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Physics Abstracts

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Interface structure at large supercooling

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Résumé. — Nous étudions la dynamique du front de croissance d'un corps pur en présence de cinétique d'interface non instantanée dans la limite de grandes surfusions. Le front plan est trouvé être stable au-dessus d'une surfusion critique $\Delta_s (> 1)$. Pour $\Delta < \Delta_s$ le front est instable vis-à-vis des perturbations de petit vecteur d'onde, $0 < k < k_0$, où k_0 s'annule exactement à la valeur critique Δ_s . Nous montrons que la dynamique du front est décrite dans la région critique par une équation aux dérivées partielles de type Kuramoto-Sivashinsky [3, 4]. Nous avons trouvé des solutions stationnaires de cette équation dans l'intervalle $(0, k_0)$ et étudié leur stabilité vis-à-vis de toute perturbation infinitésimale. Il sort de notre analyse que parmi la famille continue de solutions dans l'intervalle $(0, k_0)$, seule une bande très étroite est stable. Nos estimations laissent penser que le cristal liquide nématique [19] et/ou le cristal « colonnaire » [20] devraient permettre l'accès expérimental aux « grandes » surfusions. Ils devraient constituer par conséquent de bons candidats pour l'étude expérimentale de ce régime où une variété de comportements, tels que l'ordre, le chaos temporel, et la turbulence... devrait se manifester.

Abstract. — The front dynamics during the growth of a pure substance in the large undercooling limit including interface kinetics is analyzed. There exists a critical dimensionless undercooling $\Delta_s (> 1)$ above which a planar front is linearly stable. For $\Delta < \Delta_s$ the planar front is unstable against short wavenumbers k 's perturbations, $0 < k < k_0$, where k_0 vanishes at the critical undercooling Δ_s . Close to criticality the interface dynamics is governed by a partial differential equation of the Kuramoto-Sivashinsky [3, 4] type. We have investigated steady-state periodic solutions of this equation in the range $(0, k_0)$ and analyzed their full linear stability. It is found that among the continuous family of solutions with wavenumbers lying in the interval $(0, k_0)$, the stable ones exist only in a narrow region of this interval. From our estimates it seems that the nematic crystal [19] and/or the columnar liquid crystal [20] should allow experimental access to the « large » supercooling regime. They should therefore constitute good candidates on which to perform experiments in this regime where a rich dynamics, including order, temporal chaos, and turbulence..., is expected.

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1. Introduction.

Crystal growth provides us with fascinating examples of free boundary pattern-forming systems. This subject has known during the last decade an increasing amount of both experimental and theoretical interest. One of the extensively studied issue is that of velocity selection and side branching activity in dendritic growth [1]. The problem turned out to involve a subtle solvability mechanism, associated with the singular nature of the capillary perturbation. Most of the progress has been achieved in the small undercooling regime. There the planar front is always unstable, the interface shape is dendritic. However as the undercooling increases, surface kinetics can become of great importance. The question thus arises of whether kinetics may become decisive at large dimensionless undercooling ($\Delta > 1$). It is known that in the absence of kinetics, for example, neither a planar front nor an Ivantsov parabola (in the absence of capillary) constitutes a steady solution of the growth equations when $\Delta > 1$.

In this paper we analyze interface dynamics in the large supercooling limit. It is known that for $\Delta > 1$ the growth equations support a planar front solution moving steadily at a velocity $v = W(\Delta - 1)$, where W is a constant which is proportional to the kinetic coefficient (see below). The transition from a dendritic to a planar front structure was discussed in a recent work by Brener and Temkin [2]. Specifically it was shown that dendritic solutions exist below a supercooling $\Delta_c (> 1)$. The planar front solution, which exists at $\Delta > 1$ becomes stable above a critical undercooling $\Delta_s > \Delta_c$. It has been conjectured [2] that the solidification front should assume a periodic structure for undercoolings Δ such that $\Delta_c < \Delta < \Delta_s$. Our goal is to focus on the planar front transition. We analyze the stability of the front and find that it undergoes a morphological instability at a critical wavenumber k_0 which vanishes exactly at the undercooling Δ_s . Following Sivashinsky [3] we extract from the full growth equations, a partial differential equation that governs the front dynamics close to $\Delta = \Delta_s$. Our equation is of the Kuramoto-Sivashinsky [3, 4] type. We should mention that this is not the first time that a such treatment is used in the context of crystal growth. The first application can be traced back to Sivashinsky [5] who considered the interface instability in directional solidification of a binary alloy in the limit of a small partition coefficient. This limit provides, indeed, a small value (compared to the characteristic scale which is the inverse of the diffusion length) for the bifurcation wavenumber, which is the generic situation where one should resort to an expansion à la Sivashinsky [4]. In the small partition coefficient [5] limit the front dynamics is described by an equation somehow similar to the Kuramoto-Sivashinsky (KS) equation with a « damping » term (proportional to the interface position). A similar situation is obtained near the so-called absolute stability limit (the planar front is stable above this limit even for a vanishingly small thermal gradient) predicted by Mullins and Sekerka [6] where the bifurcation wavenumber becomes small (note that by definition near the absolute limit the thermal gradient is small). Novick-Cohen [7] included interface kinetics and a nonequilibrium partition coefficient in the analysis. Her equation is of Kuramoto-Sivashinsky type with a « damping » term, due to the thermal gradient, which reduces to a pure KS equation in the zero gradient limit. This is the limit of free growth we are considering here (in fact we assume a constant miscibility gap while Novick-Cohen [7] considered a non constant and a nonequilibrium gap).

Up to this point we will be largely repeating previous analyses [5, 7] by putting them in the context of the growth from a supercooled melt. The KS equation has also been derived in other contexts and numerous analytical and numerical investigations were devoted to it [8]. This equation admits [8], among other solutions, two stationary solutions which are called the « cellular » and « strange » solutions (see below). These stationary solutions were computed

by a forward time-dependent scheme [8]. We will compute them here using a stationary scheme. The stability of the « cellular » solution was first reported by Cohen *et al.* [9] using a direct integration of the KS equation. This solution is found to be unstable against large wavelength fluctuations [9]. The domain of stability of the cellular solution is very narrow. Using a multiscale analysis Frisch *et al.* [10] have extracted the « soft » modes from the KS equation. They brought out the viscoelastic character of the instability and confirmed (with a better accuracy) the result reported by Cohen *et al.* [9]. Here we will perform a systematic stability analysis based on the Floquet-Bloch theorem. This method is powerful if one is only interested in the stability of stationary solutions against all types of perturbations. We have confirmed the Cohen *et al.* [9] result with an accuracy as good as that of Frisch *et al.* [10].

A result found here for the first time, to our knowledge, is that the « strange » solution is also unstable against large wavelength fluctuations. The domain of stability of this solution is extremely narrow (much narrower than that of the cellular solution) so that it provides a quasi-perfect wavelength selection. This is an unusual example where the stability leads to a collapse of the band of possible wavelengths to, practically, a unique solution. Note that besides the above mentioned solutions the KS equation admits other solutions as for example oscillatory solutions [8]. It seems to us natural, as a first step, to pay attention to stationary solutions. This should not be taken to mean, however, that these are the only relevant solutions in real experiments.

Another result to be reported here is that the solution which moves with the maximum speed is marginally stable. Similar results were found in other contexts [11] and where selection was postulated (or sometimes found by a direct computation of some model equations [12]) to obey a marginal stability criterion.

Up to now [7] kinetic effects were considered as academic exercises. The main reason was that we, somehow, naively believed that kinetics would be important only, say, for growth velocities comparable to molecular speeds (in the rough part of the interface). This would, accordingly, have implied huge supercoolings, far beyond any experimental scope. Of course the absence of a complete microscopic description constitutes a major handicap for precise information on kinetics. Recently, however, directional solidification experiments [13] on impure CBr_4 have revealed an important recession of the planar front as a function of the growth speed even for growth speeds as small as a few $\mu\text{m/s}$. This is a signature of a non instantaneous kinetic effect. It is not obvious (at least to us) to have a clear argument on the domain of parameters where kinetics is decisive. Instead, we take measured values for the kinetic coefficient (from planar front recessions) and test directly their importance. There is also some numerical evidence [14] for the decisive role of kinetics in real experiments. In particular dendrites in impure CBr_4 are likely selected by kinetics anisotropy [14] rather than by interface energy anisotropy.

We will comment here on pattern selection and discuss the plausibility of experimental access to the large supercooling limit. From interface recessions measurements we evaluate an effective kinetic coefficient. Our estimates indicate that transparent materials should give access to this regime. They should therefore offer interesting examples of free boundary pattern-forming systems on which to study the large variety of front dynamics, going from order to turbulence.

2. Basic equations.

We consider the following situation : a pure solid is growing at the expense of its melt in the z -direction. The temperature far ahead of the solidification front is maintained at a constant value $T_\infty < T_m$, where T_m is the melting temperature. We consider the one sided model. This corresponds to a situation where diffusion in the solid phase is negligibly small. Of course a

one sided model is quantitatively accurate only when the solid grows from a supersaturated solution. But it is easy to show that the main conclusions are not at all altered by the one sided diffusion assumption. We will come back to this point in the last section. We consider one dimensional deformations only and assume that the system is infinite in the x -direction (on the scale of all wavelengths of interest). Let \tilde{T} denote the temperature field in the liquid phase (tilded variables refer to the physical ones). In the frame moving at a constant speed v , undetermined for the moment, the heat diffusion equation reads

$$D \nabla^2 \tilde{T} = -v \tilde{T}_{\tilde{z}} + \tilde{T}_{\tilde{t}}, \tag{1a}$$

with the condition

$$\tilde{T} = T_\infty \quad \text{at} \quad \tilde{z} = \infty. \tag{1b}$$

Differentiations are subscripted and D is the heat diffusivity of the liquid. At the liquid-solid interface the energy conservation equation takes the form

$$Lv_n = -\chi \frac{\partial \tilde{T}}{\partial \tilde{n}}, \tag{2}$$

where L is the latent heat of fusion per unit volume, χ the thermal conductivity, connected to the diffusivity D by the relation $cD = \chi$, where c is the heat capacity per unit volume. Finally v_n is the normal interface velocity. We assume that v_n is linear in the departure from equilibrium so that the modified Gibbs-Thomson equation reads

$$\tilde{T} = T_m \left(1 + \frac{\gamma \tilde{\kappa}}{L} \right) - \frac{v_n}{\beta}, \tag{3}$$

where γ is the surface tension and β a phenomenological kinetic coefficient (γ and β are taken to be isotropic), and $\tilde{\kappa}$ is the interface curvature taken to be positive for a concave solid

$$\tilde{\kappa} = \frac{\tilde{\zeta}_{\tilde{x}\tilde{x}}}{(1 + \tilde{\zeta}_{\tilde{x}}^2)^{3/2}},$$

where $\tilde{z} = \tilde{\zeta}(\tilde{x}, \tilde{t})$ is the instantaneous front position. Equations (1)-(3) support a planar front solution characterized by

$$\tilde{T}(\tilde{z}) = T_\infty + \frac{L}{c} e^{-\frac{v\tilde{z}}{D}}, \tag{4}$$

where v represents the growth velocity of the planar front, and is defined as

$$v = W(\Delta - 1), \tag{5}$$

with $W = \frac{\beta L}{c}$ and $\Delta = \frac{c(T_m - T_\infty)}{L}$ is the dimensionless undercooling. Before studying the linear stability of this solution we would like first to rewrite the basic equations in a dimensionless form. For that purpose we rescale the lengths and time by $\frac{2D}{v}$ and $\frac{4D}{v^2}$ respectively, while the dimensionless temperature is defined as $u = \frac{c(\tilde{T} - T_\infty)}{L}$. In terms of the new variables equation (1) becomes

$$\nabla^2 u = -2u_z + u_t, \tag{6}$$

and at the boundary ($z = \zeta(x, t)$) the mass conservation equation and the Gibbs-Thomson condition (Eqs. (2), (3)) transform into

$$2 + \dot{\zeta} = - (u_z - \zeta_x u_x) \tag{7}$$

$$u = \Delta + d\kappa - \frac{v}{2W} (2 + \dot{\zeta})(1 + \zeta_x^2)^{-1/2} \tag{8}$$

$d = cT_m \gamma v / 2 DL^2$ is the dimensionless capillary length. Here $\zeta(x, t)$ represents the dimensionless front position measured from $z = 0$ in the frame of reference moving at a velocity v given by equation (5) as a function of the undercooling. The linear stability analysis of the planar front is performed by looking for perturbations of the planar interface in the form $\zeta(x, t) \sim e^{\omega t + ikx}$, k is the wavenumber of the fluctuation and ω is the amplification (attenuation) rate that we want to determine. A linearization of the growth equations (6)-(8) leads to a set of two homogeneous linear algebraic equations for the interface and the temperature field amplitudes. If this set is to have a non trivial solution its determinant should vanish. This condition results in the following dispersion relation :

$$\left(2 - dk^2 - \frac{v\omega}{2W} \right) (1 + \sqrt{1 + k^2 + \omega}) = \omega + 4. \tag{9}$$

It is easy to show that setting $\text{Re}(\omega) = 0$ in equation (9) implies automatically that $\text{Im}(\omega) = 0$. This means that when looking for neutral modes we can simply set $\omega = 0$ in equation (9). Let k_0 denote the wavenumber of a neutral mode, $\omega(k_0) = 0$. It follows from equation (9) that

(i) For $d < \frac{1}{2}$ there exist two solutions, namely

$$k_0 = \left\{ \frac{2}{d} (1 - \sqrt{2d}) \right\}^{1/2} \tag{10a}$$

and

$$k_0 = 0. \tag{10b}$$

(ii) For $d > \frac{1}{2}$ there exists only one solution, $k_0 = 0$.

In other words $\omega < 0$ for all k 's when $d > 1/2$, whereas $\omega > 0$ in the interval $0 < k < k_0$ when $d < 1/2$. The critical situation occurs at $d = 1/2$. Using the definitions of d and v we obtain that this happens at a critical dimensionless undercooling Δ_s given by

$$\Delta_s - 1 = \frac{DL}{\beta T_m \gamma} \tag{11}$$

Note that Δ_s depends on the material parameters only and is always greater than unity. Δ_s defines a critical undercooling above which the planar front is stable. Note that for $\beta \rightarrow \infty$ (no kinetics) $\Delta_s \rightarrow 1$, which expresses the energy conservation in the free kinetics case. When the undercooling Δ decreases down to Δ_s the planar front becomes first unstable at a critical wavenumber $k_0 = 0$. We will take advantage of this fact to extract from the full equations of growth the only part that is relevant to the front dynamics in the vicinity of the critical undercooling Δ_s . This can be accomplished by means of the Sivashinsky [3] singular expansion.

3. Derivation of the front equation near $\Delta = \Delta_s$.

Let ε be a small parameter measuring the deviation from the critical undercooling Δ_s , and defined as :

$$\Delta = \Delta_s - (\Delta_s - 1) \varepsilon . \quad (12)$$

The linear theory is a first step in a stability analysis. Moreover it is a necessary starting point for the definition of the nonlinear problem. The first essential step in the development of the nonlinear analysis consists in specifying the characteristic time and length scales in the vicinity of threshold. This can be done by investigating the dispersion relation (Eq. (9)) in the critical region. Close to Δ_s equation (6) yields :

$$\omega = \frac{\varepsilon W}{v} \left(1 - \frac{k^2}{k_0^2} \right) k^2 + \text{higher orders} . \quad (13)$$

It follows from equation (10a) that $k_0 \sim \sqrt{\varepsilon}$. Using this result we immediately see from equation (13) that $\omega \sim \varepsilon^2$. This dictates us that the characteristic length and time scale as $\varepsilon^{-1/2}$ and ε^{-2} respectively. Our analysis follows now that of Sivashinsky. We rescale the space and time variables as follows

$$X = x \sqrt{\varepsilon}, \quad T = \varepsilon^2 t, \quad Z = z, \quad \zeta(x, t) = \varepsilon H(X, T), \quad (14)$$

where $H(X, T)$ is of order ε^0 . The functions H and u are expanded in powers of ε

$$u = u_0(Z) + \varepsilon u_1(X, Z, T) + \dots \quad (15a)$$

$$H = H_0(X, T) + \varepsilon H_1(X, T) + \dots \quad (15b)$$

Now the scheme is to insert (15) together with (14) into the basic equations (6)-(8) and deduce successively higher contributions in an expansion in powers of ε . From now on the boundary conditions at the liquid-solid interface are understood to be evaluated at $Z = 0$.

(i) *Order ε^0* :

To order ε^0 equation (9) provides

$$u_{0ZZ} + 2u_{0Z} = 0, \quad (16a)$$

where u_0 is subject to the boundary conditions (Eqs. (7)-(8)) at $Z = 0$

$$u_{0Z} = -2 \quad (16b)$$

$$u_0 = 1. \quad (16c)$$

These equations are solved by

$$u_0(Z) = e^{-2Z}, \quad (17)$$

where use has been made of the condition $u_0(Z = \infty) = 0$. Expression (17) is nothing but the planar front solution (Eq. (4)).

(ii) *Order ε* :

To order ε equations (6)-(8) read

$$u_{1ZZ} + 2u_{1Z} = 0 \quad (18a)$$

$$u_{1Z} + 2H_0 u_{0ZZ} = 0 \quad (18b)$$

$$u_1 + H_0 u_{0Z} = 0. \quad (18c)$$

The solution of this system is found to be :

$$u_1 = 2 H_0 e^{-2Z} \tag{19}$$

$H_0(X, T)$ is undetermined at this order.

(iii) *Order ϵ^2 .*

To this order u_2 satisfies the inhomogeneous bulk equation (6)

$$u_{2ZZ} + 2 u_{2Z} = - u_{1XX} . \tag{20a}$$

The contributions coming from the interface boundary conditions (7)-(8) are

$$u_{2Z} + H_0 u_{1ZZ} + H_1 u_{0ZZ} + \frac{H_0^2}{2} u_{0ZZZ} = 0 \tag{20b}$$

$$u_2 + H_0 u_{1Z} + H_1 u_{0Z} + \frac{H_0^2}{2} u_{0ZZ} = \frac{H_0 XX}{2} \tag{20c}$$

The solution of this system consists of a sum of a homogeneous and a particular solution :

$$u_2 = \left(2 H_0^2 + 2 H_1 + \frac{H_0 XX}{2} \right) e^{-2Z} + Z H_0 XX e^{-2Z} \tag{21}$$

Still at this order neither H_0 nor H_1 are known. The really interesting result appears in the next order of the expansion. The solvability condition becomes a constraint for $H_0(X, T)$ which is nothing but the nonlinear equation for H_0 that we want to determine.

(iv) *Order ϵ^3 .*

To this order the bulk equation (Eq. (6)) takes the form

$$u_{3ZZ} + 2 u_{3Z} = u_{1T} - u_{2XX} . \tag{22a}$$

Expanding the mass conservation equation (Eq. (7)) at the liquid-solid interface we obtain

$$\begin{aligned} u_{3Z} + H_0 u_{2ZZ} + H_1 u_{1ZZ} + H_2 u_{0ZZ} + \frac{H_0^2}{2} u_{1ZZZ} + H_0 H_1 u_{0ZZZ} + \frac{H_0^3}{6} u_{0ZZZZ} = \\ = H_{0X} u_{1X} - H_{0T} . \end{aligned} \tag{22b}$$

Doing the same with the Gibbs-Thomson condition we find

$$\begin{aligned} u_3 + H_0 u_{2Z} + H_1 u_{1Z} + H_2 u_{0Z} + \frac{H_0^2}{2} u_{1ZZ} + H_0 H_1 u_{0ZZ} + \frac{H_0^3}{6} u_{0ZZZ} = \\ = \frac{1}{2} \left\{ H_{1XX} - H_{0XX} - \frac{v}{W} H_{0T} + \frac{v}{W} H_{0X}^2 \right\} . \end{aligned} \tag{22c}$$

The solution of equation (22a) contains a contribution of the form $C(X, T) e^{-2Z}$ obtained by solving the homogeneous equation, plus a particular solution. Inserting this solution into equations (22b, c), we obtain two equations for the unknowns H_0, H_1, H_2 and C . One of this equation serves to express, for example, C as a function of the other unknowns. To obtain the sought equation for H_0 we proceed as follows. We multiply equation (22c) by 2 and add it to equation (22b). After this operation the terms proportional to C, H_1, H_2 cancell exactly. The remaining part is a nonlinear equation for the interface profile

$$F_\tau = - F_{XX} - \frac{1}{2} F_{XXXX} + F_X^2 , \tag{23}$$

where F and τ are rescaled variables, related to the original ones by

$$F = \frac{v}{W} H_0, \quad \tau = \frac{W}{v} T. \quad (24)$$

Equation (23) is free of any parameter. It is known as the Kuramoto-Sivashinsky [3, 4] equation. We may mention that in the usual Kuramoto-Sivashinsky equation the coefficient multiplying F_X^2 is negative. This is not relevant since equation (23) reduces to the standard form by simply replacing F by $-F$. Note that the equation derived by Novick-Cohen [7] near the absolute stability limit reduces formally to equation (23) if one takes the limit of a vanishing thermal gradient. This result is a direct consequence of the Novick-Cohen [7] study.

Note that the linear dispersion relation which follows from equation (23) takes now the form $\Omega = K^2(1 - K^2/2)$, which is simply the one given in equation (13), where Ω and K are related to ω and k by $\Omega = v\omega/\varepsilon^2 W$ and $K = k/\sqrt{\varepsilon}$ respectively. In terms of the new variables (Ω, K) the unstable domain of wavenumbers belongs to $(0, K_0 \equiv \sqrt{2})$. The Kuramoto-Sivashinsky (KS) equation has been extensively studied in the last few years [8]. As stated above this equation is free of any parameter and plays a role similar to the complex amplitude equation at the lower critical velocity for a slowly moving flat interface to become unstable in directional solidification. The linear stability result indicates that the characteristic wavenumber is given by $K = K_0 = \sqrt{2}$. The associated wavelength is $\Lambda_0 = \pi \sqrt{2}$. The KS equation has been investigated as a function of $\Gamma = L/\Lambda_0$, where L is the system size. Γ is the so-called « aspect ratio » (a denomination having likely its origin from Rayleigh-Bénard problem). As Γ increases the dynamics may evolve from order to low dimensional temporal chaos and to an increasingly complex dynamics [8].

Here we are interested in ordered solutions in an extended system. As a first step we will concentrate on steady-solutions only. The periodic solutions we will investigate were obtained before [15] from a forward time-dependent integration of the KS equation for sufficiently small aspect ratios ($\Gamma < 9$). Such calculations are of course relevant for pattern formation in a confined system. For extended systems ($\Gamma \gg 1$) the dynamical study of the KS is a formidable task, being due essentially to the exponential growth of the characteristic relaxation time as a function of Γ . In practice it is very hard to distinguish between a transient chaotic motion that will eventually stop before an ordered state takes place, and a completely permanent chaotic regime. Therefore the characterization, in particular, of periodic solutions and their stability can hardly be accomplished in practice from a forward time-dependent calculation if the system size is large enough. An alternative way, which is much more efficient, consists in solving the steady-state problem for periodic solutions and treat their full linear stability analysis by means of Floquet-Bloch theorem. This allows us to capture all types of instabilities. It turns out here that the most dangerous modes are the longwavelength ones which can be captured in a full dynamical integration only for large sizes. Of course our methodology does not tell us about metastability (if any) which may be relevant in the complete evolution of the dynamical system (see comments below). The present analysis is thought of as the first essential step in any stability problem and will allow us to give a complete stability diagram of periodic solutions in an extended system governed by equation (23).

We find here two types of steady-solutions with different ranges of wavenumbers. Unlike directional solidification problem [16] for example, the range of stable solutions is extremely narrow, so that this would correspond in practice to a quasi-perfect wavelength selection. It is not however possible to decide (at least for the authors) which of these two states would be selected if the system is in an ordered regime. We will comment on this point later.

4. Steady-state periodic solutions.

It is easy to show that equation (23) does not admit a steady-state periodic solution ($F_\tau = 0$). Indeed let Λ denote the periodicity of the solution. Integration of equation (23) over a period leads to

$$\frac{d}{d\tau} \langle F \rangle = \langle F_X^2 \rangle > 0, \tag{25}$$

where $\langle \dots \rangle$ signifies the mean value over a period. Equation (25) means that the mean interface position is permanently drifting. This indicates that steady-state solutions $F_0(X)$, if they are to exist, should move with a constant speed ν in the z -direction

$$\nu = \langle F_{0X}^2 \rangle, \tag{26}$$

where F_0 obeys the following nonlinear differential equation :

$$\nu = -F_{0XX} - \frac{1}{2}F_{0XXXX} + F_{0X}^2. \tag{27}$$

This represents a jump ν in the growth speed of that corrugated interface as compared with the speed of the plane interface. We look for solutions of equation (27) in the form

$$F_0 = \sum_{\ell=1}^{\ell=\infty} a_\ell \cos(\ell KX). \tag{28}$$

Inserting equation (28) into (27), collecting terms proportional to $\cos(\ell KX)$ we obtain a set of nonlinear algebraic equations for the coefficients a_ℓ . For all ℓ 's but $\ell > 0$ this set reads

$$\left(\frac{\ell^2 K^2}{2} - 1\right) \ell^2 a_\ell + \sum_{n=1}^{n=m} n(\ell - n) a_n a_{\ell-n} - \sum_{n=1}^{n=\infty} n(n + \ell) a_n a_{n+\ell} + \frac{1}{4} \left(\frac{\ell}{2}\right)^2 a_{\ell/2}^2 (1 - (-1)^{\ell+1}) = 0, \tag{29}$$

where $m = \frac{\ell-1}{2}$ for odd values of ℓ , and $m = \frac{\ell-2}{2}$ for even values. It is understood here that for $m = 0$ the first sum in equation (29) should be set to zero. For $\ell = 0$ equation (27) provides a relation between the velocity ν and the Fourier coefficients :

$$\nu = \frac{K^2}{2} \sum_{n=1}^{n=\infty} (na_n)^2 \tag{30}$$

The set of equations (29) are solved by means of Newton-Raphson method. Before going further we should note that our equation (27) is free of any parameter (e.g. control parameter...). The set of algebraic equations is parametrized by the basic wavenumber K only. In the interval $(0, K_0 = \sqrt{2})$, where the planar front solution is linearly unstable, we have found two types of solutions. These are the « cellular » and « strange » solutions, which have been discovered previously [8]. They are displayed in figure 1.

We have studied the linear stability of these solutions, denoted from now on by $F_0(x)$, by looking for solutions of equation (23) in the form

$$F(X, \tau) = F_0(X) + \eta(X) e^{\sigma\tau}, \tag{31}$$

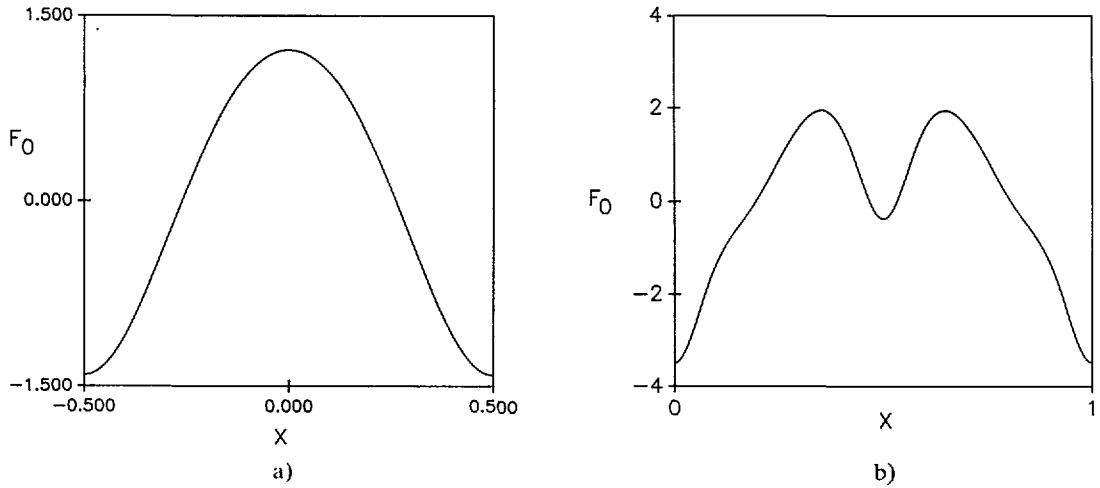


Fig. 1. — Steady-state periodic solutions. (a) : « Cellular » state. (b) : « Strange state ».

where η is a small deviation about F_0 . Inserting (31) into (27) and neglecting all but linear terms, we obtain :

$$\sigma \eta = - \eta_{XX} - \frac{1}{2} \eta_{XXXX} + 2 F_{0X} \eta_X. \tag{32}$$

Equation (32) is linear and homogeneous with a periodic coefficient $F_{0X}(F_{0X}(X + \Lambda) = F_{0X}(X))$, with $\Lambda = 2 \pi/K$. This problem is similar to that of an electron moving in a periodic potential. The general form of the eigenfunction follows from Floquet-Bloch theorem. We write it as

$$\eta(x) = \sum_{m=-\infty}^{+\infty} c_m \cos ((Q + mK) X), \tag{33}$$

where Q is a real number which belongs to the first Brillouin zone, $-K/2 \leq Q \leq K/2$. This means that we are using a reduced zone representation. Inserting equation (33) into (32) and equating similar terms on both sides, we obtain :

$$\left\{ \sigma - (Q + mK)^2 \left\{ 1 - \frac{(Q + mK)^2}{2} \right\} \right\} c_m = - \sum_{n=-\infty}^{+\infty} a_n nK \{Q + (m - n) K\} c_{m-n} + \sum_{n=-\infty}^{+\infty} a_n nK \{Q + (m + n) K\} c_{m+n}. \tag{34}$$

This is a set of linear equations for the coefficients c_n . The eigenvalue $\sigma(Q)$ is obtained by imposing a vanishing determinant. As the above system is of infinite dimension there exists in principle an infinite number of roots to the characteristic equation. Since we are interested in the location of a primary instability only, we focus attention on the branches σ whose real parts are close to the instability threshold. To investigate the roots $\sigma(Q)$ we first truncate equation (34) at a finite value m . We have checked the stability of our results by varying the value of m . We have computed the spectrum $\sigma(Q)$ for the two types of steady-solutions shown in figure 1. Figure 2 shows the range of stability for these two solutions as a function of $\Gamma = \Lambda/\Lambda_0$, where $\Lambda = 2 \pi/K$, is the actual periodicity, and $\Lambda_0 = 2 \pi/K_0$ the wavelength of the

neutral mode (« the stability length »). The interval of stability of the « cellular » solution (Fig. 1a) is found to be

$$1.195 < \Gamma < 1.305 . \quad (35a)$$

The stable domain of « strange » solutions is

$$4.22 < \Gamma < 4.23 . \quad (35b)$$

These two intervals are very narrow. In particular the one of « strange » solutions (Fig. 1b) can hardly be distinguished from a line in figure 2. This result is to be contrasted with that found in directional solidification of binary alloys at moderate speed where the band of stable solutions has appreciable width [16]. The domain of stability (Eq. (35a)) was determined first by Cohen *et al.* [9] and later by Frisch *et al.* [10] with a better accuracy. Frisch *et al.* [10] have in addition demonstrated the viscoelastic nature of the instability. It is, to our knowledge, the first time, however, that the stability of the strange solution is performed.

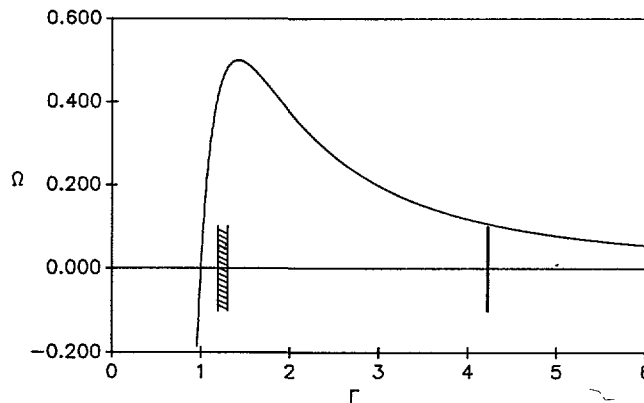


Fig. 2. — The stability diagram. The full line represents the amplification rate of the perturbation of the planar front. The dashed area represents the domain of stable cellular solutions. The domain of stability of strange solutions is so small so that it appears as a thick vertical line.

Note that in the present problem the stability analysis leads practically to a wavelength selection of the periodic structure. Of course the question of whether a system would select a « cellular » state rather than a « strange » one remains however unclear. We do not have at our disposal any criterion to answer a such question. If a variational formulation were valid, we could expect that the state of the system would be the one which minimizes the appropriate « free energy » (one state is stable and the other metastable). This denomination is, however, somehow misleading in the framework of deterministic dynamics. Indeed the final state depends on initial conditions only and can not be decided by simply looking to the « free energy » (if any). Of course fluctuations may change a such conclusion. As it is not clear whether fluctuations play an important role in nonequilibrium systems, we can simply test their importance in numerical experiments. Therefore whether fluctuations are important or not in real experiments can be checked *a posteriori* by confronting numerical results to experimental observations. We will return to the question of an experimental realization that is capable of exploring the large supercooling limit at the end of this paper.

The above discussion does not exhaust by far all scenarios of pattern selection. We can indeed imagine a competition of the « cellular » and « strange » solutions when they coexist as

two domains. We know from the Landau-Ginzburg equation describing a subcritical steady-bifurcation that in the coexistence domain the stable solution always invades the metastable one. If the bifurcation is of Hopf type [17], however, one phase may move steadily in the other one as a stable soliton (this is due to nonvariational effects). Another question of interest is to consider two coexisting semi-infinite domains. A natural question thus arises : will one domain grow at the expense of the other ? If so what determines the growth direction and the « wall » velocity. We should note that the velocity in the z direction of the « cellular » state, which lies near the maximum value (Fig. 3), is significantly bigger than that of the « strange » solution (not shown on the Fig.). It is interesting to see whether this difference may be relevant in the competition between the two states. We are planning to deal with these questions in the near future.

Another feature confirmed (see also Frisch *et al.* [10]) here for the cellular solution, which holds for the strange one also, is that the edges of the stable domains in figure 2 are limited by longwavelength propagative instabilities, which are to be contrasted with the usual Eckhaus diffusive instabilities. This feature results from the fact that in addition to the usual translational symmetry (which causes large scale phase modulations be dangerous, as expressed by the Eckhaus result), there exists in the present case another group of symmetry. To see this we first derive equation (23) with respect to X and write the resulting equation as $g_\tau = -g_{XX} - g_{XXX}/2 + gg_X$, where $g = F_X/2$, and then notice that this equation is invariant under a Galilean transformation : $g \rightarrow g + c$ and $X \rightarrow X + c\tau$, where c is a constant. Consequently the relevant modes for the dynamics are the phase of the pattern plus an additive mode, associated with large scales Galilean distortions. This means that we have a co-dimension 2 bifurcation problem with a strong coupling of modes that is capable of transforming the usual diffusive character, inherent to pure phase instabilities, into a propagative one.

Finally it is worth mentioning that the cellular solution (Fig. 1a) which moves at the maximum speed ν (Fig. 3) is marginally stable. This is not accidental but is a general property of equation (23). Indeed the linearized equation (32) has, besides the usual translational mode, another null eigen-mode F_{0A} at the maximum speed ν . To see this we simply need to differentiate the static equation (27) with respect to A

$$\nu_A = -F_{0XXA} - \frac{1}{2}F_{0XXXXA} + 2F_{0X}F_{0XA}$$

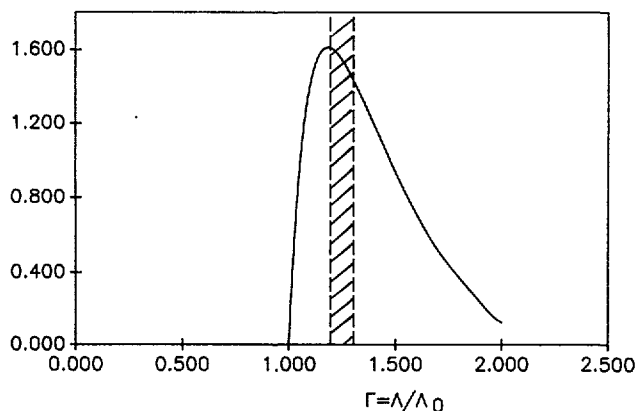


Fig. 3. — The speed of cellular solutions as a function of the reduced wavelength $\Gamma = A/A_0$. The dashed area refers to the stable band.

and then recognize that the r.h.s. of this equation is identical to that of equation (32) in which η is replaced by $F_{0,\Delta}$. It follows immediately that $\sigma = 0$ at the point where $\nu_\Delta = 0$. This result looks interesting when we know that in some contexts [11] the marginal stability has been considered as decisive, regarding pattern selection, or even demonstrated in model equations as the usual Landau-Ginzburg one [12]. Whether the fact that the marginal stability in the present case has any consequence on pattern selection is a question which needs further investigations and is beyond the scope of this paper. We would like however to make the following conjecture : if the system is initially « prepared » with a localized perturbation in an unstable situation it will likely, in view of numerical information [15], develop a turbulent regime. Even when the pattern happens to be linearly stable, the chaotic regions would not decay rapidly into a regular pattern. The ordering is, in some sense, inhibited by the propagation of disturbances, since, as mentioned above, the stable domain (Fig. 2) is limited by propagative instabilities.

5. Discussions.

In this section we would like to discuss the possibilities for the experimental realization of large undercoolings $\Delta = \Delta_s > 1$. We found in section 2 that the critical undercooling above which a planar front is stable is given by (Eq. (11))

$$\Delta_s = 1 + \frac{DL}{\beta T_m \gamma} \quad (36)$$

Δ_s is a function of the material parameters only. In general one of the major handicap for a rough estimate of Δ_s lies to the ignorance of the kinetic coefficient β . In the absence of a complete microscopic description, we will take estimated values in the literature, although some procedures for obtaining this coefficient remain questionable. We will first consider a metallic alloy. This is nickel for which rapid solidification experiments have been recently performed [18]. The parameters entering the r.h.s. of equation (36) are $D = 6.5 \times 10^{-6} \text{ m}^2/\text{s}$, $L = 2.58 \times 10^9 \text{ J/m}^3$, $T_m = 1726 \text{ K}$, $\gamma = 0.464 \text{ J/m}^2$, $\beta = 1.6 \text{ m/s K}$. We then obtain $\Delta_s \approx 14$. Using the definition of Δ we find that the required temperature T_∞ for the planar front to be stable is given by

$$T_\infty = T_m - \frac{L}{c} \Delta_s.$$

The value of the heat capacity for Ni is $c = 6.5 \times 10^6 \text{ J/m}^3$. This amounts to $T_\infty = -3795 \text{ K}$ (!). This means that we would need to cool the liquid far below the absolute zero temperature ! (which is quite amusing). It seems from this estimate that it would be impossible to explore the high supercooling regime in a pure material.

The question naturally arises of whether there exists any possibility to observe the planar front transition. We show below that this would likely be the case with an impure material where the front dynamics is mainly controlled by the (much slower) mass diffusion. This is the so-called isothermal growth, where the heat generated at the liquid-solid interface is instantaneously conducted away so that the growth is limited by the slow variable, namely the concentration of impurities. It is a simple matter to rewrite the basic equations relevant to the present situation. The main difference is that here the dimensionless supercooling Δ is defined as

$$\Delta = \frac{T_m - mc_\infty - T_\infty}{m \Delta c} \quad (37)$$

where m is the liquidus slope, c_∞ the concentration of impurities far ahead of the solidification front, Δc the equilibrium miscibility gap and T_∞ is the actual temperature of the environment in which the solid grows (Fig. 4). The critical dimensionless undercooling above which the planar front is stable is given by

$$\Delta_s = 1 + \frac{D_c L}{\beta T_m \gamma}, \quad (38)$$

which is exactly the same Δ_s for the pure material (Eq. (36)), with D substituted by D_c , the mass diffusion coefficient. We should mention that equation (38) is derived in the constant miscibility gap approximation. It can be checked that relaxing this assumption induces only minor changes. As seen from equation (38) and the definition of Δ (Eq. (37)) the advantage for considering a situation where the growth is limited by impurities diffusion is double. Firstly the fact that D_c is much smaller than D ($D_c/D \sim 10^{-3}$ - 10^{-4}) causes a drastic reduction (by a factor equal to D/D_c) of the critical dimensionless undercooling Δ_s . Secondly the physical undercooling is measured on the scale $m \Delta c$, which may be much smaller than L/c , which constitutes the appropriate undercooling scale for a pure substance. For the case of Ni, we find, by taking $D_c \sim 10^{-9}$ m²/s, $\Delta_s \sim 1 \sim 10^{-3}$. This means that the required temperature T_∞ is very close below the solidus line (Fig. 4). Such undercoolings are, by now, likely accessible in standard experiments. Of course how difficult is the realization of an undercooling $\Delta_s \sim 1$ depends on the nature of impurities (which act quantitatively on the phase diagram and therefore on the magnitude of $m \Delta c$) and obviously on their amount. More precisely the smaller $m \Delta c$ the easiest the access to the large supercooling limit. We should however point out that when $m \Delta c$ becomes smaller and smaller the disregard of heat diffusion may become questionable. We give below the condition under which our assumption is expected to be valid.

Obviously the question arises of whether a material as nickel is an appropriate candidate for the experimental investigation of the front dynamics. This is unfortunately far from being the case. The main reason is that Ni, as most of metals, does not allow an *in situ* analysis, as do organic materials which have been extremely helpful in the progress of our understanding of pattern formation in crystal growth. We are therefore naturally led to ask whether transparent materials may constitute good candidates for experimental studies. We will first concentrate on the experimental setup of Simon and Libchaber [19] who considered recently the growth of

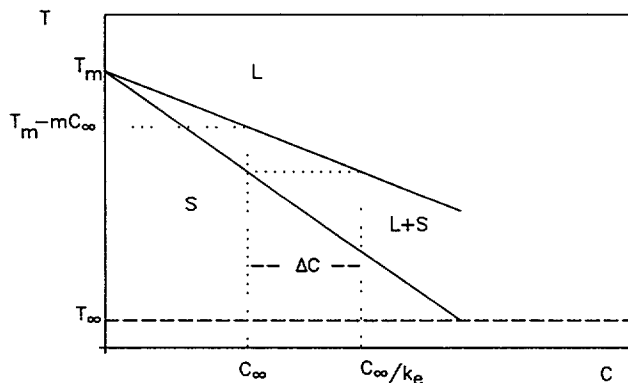


Fig. 4.— A schematic phase diagram of the coexistence of the liquid and solid phases. $\Delta c = c_\infty(1/k_e - 1)$ is the miscibility gap and k_e the equilibrium partition coefficient.

a nematic crystal with a small amount of impurities. This feature strongly favours, together with the relatively small diffusion coefficient, the experimental exploration of the large supercooling limit. Indeed the values of the material parameters entering equation (38) are $T_m = 313$ K, $D_c = 2 \times 10^{-11}$ m²/s, $L = 2 \times 10^6$ J/m³, $\gamma = 9.4 \times 10^{-6}$ J/m². Finally the kinetic coefficient β is evaluated from the planar front recession as a function of the velocity [21]. From a rough estimate we find that $\beta \sim 10^{-4}$ m/s K. This value follows from writing that the planar front recession is equal to $v/\beta G$ where G is the thermal gradient and is typically of the order of 10^3 K/m, while the recession is of about 10^{-3} m for a velocity of 10^{-4} m/s. It follows then that $\Delta_s \approx 10^2$. This value seems to be big enough. However, as stated above this undercooling is measured in $m \Delta c$ scale which is rather small. In Simon and Libchaber's [19] experiment $m \Delta c \approx 0.01$. Consequently the required temperature is of the order of a degree below the solidus line. More precisely (see Fig. 4) $T_m - mc_\infty - T_\infty = \Delta_s m \Delta c \approx 1$ K. This is a rather small difference whose experimental realization should be feasible. We should however insist on the fact that the estimated value for β must be taken with a certain caution. Indeed a recession of the front may also result from the motion of the thermal profile with the pulling velocity, due to the thermal inertia. An accurate estimate of the kinetic coefficient should be provided by measuring the actual surface temperature. We hope that this can be carried out in the near future and therefore make our predictions more precise. Note that the above value for β seems very small. Its determination follows, as stated above, from the front recession. If the recession is overestimated, which may likely be the case due to thermal inertia, then the actual value of β would be larger. If a such is the case then the required supercooling Δ_s would be even smaller than the one evaluated above.

Another point we would like to mention is that the homogeneous nucleation of the nematic crystal in the undercooled isotrope may be so pronounced to cause additional difficulties. The main reason lies to the rather low value of the surface tension. Another promising candidate is the columnar liquid crystal used by Oswald *et al.* [20] where large values of the supercooling ($\Delta \approx 0.6$) were achieved. A rough estimate [22] of the critical undercooling for the planar front to be stable provides $\Delta_s - 1 \approx 1$. We believe that a more purified material should give access to a such undercooling.

Before concluding we would like to specify the conditions under which the growth can be considered as isothermal. For that purpose we should evaluate the real interface temperature for a thin film, by taking into account the release of latent heat, and compare it to that imposed externally. For a one dimensional problem, treated here, the physical temperature T obeys the following equation

$$\frac{1}{D} T_t = T_{xx} - \frac{T - T_\infty}{h^2}, \quad (39)$$

where h is a phenomenological parameter, having the dimension of a length, and characterizes the heat exchange between the sample and the environment. Considering a symmetric heat diffusion in both phases we can show [23] that the actual interface temperature T_i for a planar front is given by

$$T_i = T_\infty + \frac{L}{c(1 + 4D^2/h^2v^2)^{1/2}}, \quad (40)$$

where v is the interface velocity (Eq. (5)). The condition for the solidification process to be isothermal is that the actual interface temperature be very close to the imposed one, T_∞ , namely

$$\frac{T_i - T_\infty}{T_m - mc_\infty - T_\infty} \ll 1. \quad (41)$$

Using the definition of Δ (Eq. (37)) we can write condition (41) as

$$\frac{T_1 - T_\infty}{\Delta m \Delta c} \ll 1. \quad (42)$$

For a sufficiently efficient heat exchange, $D^2/h^2 v^2 \gg 1$ (a situation which is always satisfied), equation (42) leads to

$$\frac{Lh\nu}{cD} \ll m \Delta c \Delta. \quad (43)$$

This gives a condition for the phenomenological parameter h for the isothermal condition to be fulfilled. This parameter is related on the other hand to the relaxation time τ of the thermal profile measured on the sample when this one is immersed in an environment with a different temperature. In other words measuring the instantaneous thermal profile from the initial time up to a time when the sample reaches a thermal equilibrium with the « reservoir » would give access to the time τ and *via* the relation $\tau = h^2/D$ the phenomenological parameter can be estimated. If one takes $\tau \approx 10$ s we find that equation (43) is always satisfied except for extremely small values of $m \Delta c$ of the order of 10^{-4} .

Our major results can be summarized as follows. (i) We have shown that the front dynamics in the large supercooling limit, where interface kinetics become important, is described by a Kuramoto-Sivashinsky equation. This is the free growth version of the Novick-Cohen [7] study. (ii) We have investigated steady-state solutions using a Newton-Raphson scheme and treated their full linear stability for an extended system. It consists of a forward application of the Floquet-Bloch theorem. We have found a drastic reduction of the band of possible wavelengths. For the « strange » solution the collapse is more dramatic. Moreover the « cellular » solution with the maximum speed is marginally stable. This situation was met in other contexts [11, 12]. But we have given to it here a general meaning. Our result on the stability of cellular solutions is in agreement with previous investigations [9, 10]. (iii) We have discussed the experimental feasibility of large supercoolings. It emerges from our calculations that this regime can be accessible with a dilute binary mixture, where the growth is limited by impurities diffusion. We believe that the nematic crystal used by Simon and Libchaber [19] and/or the columnar liquid crystal used by Oswald *et al.* [20] are promising candidates to study this regime.

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