SURFACTANT-MEDIATED SURFACE GROWTH: NONEQUILIBRIUM THEORY

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Abstract

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 a set of coupled equations are introduced to describe the coupling between a growing interface and a thin surfactant layer deposited on the top of the non-equilibrium surface. The equations are derived using the main experimentally backed characteristics of the system and basic symmetry principles. The system is studied using a dynamic-renormalization-group scheme, which provides scaling relations between the roughness exponents. It is found that the surfactant may drive the system into a novel phase, in which the surface roughness is negative, corresponding to a flat surface.

1. INTRODUCTION

Recently, there has been much theoretical interest in the statistical properties of nonequilibrium interfaces. Most of 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.[1-5] In particular, much attention has been focused on different models to describe thin-film growth by molecular-beam epitaxy (MBE).[6-14]

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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 Si(100) surface, layer-by-layer growth is limited to 3–4 monolayers (ML) due to 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.[15] Suitable surfactants such as As and Sb strongly reduce the surface free energy of both Si and Ge surfaces and cause segregation at the surface during growth.

In this paper, we 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 negative roughness exponent, which can be identified with a morphologically flat surface. A summary of the main results were presented in an earlier publication.[16]

The paper is organized as follows: Sec. 2 presents a short review of the experimental studies. Section 3 introduces the key elements of the proposed nonequilibrium theory. Section 4 presents the main results of the dynamic renormalization group (DRG) analysis, and finally, Sec. 5 reflects on open problems and possible future developments.

2. EXPERIMENTAL STUDIES ON SURFACTANT MEDIATED GROWTH

The ultimate goal in crystal growth by MBE or other vapor-phase techniques is to control and influence the growth mode of a thin film. At high temperatures necessary to obtain sufficient mobility of the surface atoms, the growth mode is determined by the interface and surface free energies and the lattice strain. Lattice strain is specially relevant in heteroepitaxial growth, when attempt is made to combine different types of atoms in a layered structure.

Depending on the surface, interface and heteroepitaxial layer's free energy, three distinct growth modes can be observed. Technologically, it is most useful if the film grows in a layer-by-layer mode (Frank–Van der Merwe), when well controlled planar morphology is obtained. The deposited atoms diffuse on the surface and stick to the edge of nucleated islands. As a result the islands grows, finally covering the whole surface and completing the layer. On the top of the completed layer, new islands start to nucleate, and the previous process is repeated. The growth has an oscillatory character in time, which can be observed using reflection high-energy electron diffraction (RHEED) or other experimental techniques.

If the overlayer does not wet the surface, islanding is observed (Volmer–Weber mode), marked by the dumping of the intensity in RHEED measurements and absence of oscillations.

And finally, if the overlayer wets the surface, but the overlayer stress is unfavorable, the film might grow in a layer-by-layer mode, followed by islanding (Stranski–Krastanov mode).

One of the most widely studied heteroepitaxial structure is obtained by growth of Si on Ge, or Ge on Si. The Ge lattice is 4% larger than the Si lattice, thus generating considerable strain influencing the heteroepitaxial growth. As a result, Ge grows on a Si(100) lattice in the Stranski–Krastanov mode, while Si on Ge follows the Volmer–Weber model.

The lattice mismatch generates islanding after 3–4 monolayers of layer-by-layer growth during Ge deposition on a Si(100). Recently Copel, Reuter, Kaxiras and Tromp proposed the use of a surfactant monolayer of As to reduce the surface free energies and effectively alter the growth mode.[15]

The microscopic mechanism responsible for the unusual effect of the As on the growth process is partially understood. The As layer, with one extra valence electron per surface atom, fills the dangling bonds of the Si(100) surface, creating a stable termination. Furthermore, As segregates to the surface during growth. Si or Ge atoms deposited on the surface covered by an As monolayer rapidly exchange sites with the As and incorporate it into the subsurface. As a result, the heteroepitaxial structure incorporates negligible quantities of As.

Two main mechanisms were proposed to explain the effect of the surfactant on the growth process.[15,17] The first is a dynamic one, based on enhanced incorporation of the growth atoms. The As atoms drive any incoming Si or Ge atom to subsurface sites due to their ability to segregate easily. For a surfactant free surface, the deposited atoms diffuse to the surface, until they reach a step or a defect, where they stick. In contrast, with surfactant the freshly arrived atoms are driven into subsurface sites by an exchange mechanism with the As atoms, their diffusion being severely curtained. Thus in the presence of a surfactant, the adatom can be incorporated without a step or a defect.

The second mechanism uses first principle calculations to explain the effect of the As atoms on the stress distribution of the surface layers. A shortcoming of this mechanism is that it predicts only an increase in the epitaxial thickness before islanding appears, but does not account for the change in the growth mode. Experimental results indicate that after about 50 ML the strain is fully relieved, suppressing the driving force for island formation.

Although probably the combination of the two effects is responsible for the suppression of islanding, the nonequilibrium theory proposed in this paper is based on the first mechanism, providing a quantitative formulation of the dynamic phenomena occurring during surfactant mediated growth.

In addition to the investigations mentioned,[15,17] a number of subsequent experiments showed that surfactants can change the surface morphology in a wide variety of systems. It was found that both Sb and As can act efficiently as a surfactant for the Si/Ge system.[17] The effect of the surfactant on the lattice strain and on the appearance of dislocations was studied in details.[18–21] Low-energy electron microscopic observations were used to gain further understanding in the local exchange mechanism between Ge and surfactant. It has been argued that surface energy anisotropy, instead of surface energy, determines the changes in the growth mode of the Ge/Si system.[22]

Further experimental investigations found that Sb alters the growth of Ag on Ag(111).[23] Since submonolayer surfactant coverages were used, a new mechanism to explain these experiments was proposed. According to this, the Sb attaches to the edge of the islands and lowers the interlayer diffusion barrier of the diffusing adatoms. The Sb moves together with the edge of the growing islands and probably is segregated at the surface when the islands coalesce.

In subsequent experiments, antimony was found to change the structure of islands in Ge/Si growth,[24] and Te was used as surfactant to sustain layer-by-layer growth of InAs on GaAs(001).[25-27]

Since the system most investigated is the Ge/Si growth with As or Sb as surfactant, in what follows such a system involving surfactant mediated growth is discussed. Whether the proposed theory applies to all the experiments mentioned, or additional effects have to be considered, is an open question, which will not be addressed here.

3. NONEQUILIBRIUM THEORY

In order to construct a nonequilibrium theory to account for the nontrivial effect of the surfactant on the growth, we have to study separately the dynamics of the interface and surfactant, and then consider the possible coupling between the two quantities.

As mentioned above, under ideal MBE conditions, relaxation proceeds via surface diffusion. Atoms deposited on the surface diffuse until they find an energetically favorable position (usually near a step or a dislocation), where they stick mostly irreversibly. The diffusive dynamics is *conservative*, i.e., it does not change the mass of the film. The only change in the mass might come from deposition or desorption.

In contrast to the ideal MBE, there is experimental evidence that surfactant mediated growth of Ge on Si proceeds by highly local Ge incorporation with minimum surface diffusion.[30] 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.[31] The simplest nonlinear growth equation with nonconserved dynamics was introduced by Kardar, Parisi, and Zhang (KPZ)[32]:

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

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

Equation (1) is the lowest order nonlinear equation compatible with the basic symmetries of a growing interface: it is isotropic in the substrate directions ($x \rightarrow -x$ transformation leaves the system invariant), and invariant to translation both in the substrate directions ($x \rightarrow x + a$) and in the growth direction ($h \rightarrow h + b$). But there is a broken up-down symmetry in h: the transformation $h \rightarrow -h$ does not leave the system invariant. The explanation to this broken symmetry is based on the existence of a preferred growth direction for the interface. In the absence of the nonlinear term λ this symmetry is obeyed as well. Another important property of this equation is that higher order nonlinear terms are irrelevant, i.e., they do not effect the growth exponents (to be defined later).

Additional terms in Eq. (1) will include the coupling to the surfactant fluctuations.

In describing the dynamics of the surfactant we shall choose as parameter the *width of the surfactant layer*, $v(x,t)$ (see Fig. 1). 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 then it has been proposed that growth equations do not depend in an explicit form on the thickness of the layer, but only on its spatial derivative, and the system remains well defined even in the presence of such a holes.

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 phenomena.[15,17]

Neglecting the desorption of the surfactant atoms, the equation governing the surfactant kinetics obeys mass conservation.

This leads to the continuity equation:

$$\partial_t v = -\nabla \cdot \mathbf{j} + \eta' \, . \tag{2}$$

where 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[6]:

$$\partial_t v = -K\nabla^4 v + \eta' \, . \tag{3}$$

Equation (3) can be obtained from Eq. (2) by using a current $\mathbf{j} \sim \nabla\mu$, where μ is the local chemical potential on the interface. Considering $\mu \sim \nabla^2 v$, i.e., depends only on the local curvature of the thickness (describing local surfactant agglomerations), we obtain Eq. (3).

To account for the coupling between the growing surface and the surfactant, it is necessary to introduce additional terms in Eqs. (1) and (3). 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. (3) must obey the required mass conservation for the surfactant.
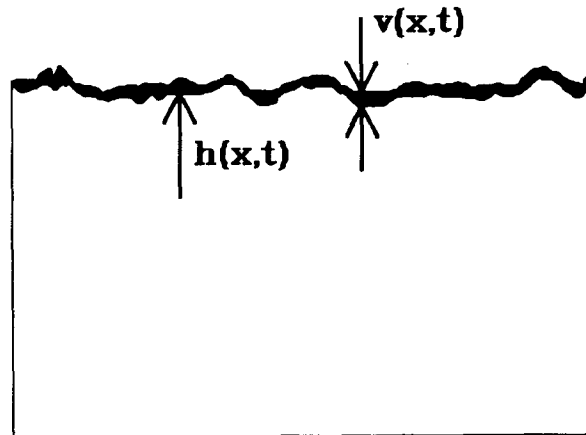
Fig. 1   Schematic illustration of the studied surfactant/surface system. The figure represents a cross section of the two dimensional surface of height $h(x,t)$ covered by a thin surfactant layer with thickness $v(x,t)$. A newly arriving atom penetrates the surfactant and is deposited on the top of the growing interface $h(x,t)$.

The simplest set of equations that satisfy the above condition is:

$$\partial_t h = \nu \nabla^2 h + \lambda(\nabla h)^2 + \beta(\nabla v)^2 + \eta_0 \tag{4a}$$

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

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

$$\langle \eta_i(x,t)\eta_i(x',t')\rangle = \mathcal{D}_i\delta(x-x')\delta(t-t'). \tag{5}$$

Here

$$\mathcal{D}_0 = D_0 \tag{6}$$

and

$$\mathcal{D}_1 = -D_1\nabla^2 = D_2\nabla^4. \tag{7}$$

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

The generic nonlinear term $(\nabla v)^2$ in Eq. (4a) can be derived using symmetry principles. In Eq. (4b) 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. Geometrical interpretation[9] 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.[33] A negative γ has the opposite effect, assigning a non-wetting character to the surfactant. Since in experiments there is no evidence of surfactant agglomeration (non-wetting 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[1]:

$$w_0^2(t,L) = \left\langle [h(x,t)-\bar{h}(t)]^2 \right\rangle = L^{2\chi_0}f(t/L^{z_0}) \tag{8}$$

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 the $\langle\ \rangle$ denotes ensemble average. The scaling function f has the properties:

$$f(u \to 0) \sim u^{2z_0/\chi_0} \tag{9}$$

and

$$f(u \to \infty) \sim \text{const.} \tag{10}$$

In a similar way one can define χ_0 and z_1 to characterize the fluctuations in the surfactant coverage $v(x,t)$.

4. ANALYTICAL STUDY

For $\beta = 0$, Eq. (4a) reduces to the KPZ equation.[1] For a one-dimensional interface the exponents can be obtained using DRG, resulting in the roughness exponent $\chi = 1/2$ and in

the dynamic exponent $z = 3/2$. For higher dimensions, unfortunately no exact results are available. But due to the non-renormalization of the nonlinear term λ, the scaling relation $\chi + z = 2$ exists between the exponents, valid in any dimension. This reduces the number of independent exponents to one. A number of conjectures exist in the literature regarding the higher dimensional exponents, but so far none of them is proved. But numerical simulations on discrete models and direct integration of Eq. (1) helped to obtain reliable estimates for the exponents in higher dimensions as well. For the physically relevant dimension, $d = 2+1$, extensive numerical simulations give $\chi_0 = 0.385 \pm 0.005$ and $z_0 \simeq 1.6$.[34] Thus the interface is rough and the roughness increases with time as $\omega_0(t) \sim t^{\chi_0/z_0}$.

For $\gamma = 0$, Eq. (4b) is the fourth order linear diffusion equation with conserved noise [Eq. (3)], which can be solved exactly, resulting in $z_1 = 4$ and $\chi_1 = 0$.[38,39]

Thus neglecting the coupling terms, Eqs. (4a) and (4b) predict rather different values for z_i and the roughness exponents χ_i. To see how the couplings change the behavior, we have investigated Eq. (4) using a DRG scheme.

For this we rewrite Eq. (4) in its Fourier components:

$$\tilde{h}(k,\omega) = \tilde{\eta}_0(k,\omega)G_0(k,\omega) - \lambda G_0(k,\omega) \int \int d^d q \, d\Omega \, q(k-q)\tilde{h}(q,\Omega)\tilde{h}(k-q,\omega-\Omega)$$
$$- \beta G(k,\omega) \int \int d^d q \, d\Omega \, q(k-q)\tilde{v}(q,\Omega)\tilde{v}(k-q,\omega-\Omega) \tag{11}$$

$$\tilde{v}(k,\omega) = \tilde{\eta}_1(k,\omega)G_1(k,\omega) + \gamma K^2 G_1(k,\omega) \int \int d^d q \, d\Omega \, q(k-q)\tilde{h}(q,\Omega)\tilde{v}(k-q,\omega-\Omega) \tag{12}$$

where $\tilde{\eta}_i(k,\omega)$, $\tilde{h}(k,\omega)$, and $\tilde{v}(k,\omega)$ are the Fourier components of the corresponding quantities and the correlators have the form:

$$G_0(k,\omega) = \frac{1}{\nu k^2 - i\omega} \tag{13}$$

$$G_1(k,\omega) = \frac{-1}{Kk^4 + i\omega} \tag{14}$$

During the DRG calculations, only one dynamic exponent $z = z_0 = z_1$ was used, valid if the Eqs. (4) do not decouple. Equations (11) and (12) are the starting point for the perturbative evaluation of $\tilde{h}(k,\omega)$ and $\tilde{v}(k,\omega)$. The basic diagrams are indicated in Fig. 2. The fast modes are integrated out in the momentum shell $e^{-l}\Lambda_0 \leq |k| \leq \Lambda_0$, and the variables are rescaled as $x \to e^l x$, $t \to e^{zl}t$, $h \to e^{\chi_0 l}h$, and $v \to e^{\chi_1 l}v$. The calculations have been performed up to one-loop order.

In what follows we shall skip most of the details of the calculation; the interested reader is referred to the literature.[40] We shall present only the main parts which are relevant to further arguments.
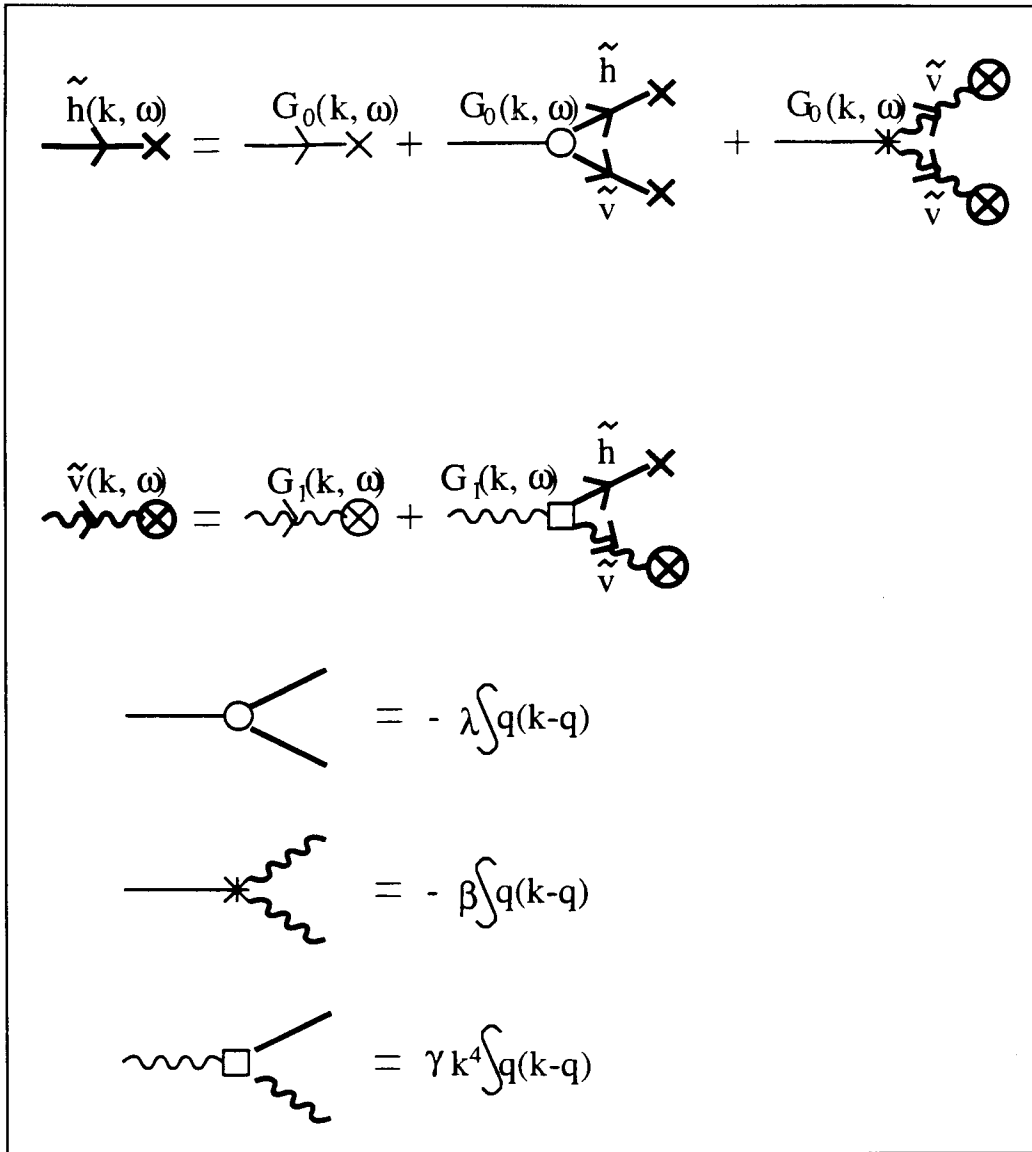
Fig. 2 Diagrammatic representation of the nonlinear integral equations [Eqs. (11) and (12)].

The first result is that the diagrams contributing to λ cancel each other, resulting in the flow equation:
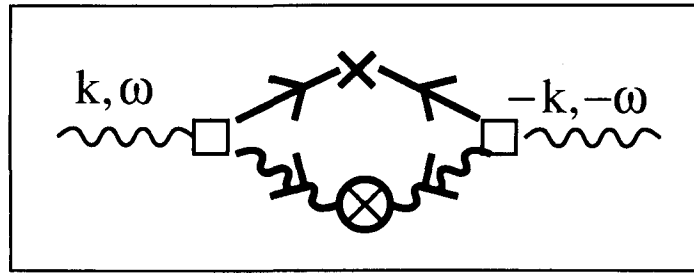
$$\frac{d\lambda}{dl} = \lambda[z + \chi_0 - 2] \tag{15}$$

providing us with the scaling relation:

$$z + \chi_0 = 2. \tag{16}$$

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 for all orders of the perturbation theory.

Fig. 3   The leading contribution to the effective noise spectral function. The encircled noise term corresponds to $\mathcal{D}_1$, and consists of D_1 and D_2 according to Eq. (7).

A second scaling relation can be obtained from the non-renormalization of the diffusion coefficient D_1:

$$\frac{dD_1}{dl} = D_1[z - d' - 2 - 2\chi_1], \tag{17}$$

resulting in:

$$z - 2\chi_1 - d' - 2 = 0. \tag{18}$$

The diagrams that contribute to D_1 (see Fig. 3) 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 Eq. (7).

These two scaling relations already indicate that the coupled interface/surfactant system is qualitatively different from the uncoupled one, for a planar interface $(d' = 2)$[16,18] gives

$$\chi_0 + 2\chi_1 = -2, \tag{19}$$

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. A correct flow must not scale the nonlinear terms β and γ to zero, which would decouple Eqs. (4a) and (4b). The finiteness of the nonlinear terms guarantee the validity of the scaling relations[16,18] as well. The integration showed the existence of the 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 the *coupled phase* exists only for $z \geq 8/3$. 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 result 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.

It is important to note that although there is no identifiable fixed point, in this phase the scaling relations[16,18] are exact. According to Eq. (16) for $z \geq 8/3$, the roughness exponent of the interface χ_0 is negative (see Fig. 4). 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 rough (without surfactant) to flat (with surfactant) interface.

The roughness exponent of the surfactant from χ_1 [Eq. (18)] is negative if $z < 4$, while for $z > 4$ it becomes positive (see Fig. 4). 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 to obtain its value (see discussion later). 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 for the uniform surfactant coverage observed experimentally.
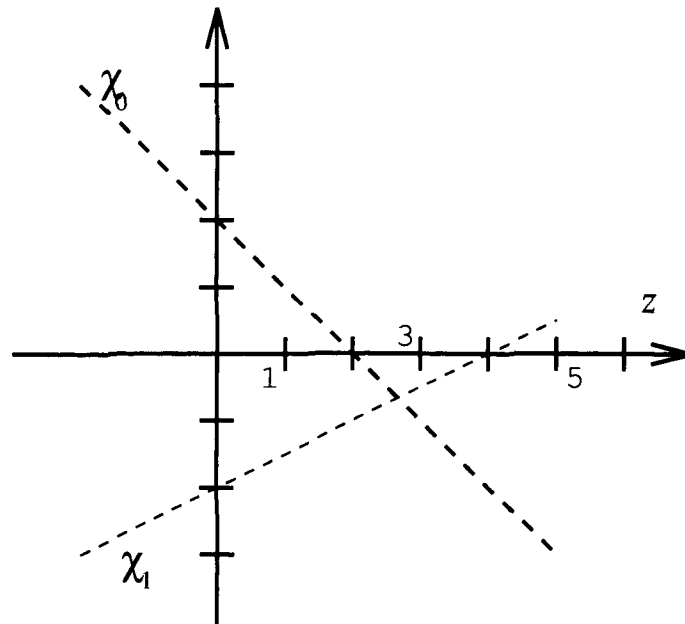
Fig. 4 The dependence of the roughness exponents χ_0 and χ_1 on the dynamic exponent z, according to the scaling relations Eqs. (16) and (18).

5. CONCLUSIONS AND FURTHER DEVELOPMENTS

In the previous sections, we introduced a set of coupled equations compatible with the basic symmetries and conservation laws of the surfactant/interface system studied experimentally. The main feature of these equations is that they predict a negative roughness exponent. We have argued that a negative roughness exponent describes a flat interface, in accord with the experimental observations. A natural question arises here: Is there any predicting power in this theory, or have experimental results merely been reproduced without generating further inquiries?

In this section, we examine the predictions made by the theory. The limits are presented as well: what are the physical ingredients we neglected, and whether and how could they be incorporated in a new theory along the presented lines.

As we have noted earlier, the analytic study does not provide us with the exact value of the exponents, but predicts that the dynamic exponent z lies in the narrow range between $8/3$ and 4. If we could measure somehow the dynamic exponent z, the scaling relations would provide us with the other exponents. In fact, if one would be able to measure experimentally any of the exponents χ_i, β_i, or z, the other exponents could be obtained via Refs. 16 and 18.

The scaling theory[8-10] predicts that an originally flat interface becomes rough as a power law of time, $w \sim t^\beta$. Since in our case β is negative, an originally rough interface becomes smooth as a power law of time, until a limiting small roughness is reached. The only difference is in the system size dependence of the roughness: while in the usual growth models, the roughness increases as a power of L, in our case the interface is smooth, with a small thermal roughness w_0, independent of the system size. Thus a possible experimental check of the previous predictions would start from an initially rough interface and monitor directly the decrease of the roughness in time and fit the obtained curve with a power law. Previous experimental results indicated that it is possible to obtain the time dependence of quantities directly related to the surface roughness.[51-55] It would be interesting to see whether for the surfactant such a study could be carried out.

Such an experiment would result in the exponent β_0 for the interface ($\beta_0 = \chi_0/z$), from which using the scaling relations z and χ_0 could be determined. Hopefully the determined z would fall between the boundaries predicted by the theory.

Further test of the theory might come from direct numerical integration of the coupled Eqs. (4), with the aim to look for the coupled phase and obtain the value of the critical exponents. Integration proved to be successful in obtaining the exponents for the KPZ equation,[37] and for checking the DRG results for other coupled systems.[45]

Constructing and investigating discrete models in the same universality class as the studied continuum equations is another efficient and frequently very accurate way to obtain the scaling exponents.[48-50,35] For nonconserved coupled equations (see later) such models have been investigated[47] and gave results in accord with the DRG[47] and numerical integration.[45]

And finally let us mention some open problems related to the presented theory. It is important to note that when introducing Eq. (4), we did not use directly the existence of the strain which appears due to the lattice mismatch. Although an important problem,[56] a continuum description of strain-induced roughening is still missing. The proposed model [Eq. (4)] is expected to describe the *coupled* surfactant/interface system, but decoupling the surfactant does not necessary 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. (4), the desorption of the surfactant atoms is neglected by considering that Eq. (4b) obeys mass conservation. Lifting the conservation law, Eq. (4b) should be replaced by a non-conservative equation. Such a system has recently been studied,[45,47] 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 Eqs. (4) 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.

Another shortcoming of the presented theory is that it does not predict oscillations in the interface roughness in the layer-by-layer growth regime, as is expected experimentally. This is due to the fact that the present continuum theory does not account for the *discreteness* of the lattice, responsible for the oscillations. But such a discrete pinning potential in principle can be introduced in Eqs. (4). The effect of such a pinning potential for both the conserved and nonconserved equation was studied in the literature.[57,58] It would be interesting to see how the coupling terms interact with the lattice potentials, and whether such a calculation leads to a coupled phase with periodic oscillations in time.

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 Eqs. (4) were: (a) no surface diffusion of the newly landed adatoms; (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, Eqs. (4) serve 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.

6. ACKNOWLEDGMENTS

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