Dynamic scaling in conserved systems with coupled fields: Application to surfactant-mediated growth

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Abstract. – We present an analytical study of the interaction of two nonequilibrium conservative fields. Due to the conservative character of the relaxation mechanism, the scaling exponents can be obtained exactly using dynamic renormalization group. We apply our results to surfactant-mediated growth of semiconductors. We find that the coupling between the surfactant thickness and the interface height cannot account for the experimentally observed layered growth, implying that reduced diffusion of the embedded atoms is a key mechanism in surfactant-mediated growth.

Presently there exists considerable interest in understanding the dynamical properties of growing nonequilibrium interfaces [1], [2]. While originally this research was motivated by studies of interface roughening, the formalism and the knowledge accumulated can be applied to a wider range of nonequilibrium phenomena [3].

In studies of interface roughening it is customary to consider only one relevant field, the height of a d-dimensional interface $h(\mathbf{x}, t)$ [4]. However, recent work indicates that in many physically relevant cases a single field is not sufficient for the complete characterization of the system [5].

In this paper we consider a coupled-field approach to discuss a technologically important problem, the growth of semiconductors by molecular beam epitaxy (MBE) in the presence of surfactants. The surfactant is a thin layer of atoms, deposited on the surface, which segregate on top of the growing interface [6]. For a complete characterization of the surfactant-interface system, one has to consider the coupling between the height of the interface and the thickness of the surfactant layer. On the assumption that the surfactant severely curtails the diffusion length of the embedded atoms, it was shown [7] that coupled continuum equations predict the existence of a phase in which both the interface and the surfactant layer are smooth. This phase is reminiscent of the layer-by-layer growth mode observed experimentally. An unresolved issue of critical importance is whether the *coupled* dynamics of the interface and the surfactant

are able by themselves to produce the smooth growth, without requiring that the embedded atoms are immobile.

In the present work we show that in surfactant-mediated growth the coupling of two conserved fields is not adequate to induce the experimentally observed smoothing effect, implying that reduced diffusion of embedded atoms is a key element in the process. We arrive at this conclusion by performing a dynamical renormalization group (DRG) study of the interaction between two fields, for which the main relaxation mechanism is conservative. Due to the conservative character of the relaxation mechanism, all the exponents can be obtained *exactly* for the fully coupled system. In addition to surfactant-mediated growth, this study allows us to discuss the possible universality classes arising from the coupling of two nonequilibrium processes, a broader question of current interest in statistical mechanics.

We study the following set of equations

$$\partial_t h = -K_h \nabla^4 h + \lambda \nabla^2 (\nabla h)^2 + \beta \nabla^2 (\nabla v)^2 + \eta_h \,, \tag{1a}$$

$$\partial_t v = -K_v \nabla^4 v + \gamma \nabla^2 [(\nabla h)(\nabla v)] + \eta_v \tag{1b}$$

as a generic model for the dynamics of two coupled nonequilibrium fields, $h(\mathbf{x}, t)$ and $v(\mathbf{x}, t)$, for which the relaxation mechanism is strictly conservative. As we discuss below, h can be interpreted as the height of a surface on which a surfactant layer of thickness v resides.

We first motivate the choice of coupled equations by symmetry arguments. To simplify the notation we assume that we have a two-component field $\psi = (h, v)$. The conservative requirement of the relaxation mechanism means that any local variation in the magnitude of ψ is the result of a transport mechanism described by the current $j_\psi = (j_h, j_v)$, such that ψ obeys the continuity equation $\partial_t \psi = -\nabla j_\psi + \eta_\psi$. In many physically relevant systems the local variations in the current are governed by the spatial variations in the local chemical potential, μ, giving $j_\psi \sim -\nabla \mu_\psi$. If a diffusion bias at step edges is present (an effect known as "Schwoebel" barrier), or gravity plays a role in the relaxation process, the chemical potential is simply proportional to the field $\mu_\psi \sim \psi$. The possible effects of terms generated by a Schwoebel barrier will be discussed below. The next relevant functional form for the chemical potential is $\mu \sim \nabla^2 \psi$, *i.e.* the potential depends on the local curvature of the field (the explicit $\nabla \psi$ dependence can be excluded since it results in an unphysical broken $x \to -x$ symmetry). Combining the above relations, we obtain

$$\partial_t \psi = -K_\psi \nabla^4 \psi + \eta_\psi \,, \tag{2}$$

which gives the linear terms in (1) [8]. In order to account for *nonequilibrium* effects, we write the current as $j_\psi = j_\psi^{\mathrm{eq}} + j_\psi^{\mathrm{ne}}$, where j_ψ^{eq} is the equilibrium part discussed previously, while j_ψ^{ne} contains the nonequilibrium terms that cannot be obtained by variations of a Hamiltonian. $\lambda \nabla^2 (\nabla h)^2$, $\beta \nabla^2 (\nabla v)^2$ and $\gamma \nabla^2 [(\nabla h)(\nabla v)]$ represent such terms, which can be associated with the local chemical potentials $\mu_\lambda^{\mathrm{ne}} \simeq (\nabla h)^2$, $\mu_\beta^{\mathrm{ne}} \simeq (\nabla v)^2$ and $\mu_\gamma^{\mathrm{ne}} \simeq \nabla h \nabla v$. The terms $\beta \nabla^2 (\nabla v)^2$ and $\gamma \nabla^2 [(\nabla h)(\nabla v)]$ are the lowest-order relevant coupling terms, while the nonlinear term $\lambda \nabla^2 (\nabla h)^2$ is generated by β and γ. In principle one can consider further nonlinear terms, but they do not add to the relevant physics [9].

If the system is strictly conservative, the noise $\eta_\psi = (\eta_h, \eta_v)$ has to obey this conservation property. It is, however, possible to have conservative relaxation processes but nonconservative noise. Accordingly, we include *both* conservative and nonconservative noise terms in (1). The noise is assumed to have zero average and correlations

$$\langle \eta_\psi(\mathbf{x}, t) \eta_\psi(\mathbf{x}', t') \rangle = \mathcal{D}_\psi \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \,, \tag{3}$$

where $\mathcal{D}_\psi = D_\psi^{\mathrm{nc}} - D_\psi^{\mathrm{c}} \nabla^2 + D_\psi' \nabla^4$. The D_ψ' term is generated by D_ψ^{nc} and D_ψ^{c}, as will be shown below.

The coexistence of the conservative and nonconservative noise terms introduces a length scale $L_\psi \sim (D_\psi^c/D_\psi^{nc})^{1/2}$ which delimits two different scaling regimes: one dominated by the conservative noise (with the system size $L \ll L_\psi$), and one dominated by the nonconservative noise ($L \gg L_\psi$). Moreover, D_h^{nc} can be different from D_v^{nc} (and similarly, $D_h^c \neq D_v^c$), which introduces two different length scales $L_\psi = (L_h, L_v)$, resulting in a rather complicated crossover behavior.

We analyzed the coupled system (1) using a DRG scheme, limiting the calculations to the one-loop approximation. Our main results are expected to be valid for higher loops as well, presuming that a coupled phase exists. After integrating out the fast modes in the momentum shell $e^{-l}\Lambda_0 \leq |\mathbf{k}| \leq \Lambda_0$, we have performed the rescaling $\mathbf{x} \to e^l\mathbf{x}$, $t \to e^{lz}t$, $h \to e^{l\chi_h}h$, and $v \to e^{l\chi_v}v$, where χ_h and χ_v are the roughness exponents of the fields h and v, respectively, and z is the dynamic exponent of the system. Since we are interested in the properties of the *coupled* phase, we assume that there is only one dynamic exponent controlling the time evolution of both fields [5].

The first important result is related to the nonrenormalization of the nonlinear term λ, $\frac{\partial \lambda}{\partial l} = \lambda[\chi_h + z - 4]$, a consequence of the invariance of eq. (1) under a generalized Galilean transformation [10]. It is interesting that the coupling to an additional field v does not destroy the validity of this transformation. A consequence of this invariance is that the flow equation for λ is free from higher-loop corrections, and the resulting scaling relation

$$\chi_h + z = 4 \tag{4}$$

is exact.

Due to the conservative nature of the relaxation process, all diagrams contributing to the flow equation of the spectral functions D_ψ^{nc} and D_ψ^c carry $\mathbf{k}^4$ terms, which add corrections only to the flow equation of the D_ψ' term (this also explains the presence of D_ψ': even if we did not include such a term, it would be induced by the other noise terms). As a result, none of the physically relevant noise terms are renormalized, resulting in the scaling relations

$$z - 2\chi_\psi - d = 0\,, \tag{5}$$

$$z - 2\chi_\psi - d - 2 = 0\,, \tag{6}$$

obtained from the flow equations for D_ψ^{nc} and D_ψ^c, respectively. Higher-loop diagrams have the same structure as the one-loop diagrams, thus they do not contribute to the flow equations, ensuring that ((5), (6)) are exact [11]. Note that (5) and (6) correspond to four equations, which can be obtained by replacing ψ with its two components (h, v). The resulting five scaling relations (4)-(6) apparently overdetermine the three independent scaling exponents χ_h, χ_v and z, but not all scaling relations are valid in the same regime. The ordering between L_h, L_v and L determines the actual scaling exponents and leads to the four possible scaling regimes summarized in table I.

TABLE I. – *Summary of the four distinct scaling regimes predicted by* (1).

Length scale	$3\chi_h$	$3\chi_v$	$3z$
$L \ll L_h, L \ll L_v$	$2 - d$	$2 - d$	$10 + d$
$L \gg L_h, L \gg L_v$	$4 - d$	$4 - d$	$8 + d$
$L_h \ll L \ll L_v$	$4 - d$	$1 - d$	$8 + d$
$L_v \ll L \ll L_h$	$2 - d$	$5 - d$	$10 + d$

a) $L \ll L_h$ and $L \ll L_v$: both equations of motion are determined by the conservative noise D_ψ^c. The exponents are determined by (4) and two additional scaling relations obtained by replacing ψ with h and v in (6). In this regime the exponents of the coupled phase are not different from that of the uncoupled conservative equation. Sun *et al.* [10] found that the nonlinear term in (1a) is relevant only for $d = 1$; for higher dimensions the scaling is correctly described by the fourth-order linear equation (2).

b) $L \gg L_v$ and $L \gg L_h$: the nonconservative noise determines the scaling exponents of the coupled phase. In this case the exponents coincide with the exponents of the nonlinear growth equation with surface diffusion [8].

c) $L_h \ll L \ll L_v$: the nonconservative noise determines the scaling of h, while the scaling of v is still determined by the conservative noise. In this case the exponents can be obtained using (4), (5) with $\psi = h$ and (6) with $\psi = v$.

d) $L_v \ll L \ll L_h$: the exponents are given by (4), (6) with $\psi = h$, and (5) with $\psi = v$.

The exponents obtained in case c) and d) are novel, resulting from the coupling between the two fields. Case c) is particularly interesting, since for $d > 1$ it predicts negative roughness exponent for v, which corresponds to a smooth morphology.

The obtained exponents depend on the existence of fixed points with nonzero coupling terms, γ and β. To search for fixed points, we integrated the DRG flow equations in the limits corresponding to a)-d). For a) we find that K_h and K_v renormalize to zero and the flow is singular. However, the singularity is not present if we choose a nonzero D_h^{nc}, when a fixed point exists. For b) and c) we find that fixed points exist, but in c) β renormalizes to zero. This suggest that for c) we have an independently fluctuating h field, that is a source of correlated noise for v through the nonzero γ coupling term. For d) all parameters increase without limit, allowing for the possibility of a nonperturbative fixed point. The validity of (1) in this regime might be questioned due to the $\chi_v = 1$ exponent, which allows for higher-order terms to become relevant.

As an application of the above results we consider homoepitaxial MBE growth in the presence of a surfactant layer. In plain MBE (without surfactant) atoms arrive on the surface, and relax by surface diffusion. Consistent with MBE conditions, desorption can be neglected. The relaxation process is then strictly conservative, originating from surface diffusion, and in the linear approximation the height of the interface, $h(\mathbf{x}, t)$, follows the linear equation (2). Since the interface is growing, *i.e.* there is a $h \to -h$ broken symmetry, nonlinear terms like $\nabla^2(\nabla h)^2$ might influence the scaling behavior. The noise term η_h has two components: a nonconservative one, describing the randomness of the deposition process, and a conservative one, describing the thermally activated random diffusion.

Under standard experimental conditions the surfactant is deposited on top of the interface at the beginning of the experiment. During growth the surfactant segregates on top of the growing interface [6]. In the linear approximation its thickness, v, is described by the linear diffusion equation (2), but with conservative noise *only*, since there is no surfactant deposition or evaporation. During growth, adatoms arrive on the surface and are deposited on top of the surfactant layer. At some point the surfactant atoms exchange positions with the newly deposited adatoms. We call subsurface diffusion the motion of the adatoms immediately below the surfactant after they have exchanged positions. Since the surfactant segregates anyhow, the role of subsurface diffusion is unknown, while its absence was assumed in order to rationalize experimental results [12]. We analyze here the case when subsurface diffusion is *not* neglected and explore the consequences from a theoretical point of view.

In order to incorporate the effect of the surfactant, and the influence of the surface mor-

phology of h on the surfactant diffusion, one has to include coupling terms into the growth equation. Symmetry principles and the conservative nature of the process leave $\gamma\nabla^2[(\nabla h)(\nabla v)]$ as a possible term to be included in the equation of motion of the surfactant. Similarly, the linear equation for h has to be augmented by $\beta\nabla^2(\nabla v)^2$ and $\lambda\nabla^2(\nabla h)^2$, as the relevant coupling and nonlinear terms, respectively. One thus arrives at the set of coupled equations (1). The difference between the full eq. (1) and the surfactant-mediated growth process comes in the noise: the equation of motion for the surfactant thickness (1b) does *not include the nonconservative noise* (since surfactant deposition or evaporation is absent). The growth equation for h includes both the conservative and nonconservative noise components. Thus eq. (1) with $D_v^c = 0$ is appropriate for surfactant-mediated growth in the regime where surface diffusion underneath the surfactant cannot be neglected.

In what follows we describe the possible scaling regimes as predicted by (1) for this particular system, linking the terms in the growth equations to experimentally measurable quantities. Since there is no nonconservative noise for the surfactant, there is only one length scale, L_h, determining the scaling behavior. The correlator D_h^c is related to the diffusion probability, *i.e.* $D_h^c \sim \exp[-F_d/kT]$, where F_d is the activation free energy for diffusion. The correlator of the nonconservative noise, D_h^{nc}, is proportional to the flux, $\Im$, thus we have $L_h \sim [\Im/\exp[-F_d/k_B T]]^{1/2}$.

For $L \ll L_h$ we are in regime a) (see table I). For $d = 2$, $z = 4$ and $\chi_v = \chi_h = 0$. Thus, the dynamics of the system is governed by the fluctuations in the interface height, h, since the exponents coincide with the exponents of (1a) with $\beta = 0$ (*i.e.* with no coupling). For short-length scales we have slow (logarithmic) roughening for the interface and the surfactant.

For $L \gg L_h$, deposition determines the scaling of h, and the model belongs to case c). For $d = 2$ we have $z = 10/3$, $\chi_h = 2/3$, and $\chi_v = -1/3$. These exponents correspond to an algebraically *roughening* interface h, covered by a *smooth* surfactant layer. Indeed, physically it is expected that the roughening of the surfactant layer cannot continue indefinitely, *i.e.* one should see asymptotically a uniform surfactant coverage, correctly predicted by the negative roughness exponent χ_v. The mechanism leading to this exponent is also intriguing: as the integration of the flow equations shows, the surface decouples from the surfactant, and fluctuates independently. However, as the surfactant is situated on the surface, it cannot decouple from h, and its scaling is influenced by h through the nonzero coupling term γ.

The most interesting prediction of our analysis is that asymptotically the interface fluctuates independently and is rough. The desired effect of the surfactant is to promote layer-by-layer growth, *i.e.* to help the interface grow smoothly. One way to achieve this is to severely curtail the diffusion length of the embedded atoms. Indeed, the growth equation for h, derived assuming reduced surface diffusion, predicts the presence of a smooth phase [7]. As we emphasized above, in this paper we focused on the case when there is atomic diffusion underneath the surfactant layer. For this case the growth equation (1) predicts that for the interface h a smooth phase does *not* exist, *i.e. subsurface diffusion* results in *roughening* of the growing interface. At the same time this equation predicts a uniform surfactant coverage, consistent with experimental observations [6].

In (1) we did not consider the terms $\nabla^2 h$ (in (1a)) and $\nabla^2 v$ (in (1b)). These terms can be generated by a Schwoebel barrier, which is present in certain MBE systems [13]. One can check that the scaling relations (4)-(6), and the exponents of table I do not change if we replace the $K_h\nabla^4 h$ and $K_v\nabla^4 v$ terms in (1) with $\nu_h\nabla^2 h$ and $\nu_v\nabla^2 v$ with positive coefficients, respectively.

The RG calculation with the Laplacian terms and the integration of the resulting flow equations need to be repeated in order to determine the stability of the new exponents.

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