, 19 (1991).
 [4] L. Golubović and R. Bruinsma, *Phys. Rev. Lett.* **66**, 321 (1991).
 [5] Z.-W. Lai and S. Das Sarma, *Phys. Rev. Lett.* **66**, 2348 (1991).
 [6] L.-H. Tang and T. Nattermann, *Phys. Rev. Lett.* **66**, 2899 (1991).
 [7] M. Copel, M.C. Reuter, E. Kaxiras, and R.M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989); M. Copel, M.C. Reuter, M. Horn von Hoegen, and R.M. Tromp, *Phys. Rev. B* **42**, 11 682 (1990).
 [8] H.A. van der Vegt, H.M. van Pinxteren, M. Lohmeier, E. Vlieg, and J.M.C. Thornton, *Phys. Rev. Lett.* **68**, 3335 (1992).
 [9] H.J. Osten, J. Klatt, G. Lippert, B. Dietrich, and E. Bugiel, *Phys. Rev. Lett.* **69**, 450 (1992).
 [10] N. Grandjean, and J. Massies, and V.H. Etgens, *Phys. Rev. Lett.* **69**, 796 (1992); see also C.W. Snyder and B.G. Orr, *Phys. Rev. Lett.* **70**, 1030 (1993); N. Grandjean and J. Massies, *ibid.* **70**, 1031 (1993).
 [11] A recently proposed model [M. Siegert and M. Plischke, *Phys. Rev. Lett.* **68**, 2035 (1992)] predicted a smooth interface, but with grooved morphology, which is not observed in the surfactant system.
 [12] E. Kaxiras, *Europhys. Lett.* **21**, 685 (1993).
 [13] R.M. Tromp and M.C. Reuter, *Phys. Rev. Lett.* **68**, 954 (1992).
 [14] In fact, even for systems with surface diffusion but without mass conservation the long time behavior is described by the KPZ equation [15]. But if surface diffusion is absent, the growth equation can have only nonconservative dynamics, as is the case with the surfactant covered Ge interface.
 [15] M. Kardar, G. Parisi, and Y.-C. Zhang, *Phys. Rev. Lett.* **56**, 889 (1986).
 [16] Throughout this paper it is assumed that the surfactant layer is very thin; thus nonlocal effects do not contribute to the dynamics. The typical experimental coverage, which is the spatial average of $v(x,t)$, is around 1 ML. For coverages smaller than 1 ML holes might appear in the surfactant layer. Since the growth equations to be proposed do not depend in an explicit form on the thickness of the layer, but only on its spatial derivative, the system remains well defined even in the presence of such holes.
 [17] P.G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
 [18] For a detailed discussion on the different conjectures on the $d = 2 + 1$ KPZ exponents and their numerical verification see [1], and also J.M. Kim and J.M. Kosterlitz, *Phys. Rev. Lett.* **62**, 2289 (1989); B.M. Forrest and L.-H. Tang, *Phys. Rev. Lett.* **64**, 1405 (1990); K. Moser, J. Kertész, and D.E. Wolf, *Physica (Amsterdam)* **178A**, 215 (1991).
 [19] T. Sun, H. Guo, and M. Grant, *Phys. Rev. A* **40**, 6763 (1989).
 [20] A correct flow must not scale the nonlinear terms β and γ to zero, which would decouple Eqs. (3a) and (3b). The finiteness of the nonlinear terms guarantees the validity of the scaling relations (7) and (8) as well.
 [21] The coupled phase is stable against small fluctuations in the coefficients and exists in a finite region of the parameter space. Since under experimental conditions small fluctuations in the value of the control parameters are always expected, the stability of the system against them ensures the persistence of the coupled phase. But large deviations of the parameters introduce instabilities, which results in the breakdown of the smooth phase. This is in accord with the experimental observation that surfactant-induced layer-by-layer growth develops only under well controlled experimental conditions.
 [22] S. Das Sarma and P. Tamborenea, *Phys. Rev. Lett.* **66**, 325 (1991); D.A. Kessler, H. Levine, and L.M. Sander, *Phys. Rev. Lett.* **69**, 100 (1992); S. Das Sarma and S. V. Ghaisas, *Phys. Rev. Lett.* **69**, 3762 (1992).
 [23] B.G. Orr, D. Kessler, C.W. Snyder, and L. Sander, *Europhys. Lett.* **19**, 33 (1992).
 [24] D. Ertas and M. Kardar, *Phys. Rev. Lett.* **69**, 929 (1992).
 [25] A.-L. Barabási, *Phys. Rev. A* **46**, R2977 (1992).