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Discontinuous Transition between Seaweed and Chaotic Growth Morphology

T. Ihle (*) and H. Müller-Krumbhaar

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

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Abstract. — We study an interface moving in a diffusion-field in the high-speed region around unit-supercooling. A tunable relaxation term in the diffusion equation allows us to obtain non-singular stationary solutions for arbitrary growth rate. We find a change-over between KPZ and Kuramoto-Sivashinsky type behavior, and a discontinuous transition between the latter and compact seaweed growth morphology which develops logarithmic singularities in finite time in qualitative agreement with computer simulations of the fully time dependent moving boundary problem in two dimensions. A special multiple-scale analysis near absolute stability yields an equation for the interface profile which reduces to the Kuramoto-Sivashinsky equation and an equation known from directional solidification in some limit

Introduction

Pattern formation in nonequilibrium systems [1,2] typically occurs when two possible phases of a system are driven out of coexistence so that one of the phases grows at the expense of the other phase. Implicitly it is assumed here that the two phases do not mix perfectly but are separated by an interface which moves during the growth. Some of the basic questions one would like to answer in this context concern the kind of structures that can be formed by such an advancing interface and how the structures and the conditions under which they are formed can be characterized.

The growth of a crystal from the melt or from a solution is a typical example for such a pattern forming process. This type of phase change usually requires the transport of at least one conserved quantity, the solute material or the latent heat of solidification, which is transported *via* diffusion. This is the so-called *Stefan-problem* [3] or *moving boundary problem*.

It is known since about three decades [4] that a nucleus of the new phase growing at the expense of the unstable phase becomes unstable as its radius becomes bigger than a few times the critical radius. If the surface tension is anisotropic, for example due to crystalline anisotropy, it is generally believed that the nucleus finally deforms into a dendritic pattern like a snowflake [2,5]. The limit of vanishing anisotropy, however, is much less clear.

There has been a recent attempt to formulate a theory [6,7] for the fundamental morphologies and the most relevant parameters controlling their appearance.

(*) Author for correspondence (e-mail: t.ihle@kfa-juelich.de)

1. The Diffusion-Relaxation Model

We will use a modification of a standard model for solidification. The model describes diffusion of heat or of a chemical component in the bulk of a two-phase system such as a freezing solid in contact with its melt. The interface is assumed to be in local thermal equilibrium, the liquid far ahead of the solid-liquid interface is supercooled. The boundary condition at the advancing interface is influenced by the structure of the moving interface, which is also changing with time. This makes the problem highly nonlinear. Since the actual shape and position of the boundary is not fixed, a further condition is needed. This is the respective conservation law for heat or matter at the advancing interface: For a liquid-solid transition latent heat is released during freezing, which must be transported away into the supercooled liquid by a diffusion current. The gradient of the diffusion field at the interface accordingly is proportional to the local speed of advancement of the interface. We discuss here a modified version of the so-called one-sided diffusion model [2,14,17] where diffusion is only considered in the phase ahead of the advancing interface, in order to keep the equations as simple as possible.

$$\frac{\partial}{\partial t} u(x, z, t) = D (\nabla^2 u(x, z, t) - \lambda u) \quad (1)$$

$$u_s^0 = \Delta - d_0 K - \beta v_n \quad (2)$$

$$v_n = -D \hat{n} \cdot \nabla u_s \quad (3)$$

(1) is the fully time-dependent diffusion equation (*i.e.* without *quasistationary* approximation [17]), (2) is the boundary condition for the diffusion field u at the interface, at infinity one has $u = 0$. (3) is the conservation law for the solute or impurity at the interface, v_n is the normal velocity of the moving boundary and here the special case of a constant jump of unit height in the concentration u across the interface is assumed. $u(x, z, t)$ is the normalized diffusion field [2,5], $\Delta = 0 \dots 1$ is the normalized dimensionless supercooling, D the diffusion coefficient, d_0 the capillary length. The specific modification introduced here is the parameter λ as a relaxation coefficient which is zero in the standard model [2]. Furthermore β is the kinetic coefficient, and K the curvature of the interface. Furthermore, the Mullins-Sekerka length $\rho_{MS} = 2\pi\sqrt{d_0\ell_D}$ is important to characterize interface instabilities, with $\ell_D = 2D/v$ being the diffusion length.

Without the relaxation term in the diffusion equation a bounded stationary pattern is only possible at unit undercooling $\Delta = 1$ because of energy conservation. At smaller undercooling a seaweed-pattern will form with infinitely deep grooves filled with liquid in the stationary pattern.

It would be convenient for an analytical investigation of the doublon structure to represent the solid-liquid interface by a single-valued function and to expand around a stationary flat interface.

In order to make such an expansion around a flat interface, we have to modify the conservation of energy or mass, respectively. This is the reason for introducing a small relaxation term $\lambda > 0$ into the diffusion equation (1) which forms together with the boundary conditions (2,3) the full diffusion-relaxation model. Physically this term describes a global loss of heat or mass due to a non-ideal isolation of the system to the outside [22]. Practically this occurs under growth conditions where the system is almost two-dimensional so that the exchange with the environment takes place in the third dimension. If the undercooling approaches one, this correction becomes infinitesimal.

From (1-3) we obtain a condition for the velocity of a stationary flat interface moving at constant rate:

$$\lambda l^2 = \frac{4}{b^2} (1 - b) \quad b = \Delta - \beta v \tag{4}$$

In the limit of vanishing kinetic coefficient β the equation simplifies to

$$v = \frac{D \sqrt{\lambda} \Delta}{\sqrt{1 - \Delta}} \tag{5}$$

Otherwise we obtain a third order equation for the velocity which has for all undercoolings $\Delta > 0$ a positive and bounded solution. At $\Delta = 1$ and for $\lambda \beta^2 D^2 \ll 1$ one obtains an approximate solution:

$$v \approx D^{2/3} \left(\frac{\lambda}{\beta} \right)^{1/3} \quad (\Delta = 1). \tag{6}$$

This means that an arbitrary value for the velocity of the planar front can be adjusted by means of infinitesimal small relaxation and kinetic coefficients λ and β , respectively. The kinetic coefficient cures the divergence of the velocity at $\Delta = 1$ as it is well-known. The combination with a nonzero value of λ allows for a smooth crossover from the already known results [25] in the kinetic regime with $\Delta > 1$ to the interesting regime with $\Delta < 1$.

At first we investigate the linear stability of a flat interface starting from the stationarity condition (4) by introducing a perturbation $\zeta(x, t) = \zeta_{q, \omega_q} \exp(\omega_q t + i q x)$ of the interface in z -direction (normal to the interface) and a corresponding perturbation of the diffusion field.

For simplicity we use in all following equations dimensionless quantities like the relaxation coefficient $\tilde{\lambda}$, capillary length d , relaxation rate ω , wave number k , and kinetic coefficient $\tilde{\beta}$ obtained by normalization with the diffusion length $l = 2D/v$ for length scales and by the diffusion coefficient D and diffusion length for time scales: $\tilde{\lambda} = \lambda l^2$, $d = d_0/l$, $\omega = l^2 \omega_q / D$, $k = ql$ and $\tilde{\beta} = D\beta/l$.

This gives the following dispersion relation for the growth rate ω of a small amplitude perturbation as function of its wave number k :

$$2a + dk^2 + (1 + \tilde{\beta})\omega = \sqrt{a^2 + k^2 + \omega} (2 - dk^2 - \tilde{\beta}\omega) \tag{7}$$

with the parameter $a = \sqrt{1 + \tilde{\lambda}} = 2/(\Delta - \beta v) - 1$.

In this normalization the dimensionless diffusion-length now has the value *one* and the dimensionless speed of the planar front has the value *two*.

First we restrict our consideration to the case of zero kinetic coefficient $\beta = 0$. Now the undercooling Δ must be smaller than 1. At unit undercooling the parameter a defined just above also is equal to one.

As long as $1 - \Delta$ is kept fixed we can expand ω in powers of k^2

$$\omega = c_1 k^2 + c_2 k^4 + O(k^6). \tag{8}$$

and then one obtains from (7) the coefficients

$$c_1 = \frac{1 - d(a + a^2)}{a - 1} = \frac{\epsilon \Delta}{2(1 - \Delta)} \tag{9}$$

$$\begin{aligned} c_2 &= \frac{\Delta - 2d}{32(\Delta - 1)^3} \{8d - 14d\Delta + \Delta^2(1 + 4d)\} \\ &= -\frac{1}{\Delta - 1} \left\{ \frac{\Delta^3(\Delta - 3)}{8(\Delta - 2)^2} + O\left(\frac{\epsilon}{(1 - \Delta)}\right) \right\} \end{aligned} \tag{10}$$

(We show here for simplicity only the special case of $\beta = 0$, while the coefficients have been evaluated for arbitrary β . The expansion (8) into powers of k^2 converges safely only for $k^2\epsilon/(1 - \Delta)^2 < 1$. The derivation of a local equation — as done in the following — requires $\epsilon < 1 - \Delta$ for the case of $\beta = 0$).

It follows from equation (7) that at $1 - d(a + a^2) \leq 0$ the interface is absolutely stable [25] which means that for arbitrary wavenumber k the real part of ω is not greater than zero. Therefore we have defined here the small expansion parameter ϵ so that $\epsilon = 0$ marks the limit of absolute stability:

$$\epsilon = 1 - d(a + a^2), \quad \text{with} \quad a = \sqrt{1 + \tilde{\lambda}} = \frac{2}{\Delta - \beta v} - 1. \tag{11}$$

In other words, ϵ measures the distance from the stability threshold. This parameter therefore discriminates between various growth modes. Combining the stationarity condition (4) with equation (11) eliminates the diffusion length and allows to express ϵ by means of the normalized relaxation strength $d_0 \sqrt{\tilde{\lambda}}$ and the undercooling:

$$\epsilon = 1 - d_0 \sqrt{\tilde{\lambda}} \frac{2 - b}{b\sqrt{1 - b}}, \quad b = \Delta - \beta v \tag{12}$$

Figure 2 shows the absolute stability curve $\epsilon = 0$ in the space $d_0 \sqrt{\tilde{\lambda}}$ versus Δ . (Further details of Fig. 2 will be given later).

For k between 0 and k_s the growth rate ω is positive with $\omega \sim \epsilon^2$ and $k_s \sim \sqrt{\epsilon}$. Near absolute stability $\epsilon = 0$, it is possible to derive a local differential equation for the height profile by a singular expansion method first used in the context of crystal growth by Sivashinsky [23] and others [22, 24, 25]. This procedure will be performed below for the present variant of the model system.

The expansion (8) is only valid when $\epsilon \ll 1 - \Delta$, because the higher the power in k the higher powers of $\epsilon/(1 - \Delta)$ appear in the coefficients. A violation of this condition would make the series divergent even in the relevant unstable k -band $0 \leq k \leq k_s$.

In the following considerations we will now investigate the role of the kinetic coefficient $\tilde{\beta}$ together with the relaxation parameter $\tilde{\lambda}$. The equations (1-3) are conveniently transformed into a frame moving along with the flat interface:

$$u_t = \nabla^2 u + 2u_z - \tilde{\lambda} u \tag{13}$$

$$u|_{\text{Inter}} = \Delta + d \frac{h_{xx}}{(1 + h_x^2)^{3/2}} - \tilde{\beta} \frac{h_t + 2}{(1 + h_x^2)^{1/2}} \tag{14}$$

$$2 + h_t = -(u_z - h_x u_x)|_{\text{Inter}}. \tag{15}$$

$h(x, t)$ describes the position of the interface in the moving frame.

2. Multiple Scale Analysis

A multiple scale analysis is being performed by appropriately changing time and length scales for the slow variables. This scaling of time and length parallel to the interface follows from the dispersion relation with small parameter ϵ according to

$$\begin{aligned} X &= \epsilon^{1/2} x \\ Z &= z \\ T &= \epsilon^2 t. \end{aligned} \tag{16}$$

Since the height profile is a straight line at $\epsilon = 0$ and the diffusion profile should have no X dependence the height function $h(X, T)$ and the diffusion field $u(X, Z, T)$ are expanded in the

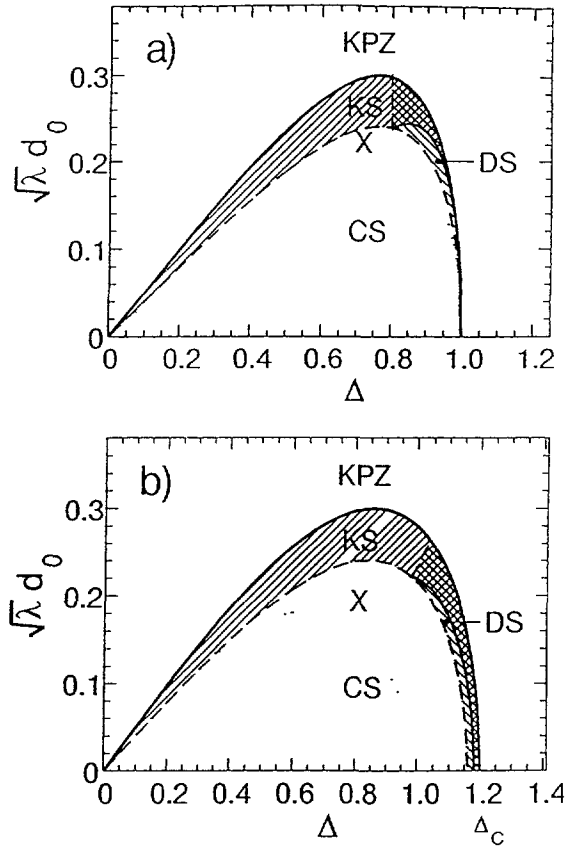


Fig. 2. — Kinetic phase-diagram in the space of supercooling Δ and normalized strength of the relaxation parameter $d_0\sqrt{\lambda}$. a): The kinetic coefficient β is zero, which is a singular case. b): Nonzero kinetic coefficient $D\beta/d_0 = 0.2$ which defines $\Delta_c = 1 + D\beta/d_0$. The topmost full line, which gives a lower bound to the region marked KPZ, is the limit $\epsilon = 0$ of absolute stability. Above that line a flat interface is absolutely stable. Below that line ϵ becomes positive and a flat interface becomes unstable against spatial modulations. The dynamics in the stable region is described by the KPZ-equation (KPZ), equation (24). The KS-equation (KS), equations (18, 50), is only valid in a small region below the curve $\epsilon = 0$ of absolute stability, which is bounded by $\epsilon \ll 1$ and $\epsilon \ll \Delta_c - \Delta$. A precise value for this bound is not known, but schematically we give here $\epsilon < 0.2$ (dashed) and $\epsilon < \Delta_c - \Delta$ (full). At sufficiently high supercoolings there exists another local equation (DS), equation (46), which is valid for arbitrary values of $\epsilon/(\Delta_c - \Delta)$ (but still bounded by some ϵ and small $\Delta_c - \Delta$). The ranges of validity of the KS- and the DS-equations overlap in a region near $\Delta = 1$. For smaller values of the relaxation parameter one must expect a transition region (X), which cannot be properly described by a strictly local equation. At even lower values of λ one reaches the “compact seaweed”-region (CS) consisting finally of stable doublons.

following way:

$$\begin{aligned}
 u(X, Z, T) &= u_0(Z) + \epsilon u_1(X, Z, T) + \epsilon^2 u_2(X, Z, T) + \dots & (17) \\
 h(x, t) &= \epsilon H(X, T) \\
 H(X, T) &= H_0(X, T) + \epsilon H_1(X, T) + \epsilon^2 H_2(X, T) + \dots
 \end{aligned}$$

Now the problem (13-15) can be solved order by order in ϵ (details are for instance in [25]). Keeping terms up to third order one obtains a closure condition which finally yields the Kuramoto-Sivashinsky (KS) equation [26-28]:

$$H_{0T} = -a_1 H_{0XX} - a_2 H_{0XXX} + H_{0X}^2 \quad (18)$$

with

$$a_1 = \frac{b^2}{2\{b(1-b) + \tilde{\beta}(2-b)\}} \quad (19)$$

$$a_2 = \frac{b^4(3-b)}{8(2-b)^2\{b(1-b) + \tilde{\beta}(2-b)\}} \quad (20)$$

The derivation of (18) in principle is an asymptotic gradient expansion of H_0 , the linear part being in agreement with the linear spectrum (7). In the limit of a vanishing relaxation coefficient λ the known equation for the kinetic regime at $\Delta > 1$ [22, 25] is recovered with coefficients:

$$a_1 = \frac{1}{2\tilde{\beta}} \quad (21)$$

$$a_2 = \frac{1}{4\tilde{\beta}}, \quad (22)$$

The nonlinearity H_X^2 is of purely geometric origin, it comes from the expansion of the square root in the relation of the normal growth velocity depending on the evolution of the height profile:

$$v_n = \frac{2 + h_t}{\sqrt{1 + h_x^2}} = 2 + F. \quad (23)$$

with v_n being the dimensionless normal velocity and F a function of derivatives of the height profile $h(x, t)$. The right hand side of this equation can be obtained from the observation that for a completely flat interface all derivatives of $h(x, t)$ must vanish.

Therefore the KS-equation (18) can be found immediately by combining the dispersion relation (8-10) with this relation which gives the exact value of one for the coefficient of the nonlinearity h_x^2 .

Since this consideration is independent of the sign of the threshold parameter ϵ , equation (11), it is also valid in the stable region $\epsilon < 0$ and one obtains in this case a Kardar-Parisi-Zhang (KPZ) equation [29] (here without the noise term it is actually Burgers equation [30, 31]):

$$h_t = -\frac{\epsilon\Delta}{2(1-\Delta)} h_{xx} + h_x^2 + O(h_{xxx}) \quad \epsilon < 0. \quad (24)$$

This equation together with the KS-equation (18) describes the neighborhood of the limit of absolute stability near $\epsilon = 0$ (11) which does now exist for arbitrary values of the dimensionless supercooling Δ due to the nonzero value of the relaxation constant λ .

3. Higher Order Expansion

It is instructive to perform the singular expansion (17) in fourth order of ϵ . The solvability condition obtained by the same way as in the third order consists of an equation for the function

H_1 which is coupled to the already known function H_0 :

$$H_{1T} = C_1 H_{1XX} + C_2 H_{1XXXX} + C_3 H_{0XXXX} + C_4 H_{0XXXXX} + C_5 H_{0XXT} + C_6 H_{0X} H_{0XXX} + C_7 H_{0XX}^2 + 2H_{0X} H_{1X} . \tag{25}$$

Twicewise differentiating of the KS-equation (18) gives an expression for $H_{0_{XXT}}$ in terms of pure spatial derivatives of H_0 . Inserting this expression into (25) cancels the term $H_{0X} H_{0_{XXX}}$ as expected by symmetry reasons and changes the coefficients C_3, C_4, C_7 . Equation (25) becomes then:

$$H_{1T} = -G_1 H_{1XX} - G_2 H_{1XXXX} - G_3 H_{0XXXX} - G_4 H_{0XXXXX} - G_5 H_{0XX}^2 + 2H_{0X} H_{1X} \tag{26}$$

Remembering that the searched solution $H(X, T)$ is a sum of H_0 and ϵH_1 it becomes clear that the coupling term $2H_{0X} H_{1X}$ expresses simply the existence of the nonlinearity H_x^2 in the equation for the summed up profile H . Therefore we can combine the two expressions (18,26) to a modified KS-equation in terms of the old variables $x, t, h(x, t)$ as:

$$h_t = -\epsilon G_1 h_{xx} - (G_2 + \epsilon G_3) h_{xxxx} - G_4 h_{xxxxx} - G_5 h_{xx}^2 + h_x^2 . \tag{27}$$

with the following coefficients:

$$\begin{aligned} G_1 &= \frac{b^2}{R} \\ G_2 &= \frac{b^4(3-b)}{4(b-2)^2 R} \\ G_3 &= \frac{b^5(-3b^2+10b-4)}{4(b-2)^2 R^2} \\ G_4 &= \frac{b^6}{16(b-2)^3 R^2} \left\{ b(b+1)(b-4) - 2\tilde{\beta}(b^2-6b+10) \right\} \\ G_5 &= \frac{b^3(b-1)(b-3)}{2(b-2)^2 R} , \end{aligned}$$

with $R = 2b(1-b) + 2\tilde{\beta}(2-b)$ and $b = \Delta - \beta v$.

It contains in addition to new linear terms, which can be found more easily by linear stability analysis, a new nonlinearity h_{xx}^2 . This nonlinearity has the “wrong” sign, *i.e.* it limits the validity of the KS-equation very close to the absolute stability as will be discussed further below.

4. Expansion near Undercooling $\Delta = 1$

As already mentioned in the discussion of the dispersion relation after equation (11) it is seen from the coefficients of the KS-equation that its validity is limited to the case $\epsilon \ll 1 - \Delta$ or $\epsilon \ll b(1-b) + \tilde{\beta}(2-b)$ with $b = \Delta - \beta v$, respectively. The dispersion relation (7) agrees in the limit $\tilde{\beta} = 0$ and $\Delta = 1$ with the dispersion relation of directional solidification [32, 33] at the high velocity threshold with vanishing temperature gradient. This suggests an alternative *analysis of the dispersion relation (7) but now for parameters in the range $1 - \Delta = O(\epsilon)$* . For simplicity we restricted the following considerations to $\tilde{\beta} = 0$ and hence $\Delta < 1$.

As expected we find that the width of the unstable band of wavelengths scales as $q_s \sim \sqrt{\epsilon}$, but the rate scales now as $\omega \sim \epsilon$. Therefore we choose the following rescaling [32]:

$$\begin{aligned} X &= \epsilon^{1/2} x \\ Z &= z \\ T &= \epsilon t \\ H(X, T) &= h(x, t) \\ \alpha &= (1 - \Delta)/\epsilon \end{aligned} \tag{28}$$

and repeat the singular expansion similar as in [33–35] while the new parameter α characterizes the scaling regime.

First we have to expand the parameter λ in powers of ϵ by means of the stationarity condition (11) $1 + \tilde{\lambda} = (2/\Delta - 1)^2$ and the definition of α :

$$\tilde{\lambda} = 4\alpha\epsilon + 8(\alpha\epsilon)^2 + O(\epsilon^3) \tag{29}$$

The capillary length d has also to be expressed in powers of ϵ :

$$\begin{aligned} d &= \frac{1 - \epsilon}{a + a^2} \\ &= \frac{1}{2} - \epsilon \frac{3\alpha + 1}{2} + \epsilon^2 \left(2\alpha^2 + \frac{3}{2}\alpha \right) + O(\epsilon^3) \end{aligned} \tag{30}$$

with $a = 2/\Delta - 1$. Written in terms of the rescaled variables and neglecting terms of order ϵ^3 the model equations (13-15) become: ($\tilde{\beta} = 0$)

$$u_{ZZ} + 2u_Z = 4\alpha\epsilon u + 8(\alpha\epsilon)^2 u + \epsilon u_T - \epsilon u_{XX} \tag{31}$$

$$u|_{\text{Inter}} = 1 - \alpha\epsilon + \left(\frac{1}{2} - \epsilon \frac{3\alpha + 1}{2} \right) \frac{\epsilon H_{XX}}{(1 + \epsilon H_X^2)^{3/2}} \tag{32}$$

$$2 + \epsilon H_T = -(u_Z - \epsilon H_X u_X)|_{\text{Inter}} . \tag{33}$$

The two boundary conditions (32,33) are defined at $Z = H(X, T)$, which is of order one. Therefore we expand them at $Z = H_0(X, T)$ and not at $Z = 0$ as in the derivation of the KS-equation.

At each power in ϵ one obtains a set of three equations (Equation of Motion (EoM), Gibbs-Thomson relation (GT) and Continuity relation (Cont)) :

Order (ϵ^0):

$$\text{EoM} \quad u_{0ZZ} + 2u_{0Z} = 0 \tag{34}$$

$$\text{GT} \quad u_0|_{Z=H_0} = 1 \tag{35}$$

$$\text{Cont} \quad u_{0Z}|_{Z=H_0} = -2 \tag{36}$$

The solution is easily found to be

$$u_0 = \exp(-2Z + 2H_0) \tag{37}$$

Order (ϵ^1):

$$\text{EoM} \quad u_{1ZZ} + 2u_{1Z} = u_{0T} - u_{0XX} + 4\alpha u_0 \tag{38}$$

$$\text{GT} \quad u_1 + u_{0Z} H_1|_{Z=H_0} = -\alpha + \frac{H_{0XX}}{2} \tag{39}$$

$$\text{Cont} \quad u_{1Z} + u_{0ZZ} H_1|_{Z=H_0} = H_{0X} u_{0X} - H_{0T} \tag{40}$$

The solution is

$$u_1 = \{H_0 H_T - H_0 H_{0XX} + 2\alpha H_0 - 2H_0 H_{0X}^2 + 2H_1 + H_{0XX}/2 - \alpha + Z(-H_{0T} + H_{0XX} - 2\alpha + 2H_{0X}^2)\} \exp(-2Z + 2H_0) \tag{41}$$

Order (ϵ^2):

$$\text{EoM} \quad u_{2ZZ} + 2u_{2Z} = u_{1T} - u_{1XX} + 4\alpha u_1 + 8\alpha^2 u_0 \tag{42}$$

$$\begin{aligned} \text{GT} \quad & u_2 + u_{1Z} H_1 + u_{0Z} H_2 + \frac{1}{2} u_{0ZZ} H_1^2 \Big|_{Z=H_0} \\ & = \frac{1}{2} H_{1XX} - \frac{3\alpha + 1}{2} H_{0XX} - \frac{3}{4} H_{0XX} H_{0X}^2 \end{aligned} \tag{43}$$

$$\begin{aligned} \text{Cont} \quad & u_{2Z} + u_{1ZZ} H_1 + u_{0ZZ} H_2 + \frac{1}{2} u_{0ZZZ} H_1^2 \Big|_{Z=H_0} \\ & = -H_{1T} + H_{0X} u_{1X} + H_{1X} u_{0X} + H_1 H_{0X} u_{0XZ} \Big|_{Z=H_0} \end{aligned} \tag{44}$$

In the following we will need only the inhomogeneous parts B and D of the solution u_2 :

$$u_2 = (A + BZ + DZ^2) \exp(-2Z + 2H_0) \tag{45}$$

which can be found by a tedious but straightforward calculation.

Comparison of the left hand sides of the boundary conditions, for instance (43,44), shows that they only differ in one additional Z -derivative. Since all solutions u_i necessarily contain the exponential factor $\exp(-2Z)$ the addition of the Gibbs-Thomson equation (multiplied by a factor of 2) to the continuity equation kills all contributions arising from the homogeneous parts of the solutions u_i . In the zeroth and first order of ϵ this operation gives only zero.

In the second order a solvability condition for the profile H_0 in the form of a local evolution equation is obtained:

$$\begin{aligned} H_{0TT} - 3H_{0XXT} + 4H_{0XX} + 2H_{0XXX} + 8\alpha(H_{0T} - H_{0X}^2) \\ + 3(H_{0X}^2)_{XX} + 2(H_{0X}^3)_X - 2(H_{0X}^2)_T - 2H_{0T} H_{0XX} = 0 \end{aligned} \tag{46}$$

It contains only derivatives of H_0 because of the translational invariance in Z direction.

As expected, in the limit of $\Delta = 1$, *i.e.* $\alpha = 0$, the equation agrees with the equation (4.1) in [32] for directional solidification at high speed but now in the limit of vanishing temperature gradient.

In the other limit of $\alpha = (1 - \Delta)/\epsilon \gg 1$ the KS-equation (18) up to terms of order $(1 - \Delta)$ is recovered. See Figure 2 for a comparison of the range of validity of the different effective equations. The limit $\alpha \rightarrow 0$ essentially means that the relaxation term λ goes to zero. When α goes to infinity the deviation from absolute stability $\epsilon = 0$ disappears.

5. Stationary Solutions

We will now discuss consequences of equation (46). Its stationary version reads:

$$\frac{d}{dX} \{y_{XX} + (2 - v)y + y^3 + 3yy_X\} + 4\alpha(v - y^2) = 0, \quad y = H_X \tag{47}$$

where “stationary” means that the pattern is time independent in a frame which moves with the constant velocity $2 + v$ compared to the planar front with dimensionless velocity 2.

By means of the transformation $z(X) = \exp\{H(X)\}$ the nonlinear equation (47) which is actually a modified Duffing-oscillator can be reduced to a linear equation in the limit $\alpha = 0$:

$$\frac{d}{dX} \left\{ \frac{z_{XXXX} + (2-v)z_X}{z} \right\} + 4\alpha \left\{ v - \left(\frac{z_X}{z} \right)^2 \right\} = 0. \quad (48)$$

An exact periodic solution for $\alpha = 0$ can be easily given:

$$H(X) = h_0 + \ln |A_1 \cos \sqrt{2-v}X + A_2 \sin \sqrt{2-v}X + 1|. \quad (49)$$

For certain parameters A_1 and A_2 there is the possibility of infinitely deep gaps in the height profile. Asymptotically these gaps behave like $\ln(X)$ or $\ln(X^2)$ at small X .

The full dynamical equation (46) was integrated by means of a fifth-order Gear's backward difference method [36] with a finite-difference evaluation of the Jacobian using the routine DIVPAG from the IMSL-library. It turned out that a spectral method for evaluating the spatial derivatives showed numerical instabilities for small $\alpha \approx 0.1$. Therefore the spatial derivatives were evaluated by traditional finite differences.

The KS-equation in one dimension has two stable bands of periodic solutions [25]. In analogy we here (46) also look for periodic solutions, expecting that they will develop deep grooves which ultimately become infinitely deep. In order to separate the contributions from various wavenumbers we used periodic boundary conditions with a small periodicity so that only one mode was linearly unstable on the flat interface. Starting from the Kuramoto-Sivashinsky limit of high α a stable periodic solution is found down to a critical value of $\alpha_{\text{crit}} \approx 0.01 \dots 0.1$, its precise value depending on the imposed periodicity length. Since these amplitude equations (27,46) usually originate from asymptotic expansions it is not *a priori* clear, how many terms should be taken into account for a best approximation of the original problem. Accordingly the precise value of α_{crit} also depends on the number of terms included in the expansion.

At smaller α infinitely deep grooves are forming. It is shown in Figure 3 that after an initial variation the pattern settles into a plateau-state with very small but still growing amplitude. After some time suddenly a singularity develops. The time t_D before this happens scales with the parameter α (28) as $t_D \sim 1/\sqrt{\alpha_{\text{crit}} - \alpha}$ for small deviations of α from α_{crit} . The nature of the finally reached singularity $\ln(X)$ or $\ln(X^2)$ is not changed by $\alpha \neq 0$ as seen in equation (46), because $H_X^2 \ll H_{XX}^2$, $X \rightarrow 0$, and $H_T = O(1)$. The singular structure $\sim \ln(X)$ of the local equation (46) results simply from the gradient expansion (after Eq. (28)). That means there is always more than one term containing the highest number of X-derivatives which can only be balanced by $H \sim \ln(X)$ near the singularity. Of course at the singularity the gradient expansion breaks down since higher derivatives cannot be neglected. Hence the precise structure of the forming gaps in the real system cannot be obtained from the local expansion. But from the theory of channel growth [15] we know that there is a logarithmic behavior in such gaps, which agrees here by accident. More details will be discussed further below.

If one chooses an initial condition with an amplitude bigger than some critical value the singularity forms even if α is larger than the critical value α_c . The critical amplitude above which a perturbation will grow without bound must be the larger with increasing deviation of α from α_c .

The same effect has been observed in the dynamical integration of the rescaled version of the KS-equation (27):

$$H_T = -H_{XX} - H_{XXXX} + \frac{1}{2}H_X^2 - \epsilon H_{XX}^2 + O(H_{XXXXXX}), \quad (50)$$

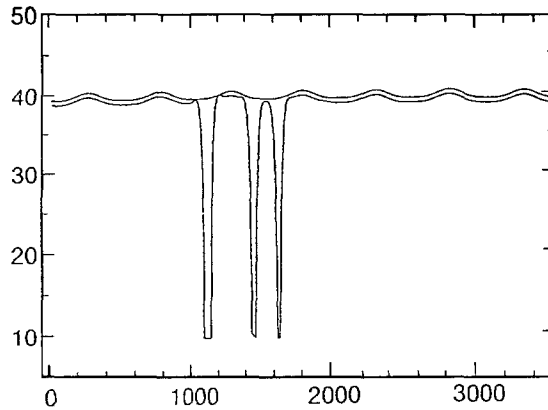


Fig. 3. — A simulation of the model equations (1-3) with periodic boundary conditions (for details see [18]) quite close to the absolute stability limit. Starting from a small sinusoidal perturbation the pattern saturates initially to a bounded state with small amplitude (upper curve). Note that this state already differs significantly from a state described by the KS equation, since here the curvature at the tips of the pattern is stronger than at the grooves. At a later time (lower curve) there is a very fast jumplike formation of deep holes in a few of these grooves. Parameters: $\Delta = 0.7$, $d_0 = 6$, $\epsilon = 0.0845$, $\beta = 0$, $D = 1$. All lengths are given in internal units δx of the spacing of the diffusional grid.

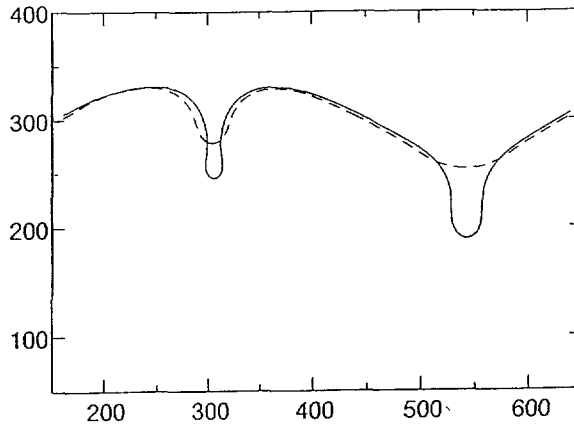


Fig. 4. — The formation of a doublon at moderate relaxation. The initial condition was a doublon with a small groove (dashed curve) which develops to a deep groove (depth $\approx 1.7l_D$, solid curve). Note, that the doublon structure is still clearly visible despite the perturbation by the relaxation term. Especially the distance between the two asymmetric parts remains a well defined quantity. Parameters: $\Delta = 0.7$, $d_0 = 3.85$, $\epsilon = 0.66$, $\beta = 0$, diffusion length $l_D = 2D/v = 49.4$, $D = 1$. As in the previous figure all lengths are given in units δx of the diffusional grid.

where higher order linear terms are neglected for simplicity. For a small aspect ratio $\Gamma = L/(2\sqrt{2}\pi) = 0.89$, L being the periodicity length, we find the usual stable stationary solutions which have sharper curvature at the grooves than at the tips due to the nonlinearity H_X^2 . If ϵ is increased there is a critical value ϵ_c above which singularities are formed.

The physical mechanism for the formation of this finite time singularity is quite simple. Suppose we have an initial condition $H = A(t=0) \cos(qX)$ with q in the unstable wave number band. Initially this mode grows exponentially in time due to the linear instability. Now the nonlinearity H_X^2 becomes active and increases the steepness of the profile, *i.e.* generates higher modes like $\cos(2qX)$, $\cos(3qX)$ and so on. This results in a sharper change of the profile in the grooves than at the tips and the stabilizing H_{XXXX} term compensates the destabilizing H_{XX} term in the grooves more than at the tips. This leads to a constant shift of the pattern, but the distance between tips and grooves saturates, *i.e.* the pattern becomes stationary in a moving frame. If the amplitude of this stationary pattern is of the order of $1/\epsilon$ the term H_{XXXX} is not able to balance the nonlinear contribution $-\epsilon H_{XX}^2$. That means that the depth of the grooves becomes larger and the nonlinearity becomes more dominant and so on. Finally we obtain from (50) for very deep grooves the approximative evolution equation for the depth $a_1(t)$ of the groove :

$$\dot{a}_1 \sim \epsilon q^4 a_1^2 \quad (51)$$

with the solution

$$a_1(t) = \frac{a_1(0)}{1 - \epsilon q^4 a_1(0) t} \quad (52)$$

If we assume $a_1(0)$ of order $1/\epsilon$ and q of order one, the time difference between reaching the critical amplitude and the formation of an infinite groove is of order 1.

For a more quantitative description one may transform equation (50) into Fourier space assuming a symmetric pattern $H(X) \approx \sum_{j=1}^3 a_j(t) \cos(jqX)$ with amplitudes $a_j(t)$ and the basic wavenumber $q = 2\pi/L$. Since only one mode is linearly unstable it should be a good approximation to set all modes higher than three to zero. This simplifies the problem to three equations for the temporal evolution of the modes

$$\begin{aligned} \dot{a}_1 &= a_1 \omega_1 + a_1 a_2 P_0 + a_2 a_3 P_1 \\ \dot{a}_2 &= a_2 \omega_2 + a_1 a_3 P_2 - a_1^2 P_3 \\ \dot{a}_3 &= a_3 \omega_3 - a_1 a_2 P_4 \end{aligned} \quad (53)$$

with $q = 2\pi/L$, $\omega_j = j^2 q^2 (1 - j^2 q^2)$ and

$$\begin{aligned} P_0 &= q^2 (1 - 4\epsilon q^2) \\ P_1 &= 3q^2 (1 - 12\epsilon q^2) \\ P_2 &= \frac{3}{2} q^2 (1 - 6\epsilon q^2) \\ P_3 &= \frac{1}{4} q^2 (1 + 2\epsilon q^2) \\ P_4 &= q^2 (1 + 4\epsilon q^2) \end{aligned} \quad (54)$$

The time derivatives are set to zero and we obtain the three modes of the stationary solution:

$$\begin{aligned} a_1 &= \sqrt{\frac{a_2 \omega_2}{P_3 - a_2 P_2 P_4 / \omega_3}} \\ a_2 &= -\frac{P_0 \omega_3}{2P_1 P_4} \pm \sqrt{Q} \\ a_3 &= \frac{a_1 a_2 P_4}{\omega_3} \end{aligned} \quad (55)$$

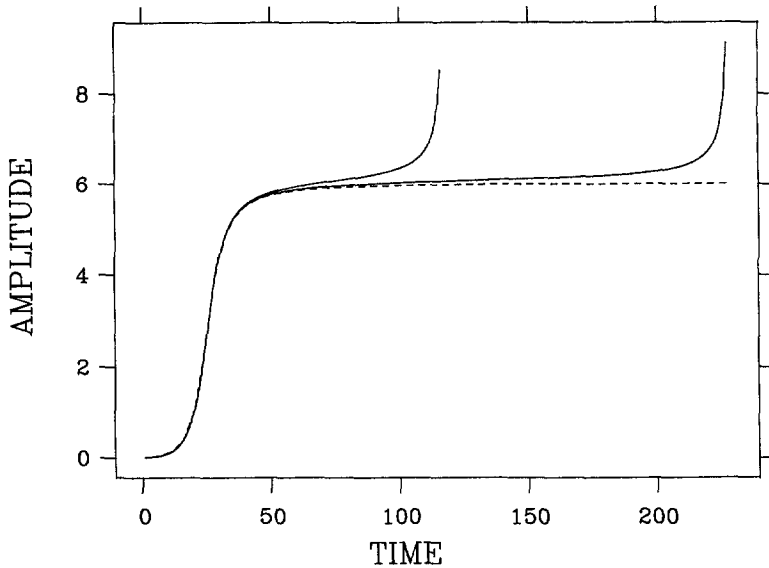


Fig. 5. — Temporal evolution of the basic mode a_1 after equation (53) for $\epsilon_1 = 0.244$ and $\epsilon_2 = 0.2438$ which are right above $\epsilon_{crit} = 0.24375$ and therefore show a finite time singularity. The length of the flat plateau scales as $(\epsilon - \epsilon_{crit})^{-1/2}$. The dashed line shows the temporal evolution at $\epsilon = 0.24372 < \epsilon_{crit}$ which has no divergence.

with

$$Q = \left(\frac{P_0 \omega_3}{2P_1 P_4} \right)^2 - \frac{\omega_1 \omega_3}{P_1 P_4} \tag{56}$$

That means there are two stationary solutions as long as the quantity Q in the square root is positive. An integration of the dynamical equation (50) showed, that only the solution with the bigger amplitude is stable. This was confirmed by finding the eigenvalues of the stability matrix obtained by linearization around the stationary state. If Q approaches zero the two states get closer to each other and one of their eigenvalues approaches zero. If $Q = 0$ there is only one marginal stable state, *i.e.* one eigenvalue is zero and the second time derivative of the three modes also becomes zero. We denote the amplitudes of this state as the critical amplitudes and the corresponding ϵ as ϵ_{crit} . If $Q < 0$ there is no nontrivial stationary state, but the second property of the critical state is maintained namely that the second time derivative is zero for a state which is very close to the critical one. If ϵ is a little above the critical value, the amplitude seems to reach a stationary state at time t_S , Figure 5. Then a flat plateau is forming characterized by a very small constant growth of the amplitude. At time t_D the amplitude goes rapidly to infinity. At time t_M in the middle of the plateau there is a turning point for the evolution of the amplitudes, *i.e.* $d^2/dt^2 a_i = 0$ (53). The amplitudes at this turning point are very close to the critical amplitudes corresponding to $\epsilon = \epsilon_{crit}$. Expanding in time around this point yields:

$$a_i = v_i + c_i \Delta t^2 + O(\Delta t^3) \tag{57}$$

The existence of such a turning point explains the constant slow growth of the amplitude of the pattern after the initial saturation. The initial saturation at t_S and the singularity at t_D correspond in this picture to the case that the term containing Δt^2 competes with the constant

velocity term, *i.e.* they are of the same order and Δt becomes

$$\Delta t = (t_D - t_S)/2 \approx \sqrt{\left| \frac{v_i}{c_i} \right|}. \quad (58)$$

Furthermore it can be shown that v_i scales like $v_i \sim \delta\epsilon = \epsilon - \epsilon_{\text{crit}}$, where ϵ_{crit} corresponds to the critical state with $Q = 0$, and c_i scales as $c_i \sim \delta\epsilon^2$. Hence the length of the plateau $t_D - t_S$ scales like $1/\sqrt{\delta\epsilon}$ which was confirmed by dynamical simulations of equation (50). At times larger than t_D the evolution of the amplitude is described by equations (51, 52). From the condition $Q = 0$ the critical ϵ_{crit} was obtained by

$$\epsilon_{\text{crit}} = \frac{1}{4q^2(1-3b)} \left(1 + b - 2\sqrt{b(1+b)} \right), \quad b = \frac{-12\omega_1}{\omega_3} \quad (59)$$

Note that this expression remains finite at $b = \frac{1}{3}$.

This gives $\epsilon_{\text{crit}} = 0.24375$ and $u_{ss,\text{crit}} = 2(a_{1,\text{crit}} + a_{3,\text{crit}}) = 13.0$, with $L = 7.8677$ which is very close to the values $\epsilon_{\text{crit}} = 0.22918$ and $u_{ss,\text{crit}} = 11.30$, obtained from the dynamical simulations of (50). The error becomes bigger if L is larger, because then the linear damping of the second and third mode is smaller. For instance at $L = 10.54$ equation (59) yields $\epsilon_{\text{crit}} = 0.37$, but the dynamical simulation gives $0.2955 < \epsilon_{\text{crit}} < 0.296$.

In conclusion the formation of singularities is due to the nonexistence of a curved stationary solution apart from a flat interface (at least in this approximation which neglects modes higher than three). The critical ϵ and the critical amplitude can be found from equation (59) with an error less than 25% in comparison with direct numerical simulation of equation (50).

6. Numerical Simulations and Conclusions

The numerical method to solve the *Stefan-Problem* (1-3) is the same as the one previously used for the standard growth model without relaxation [18]. There the method is described in detail and we shall only mention some basic features here. First the solid-liquid interface is handled explicitly, *i.e.* the interface is discretized and represented by a set of points. The two-dimensional diffusion field u is discretized too on a simple square grid.

After setting initial values for the interface position as well as for the diffusion field, a diffusion step by means of the discretized version of the diffusion equation (1) is performed

$$u_{i,j}^{n+1} = u_{i,j}^n + \frac{D \Delta t}{\Delta x^2} (u_{i+1,j}^n + u_{i-1,j}^n + u_{i,j+1}^n + u_{i,j-1}^n - 4u_{i,j}^n) - D \Delta t \lambda u_{i,j}^n. \quad (60)$$

with a small time step $\Delta t < (\Delta x)^2/(4D)$, where Δx is the lattice unit of the diffusional grid. Then the gradient of the new diffusion field is determined at the interface and each point of the discretized interface is advanced by the distance $v_n \Delta t$ according to equation (3). After that the boundary condition (2) has to be incorporated into the diffusion field. The whole procedure is now repeated beginning with the diffusion step and so on. The moving interface was always kept approximately at the center of the lattice, which allows growth over any distance. The distance between the moving front and the end of the periodic channel far inside the liquid was at least five diffusion lengths, in order to keep the growth unaffected by boundary effects.

Since anisotropy is an important parameter for the selection of dendrites the artificial anisotropy introduced by the square diffusional lattice has to be reduced.

Therefore two or four independent diffusion lattices are used which are rotated and shifted against each other. In each time step the diffusion equation is solved independently on all

lattices. We then locally advance the moving boundary independently on all lattices and average the resulting new boundary position over all lattices.

For free dendritic growth it was shown that this averaging is crucial at small anisotropy. Without that a dendrite would grow twice as fast at capillary anisotropy $\epsilon_4 \approx 0.05$, defined by $d_0 \rightarrow d_0(1 - \epsilon_4 \cos 4\Theta)$ in equation (2).

In order to observe the transition from the seaweed structure to the Kuramoto-Sivashinsky type chaotic behaviour [28] we used a stationary doublon finger structure [18] at $\Delta = 0.7$ as initial condition and switched on the relaxation term in the diffusion equation with a small dimensionless relaxation parameter $A = d_0 \sqrt{\lambda}$. After reaching a new stationary state the relaxation was further increased at constant undercooling Δ . Besides an increasing stationary velocity and decreasing distance of the two tips the doublon finger structure survives this process up to very large relaxation parameter λ . Of course now the gap between the fingers has no longer an infinite depth, since slow growth deep inside the gap is possible due to the relaxation term. At some value of A between 0.1 and 0.27 there is a crossover between a gap with an infinite slope h_x and one with a finite slope.

A simulation with periodic boundary conditions on one grid and an initial condition of a slightly perturbed flat interface with seven bumps and $A = 0.27$, *i.e.* $\epsilon = 0.0845$, showed the following behaviour. The amplitude of the perturbation converges quickly (on the time scale of the derived KS-equation) to a state, which seems to be stationary, since the amplitude increases extremely slowly. At a later state it comes to a jump-like formation of deep grooves in some but not all gaps of the interface. Since the gaps which remain stable and bounded have almost the same form as the gaps which later develop deep grooves we conclude that we are near the threshold of a discontinuous transition between a bounded structure and a structure with deep grooves of order diffusion length. The first state corresponds to the Kuramoto-Sivashinsky equation and is metastable, *i.e.* by accident in some of the gaps the numerical fluctuations have pushed the pattern across the critical amplitude. The formation of the holes is the birth of the doublon finger structure or compact seaweed morphology.

The holes are not infinitely deep in reality due to the relaxation parameter $\lambda > 0$ as suggested by the analysis of the local equation. But this saturation of the depth is beyond the validity of the perturbation expansion, since the depth is of the order of the diffusion length and nonlocal effects are becoming important. Furthermore the validity of the expansion is probably restricted to profiles with $H_X^2 \ll 1$, since an expansion of $\sqrt{1 + H_X^2}$ is involved in the calculation.

On the other hand we can assume that the normal velocity v_n of the interface can only depend on intrinsic properties of this curve like, for example, the curvature and derivatives of it along the curve [37, 38] and of their history. That means there must be an equation of the form

$$v_n = 2 + a_1 K + a_2 \frac{d^2 K}{ds^2} + \dots + b_1 K^2 + b_2 \left(\frac{dK}{ds} \right)^2 + F \tag{61}$$

where K is the local curvature, s is the arclength and F consists of higher order nonlinear terms which represent the history of the curve, for instance terms containing \dot{K} , and terms which are due to the change of the arclength. Note that only terms with even powers of s are allowed, since the velocity must be invariant under $s \rightarrow -s$. If we expand (61) for $K \ll 1$ we can find all linear coefficients a_i and the first nonlinear coefficient b_1 by using (23) and comparison with the KS-equation (27). The generalized equation (61) is valid as long as the minimum radius of curvature is much bigger than the diffusion length. In the deep gaps this is of course not fulfilled.

At $\epsilon = 0.0845$ we are far away from the calculated threshold at $\epsilon_{\text{crit}} \approx 0.3$ and $\alpha = (1 - \Delta)/\epsilon = 3.55$ is far away from $\alpha_{\text{crit}} \leq 0.1$. We checked that the numerical fluctuations are much too small to destabilize the bounded state.

Therefore we can assume that this destabilization is caused by other dangerous nonlinearities higher than H_{XX}^2 in the local equation, may be like $H_{XX}H_{XXXX}$, H_{XX}^3 or H_{XXXX}^2 . Inserting test-wise such terms with the right sign into the Kuramoto-Sivashinsky equation we observed a rapid decrease of the critical coefficient of these terms.

Finally we can say that at relative small distance from the absolute stability limit the bounded solutions of the derived KS-equation (18) are unstable against finite size perturbations which leads to a very quick formation of deep grooves. Although the mechanism leading to these singularities seems very similar to that of a KS-equation modified with a H_{XX}^2 nonlinearity, we could exclude this possibility by comparison with fully dynamical simulations of the basic equations. We expect higher order nonlinear terms in the local equation, which we did not derive here, of the form $H^{(2n)} * H^{(2m)} * \dots$ which act in the grooves of a curved bounded interface and shift ϵ_{crit} to a value significantly smaller than 0.08. Some basic results of the present analysis have been compiled in Figure 2.

In summary our diffusion-relaxation model matches up to the various isolated investigations for this interfacial pattern formation process and gives a very suggestive semi-quantitative explanation for the formation of the deep grooves observed in the seaweed or doublon-morphology. There are still some questions open, for example concerning the connection between the different types of periodic solutions of the KS-equation with the doublons or the precise point of the transition from a closed interface to one with the infinitely deep grooves. The analysis of this model in particular opens a possibility to study the formation of grooves at low values of the driving force where the kinetic coefficient is not the rate-determining factor and where the various relevant length-scales may be better separable. We hope to report on further details in the future.

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