Growth-Morphologies in Solidification and Hydrodynamics*

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The evolution of interfacial patterns during growth processes is shortly summarized. The analogy between hydrodynamic dewetting patterns and diffusion controlled growth patterns is demonstrated. A phase-field method for the treatment of hydrodynamic flow with free interfaces is presented and illustrated with some examples.

I. INTRODUCTION

In first order phase transitions a critical nucleus is formed by thermodynamical fluctuations. This nucleus afterwards grows in a deterministic way to in principle arbitrarily large size scales, thereby being subject to various growth instabilities. The growth of a crystal from the melt or from a solution is a typical example for such a process [1,2].

FIG. 1. Morphology diagram of diffusional growth patterns in two dimensions. Plotted is the driving force Δ versus crystalline anisotropy ϵ . In the inserts, D stands for 'dendrites' S for 'seaweed', C for 'compact' and F for 'fractal'.

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.

Various growth patterns are encountered, depending on the strength of the driving force (i.e. deviation from thermodynamic equilibrium), crystalline anisotropy and 'noise' or fluctuations [3]. In two dimensions, a theory was recently formulated resulting in a morphology diagram [2] of diffusional growth patterns, Fig.1.

FIG. 2. Growing seaweed-structure. The basic growth elements appearing finally in d) and e) are 'Doublon'-structures. (Result of phase-field simulations)

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II. PHASE FIELD MODEL

We have used a *phase-field model* ([2,4] and refs. therein) to simulate solidification under control of a diffusion-field in a channel over long times. The standard version of a phase-field model describes the time-evolution of an order-parameter field ϕ which is not conserved, but which is coupled to at least one second field u which obeys a continuity equation. This field u describes a conserved variable like energy or a chemical component. The equations of motion can be derived from a functional for the appropriate thermodynamic potential of the system. They can be written as a set of coupled partial differential equations in time and space, here given for the phase ϕ (solid vs. liquid), temperature T and chemical concentration C :

$$\begin{aligned} \tau \frac{\partial \Phi}{\partial t} &= \xi^2 \nabla^2 \Phi + V_0 (\Phi - \Phi^3) + M_0 \frac{1-\Phi^2}{(1+\Phi^2)^2} (C+T-1+\Gamma(\Phi)) \\ \frac{\partial C}{\partial t} &= \nabla (D_C \nabla (C - \Gamma(\Phi))) \\ \frac{\partial T}{\partial t} &= \nabla (D_T \nabla T) - \frac{\partial \Gamma(\Phi)}{\partial t} \end{aligned} \quad (1)$$

with $\Gamma \approx (\Phi + 1)/2$. M_0 , V_0 and ξ are parameters which define details of the interface properties. D_C and D_T are diffusion constants.

The stationary growth of an evolving pattern like the doublons in Fig.2 e) is controlled by two parameters, which give the selection conditions. For a single diffusion field these conditions are the Ivantsov-relation relating the Peclet-number p_T (see below) with the driving force or dimensionless supercooling Δ [1]

$$\Delta = \sqrt{p_T \pi} e^{p_T} \operatorname{erfc}(\sqrt{p_T}) \equiv \operatorname{Iv}(p_T),$$

together with the selection criterion for the dimensionless velocity σ :

$$\sigma = \frac{2 d_0 D_T}{v R^2} = \frac{d_0 v}{2 D_T p_T^2}.$$

For two fields (heat and matter), we have two Peclet-numbers, the thermal and the chemical Peclet-number: $p_T = \frac{v R}{2 D_T}$ and $p_C = \frac{v R}{2 D_C}$; stationary: $D_T p_T = D_C p_C$. The first stationarity condition is a generalized Ivantsov-relation

$$\Delta = \operatorname{Iv}(p_T) + \frac{m_L C_\infty (1-k)}{L/c_p} \frac{\operatorname{Iv}(p_C)}{[1 - (1-k) \operatorname{Iv}(p_C)]} \quad (2)$$

and the second a generalized selection criterion [5]:

$$\sigma \simeq \varepsilon^{7/4} \cdot \left(\frac{1}{(1+p_T^2 \varepsilon)} + \frac{2}{(1+p_C^2 \varepsilon)} \frac{D_T m_L (1-k) C_\infty c_p / L}{D_C [1 - (1-k) \operatorname{Iv}(p_C)]} \right), \quad (3)$$

where k is the segregation coefficient, L is the latent heat, m_L is the slope of the liquidus-line, ε is the strength of

crystalline anisotropy and C_∞ is the concentration of the bulk liquid.

Note that eqs.(2) and (3) are obtained for a typical dilute solution, while eq. (1) for simplicity holds for a constant miscibility gap. Our computer-simulations with the two-field phase-field model were in satisfactory agreement with these formulas.

Since phasefield calculations have proven to be computationally very efficient in diffusion limited crystal growth, it arises naturally to extend this approach to phenomena involving convection and external fields.

III. DEWETTING

In the phenomenon of partial wetting [6–8] a thin film of well-defined thickness is formed on the surface of a substrate. The external forces responsible for this film in addition to the cohesive forces between water molecules are Van-der-Waals forces and polar forces from the substrate.

FIG. 3. Amplitude of the phase-field over the two-dimensional substrate-surface. The front between the dry and the wet part is clearly visible as a smoothed step-function.

Recently beautiful experiments have been performed by Lipson et al. [9], Herminghaus et al. [10], continuing and extending earlier work by Reiter [11] and Brochard-Wyart et al. [12]. In the experiments of Lipson's group [9] it was found that the patterns observed in the early stages of pattern formation correspond to seaweed patterns as shown in Fig.2. This is to be expected since in the limit of creeping flow, corresponding to low Reynolds-numbers or high viscosity, the hydrodynamic flow equation for dewetting degenerates to a diffusion equation of Cahn-Hilliard type [13] with an effective diffusion constant inversely proportional to the viscosity:

$$\frac{\partial u}{\partial t} = D_{eff} \Delta u - \lambda_{eff} u \quad (4)$$

D_{eff} and λ_{eff} are derived from a linearisation of the hydrodynamic equations [14].

IV. PHASE-FIELD MODEL FOR HYDRODYNAMICS

Since the late stages of pattern formation in thin film growth were found to be governed by hydrodynamics, we coupled the phasefield equations to a simplified Marker-and-Cell-Procedure [15]. The phasefield ϕ enters the incompressible Navier-Stokes equations

$$\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \nabla) \vec{u} = \frac{1}{\rho} (-\nabla p + \eta \Delta \vec{u} + \vec{f}_s) \quad (5)$$

$$\nabla \cdot \vec{u} = 0 \quad (6)$$

through the surface force

$$\vec{f}_{s0} = \gamma K \vec{n} \delta(\vec{x} - \vec{x}_s) = \gamma K \frac{1}{2} \nabla \phi, \quad (7)$$

where K is the local curvature of the phasefield ϕ , γ the surface tension and the delta function taking into account the position of the interface. The Navier-Stokes equation couples back into the equation of motion for the phase field via an advection equation:

$$\frac{\partial \phi}{\partial t} = -\vec{u} \cdot \nabla \phi + F\{\phi\}, \quad (8)$$

with the nonlinear phasefield operator

$$F\{\phi\} = \frac{1}{\tau} \{ \xi^2 \vec{n} \cdot \nabla (\vec{n} \cdot \nabla \phi) + V_0 (\phi - \phi^3) \} \quad (9)$$

according to previous experience [4,15].

FIG. 4. Dewetting process in 1+1 dimensions (full line) and diffusion-model eq. (4) (dotted line) at time $t=1000$.

To include the external Van-der-Waals and polarizing forces which cause the phenomenon of partial wetting we add an additional surface force

$$\vec{f}_{s1} = \delta(\vec{x} - \vec{x}_s) \vec{n} \cdot (\vec{n} \cdot \nabla \Psi(z)), \quad (10)$$

resulting from a double minimum potential $\Psi(z)$ and acting on the interface.

Therefore the total force on the interface coupling into the Navier-Stokes equation is :

$$\vec{f}_s = \vec{f}_{s0} + \vec{f}_{s1}. \quad (11)$$

Naturally, a first application of the resulting algorithm was to simulate the high viscosity limit of a 1+1 dimensional system.

In Fig.4 we compare the simulation results with the diffusional Cahn-Hilliard model for wetting-dewetting. The x coordinate represents the direction parallel to the surface of the substrate, which is located at $z = 0$. The z coordinate of the interface represents the normal direction away from the substrate into the gas-phase and therefore the local height of the liquid film. The original front between the dry and the wet part of the substrate was given as a step function (dashed line). During the dewetting process the front moves towards the wet part (Fig.5), forming a distinct bump on the wet side right of the moving front

FIG. 5. Velocity-field for flow corresponding to Fig.4 (arbitrary units).

V. HIGHER REYNOLDS NUMBERS

Our interest is now to understand what happens, if the conditions for replacing the Navier-Stokes-equations by an effective diffusion equation are no more valid.

For higher Reynolds numbers significant changes due to increasing vorticity in the inertial range of wavelengths should be expected. The following figures show some of our results for much smaller viscosities. Deviating from the diffusional behavior in the high viscosity limit, the interface "overshoots" its equilibrium height and relaxes oscillatory into its final position, thereby reaching Reynolds numbers of order 150. These oscillations in the minimum of the effective interface potential Ψ can mathematically be described as gravitationally

driven surface waves with an effective $g_{eff} = \frac{\Psi''}{\rho}$ and corresponding group velocity :

$$v_{gr} = \frac{1}{2} \sqrt{\frac{\Psi''}{\rho k \tanh(kh)}} \left[\tanh(kh) + \frac{kh}{\cosh^2(kh)} \right] \quad (12)$$

Thus, for an experimental realization of these surface oscillations, a simultaneous measurement of wavelength, equilibrium height and group velocity can yield the second derivative Ψ'' of the effective interface potential at the equilibrium height (h_{eq} is given by the prewetting line).

FIG. 6. Dewetting film like shown in Fig.4 but now for high Reynolds numbers $Re \approx 100$. The surface-wiggles can be identified as "gravitational waves" in the attractive field of the substrate.

VI. SUMMARY

We have constructed a model together with a numerical scheme which allows us to examine the structure formation at interfaces (possibly reactive) when diffusion as well as convection acting on different time scales and further external fields are involved, as in the case of thin film growth. The model shows reasonable quantitative agreement with an effective diffusion-model (Cahn-Hilliard-type) in the range of Reynolds numbers below the order of unity. For higher Reynolds numbers the appearance of characteristic surface oscillations permits a measurement of the second derivative of the effective interface

potential on the prewetting line. For 2+1-dimensional simulations of the Navier-Stokes equations the Mullins-Sekerka instability of the dewetting film was confirmed, including capillar damping in the stable regime.

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