Interface dynamics in a mean-field lattice gas model

Jean-François Gouyet and Mathis Plapp #
Laboratoire de Physique de la Matière Condensée,
École Polytechnique, F-91128 Palaiseau, France

Keywords : Interface dynamics, dendritic growth, spinodal decomposition, surface modes.

Abstract :

A mean-field approximation of stochastic lattice gas models with attractive nearest-neighbour interaction allows to write generalized Cahn-Hilliard equations. We use such equation to perform numerical simulations in two dimensions of the growth of regular "snowflakes." It naturally shows curvature and kinetic effects at the interface as assumed by the classic phenomenological equations of dendritic growth. In addition, we find solute trapping. The dendrite tips are stabilized by the Gibbs-Thomson boundary condition. We calculate the surface tension and show that it has the expected angular variation. We compare our model to other microscopic growth models and the phase-field models and discuss the influence of noise.

Stationary interface states advancing with constant velocity are also investigated. We present numerical results as well as a continuum approximation which gives an analytic expression for the shape correction in the limit of not too large interface velocities. We observe departure from local equilibrium at the interface and solute trapping. The associated kinetic coefficients are calculated. The two effects are found to be related. We finally give an expression for the interface mobility and derive a relation between this mobility and the kinetic coefficients.

We also examine droplets and stripes of unstable A-B compounds with vacancies (ABv model) immersed in a stable vapor. We observe the appearance of ordered structures starting from the surface and propagating into the bulk.We calculate the characteristic lengths and the propagation velocities of these patterns using a linear stability analysis. We show that the thickness of the ordered layer depends on the model parameters and the strength of the initial noise.

Introduction

The study of moving interfaces is an old subject [1]. Two well-known and extensively studied processes where interface dynamics play a crucial role are spinodal decomposition (spontaneous phase separation) and dendritic growth. The classical models used to describe the interface kinetics are continuum phenomenological models: the Cahn-Hilliard equation [2] for phase separation, and simple diffusion equations with interface Gibbs-Thomson boundary conditions in the case of dendritic growth [3,4]. The latter models have the advantage to direct the effort only upon the interface which is sharp, and leads via the constraints to a non trivial free boundary problem, while a simple diffusion equation is needed in the bulk. It has the inconvenient that we have no access to the physical parameters which must be introduced phenomenologically : there is a missing link between the microscopic description of the kinetics of evolution of the particles in the system and the above phenomenological equations.

Various attempts have been made recently to fill this gap [5-8]. We start from a stochastic lattice gas with attractive nearest neighbours interactions from which we build mean field kinetic equations.

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present address: Physics Department, Northeastern University, Boston, Massachusetts 02155

The mean field approximation changes the stochastic process into a set of coupled non-linear difference equations without noise. It is then possible at this level to make a bridge between these equations and the phenomenological Cahn-Hilliard equations in which usual forms of the free energy and chemical potentials appear.

Such a model is not limited to binary AB alloys or to Av systems (species A and vacancies) and it is possible in this approach to write generalised Cahn-Hilliard equations for ABv model alloys, for eutectics, or to simulate the kinetics in presence of solidus/liquidus coexistence curves.

Considering first an AB system, we will recall its two-phase coexistence behaviour below a critical temperature, and the corresponding first order phase transition. Concerning the dynamics, we have here the possibility to choose a more realistic microscopic dynamics, in contrast to the usual Kawasaki dynamics which is appropriate to spin exchange and magnetic systems. We will then examine the dynamics of a moving interface and show that this approach allows to determine analytically the various parameters controlling the growth of dendrites: the orientation dependent surface tension and its anisotropy, the kinetic coefficient or the surface mobility. These analytic expressions are functions of the microscopic physical parameters of the system.

Then we will improve the microscopic description by looking to ABv systems, that is to say two interacting components A and B containing a certain amount of vacancies (v). Such a system is more realistic, as the interdiffusion of A and B particles is essentially mediated by the vacancies involving a much lower energy cost. For this situation we have studied the evolution of a free droplet of A-B compounds with few vacancies initially in equilibrium at high temperature with its vapor formed by vacancies with few A-B, then quenched below the critical temperature. We will show that ordered structures spread at the surface and propagate into the bulk, with characteristics very different than those which appear in the bulk. In addition the surface itself becomes unstable and wavy. We show that the thickness of the ordered layer depends on the model parameters and on the strength of the initial noise.

The mean-field model

We consider a square lattice of N sites (coordination number z=4). Particles (A) are located on sites and $n_i=\{0,1\}$ denotes occupation ($n_i=1$) or non occupation ($n_i=0$) of site **i** by an A; $n_i=0$ corresponds to an empty site (v) or to occupation by the other species B in a binary A-B model. Double occupancy of a site is forbidden, and there exists an attractive interaction ($\varepsilon_{AA}=\varepsilon>0$) between nearest neighbour particles. This allows to define a Hamiltonian,

$$H=-\varepsilon\sum_{\langle \mathbf{i},\mathbf{j}\rangle} n_{\mathbf{i}}n_{\mathbf{j}}-\mu_0\sum_{\mathbf{i}} n_{\mathbf{i}}\ , \qquad (1)$$

In the case of an A-B compound, $\varepsilon=\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB}$.

To define the dynamics we suppose here that the particles can jump to nearest neighbouring empty sites: this corresponds in the case of A-B alloys to the simple exchange diffusion mechanism. A general master equation can be easily written for such a dynamics, but as it is untractable, simplifications are needed. The simplest is to consider a mean-field approximation and to determine the kinetic equation satisfied by the average concentration $p_i=\langle n_i\rangle$.

It can be easily verified that the continuity equation,

$$\frac{\partial}{\partial t}p_{\mathbf{i}}=-\sum_{\mathbf{k}} j_{\mathbf{ik}}\ , \qquad (2)$$

corresponds to currents j_{ik} along the link **i-k**, of the form

$$j_{\mathbf{ik}}=\langle\, n_{\mathbf{i}}\,(1-n_{\mathbf{k}})\,w_{\mathbf{ik}}(\{n\})-n_{\mathbf{k}}\,(1-n_{\mathbf{i}})\,w_{\mathbf{ki}}(\{n\})\,\rangle\,.$$

The factors $n_i(1-n_k)$ take care of the exclusion principle: the initial site must be filled, the final site empty. $w_{ik}(\{n\})$ are transition probabilities depending on the local configuration. The physical picture behind our model is that the lattice points are located at the equilibrium positions of atoms in a crystal structure. Then an atom is trapped at its site in a potential well whose depth depends on the local configuration. As the thermal energy is supposed small compared to the barrier heights, the jump probabilities follow an Arrhenius law. We assume the barrier height to be the energy necessary for the particle to reach the saddle point between the initial **i** and final **k** sites: it does not depend on the final site environment. This leads to

$$w_{\mathbf{ik}}(\{n\})=w_0\,\exp\left(-\frac{\varepsilon}{kT}\sum_{\mathbf{a}} n_{\mathbf{i+a}}\right). \qquad (3)$$

w_0 is the jump frequency of an isolated particle, which sets the overall time scale and will be taken to unity for convenience. Here and in the following, **a** will denote a lattice unit vector, and summation

over **a** means summation over all nearest neighbours. Let us remark that this expression differs from the usual Monte Carlo rule, where the transition rate is proportional to exp(–ΔH/2kT) with ΔH being the energy difference between initial and final state. In deriving expression (3) we have chosen a form which allows a direct comparison with usual thermodynamics (see ref. [7] for discussion).
We have shown [7,9] that the currents can be written in the form of a generalised transport equation,

$$j_{\mathbf{ik}} = - M_{\mathbf{ik}} \, (\mu_{\mathbf{k}} - \mu_{\mathbf{i}}) \tag{4}$$

where $\mu_{\mathbf{i}}$ is the local chemical potential on site **i**, and $M_{\mathbf{ik}}$ the mobility along the link **i-k**.

$$\mu_{\mathbf{k}} = -\varepsilon \sum_{\mathbf{a}} (p_{\mathbf{k+a}} - p_{\mathbf{k}}) - z\,\varepsilon \left(p_{\mathbf{k}} - \frac{1}{2}\right) + kT \log \frac{p_{\mathbf{k}}}{1 - p_{\mathbf{k}}} \,. \tag{5}$$

Simplified expressions for the mobility can be derived in some circumstances. In homogeneous systems, we have directly

$$M_{hom}(p) = \frac{p\,(1-p)}{kT} \exp(-\kappa z p) \tag{6}$$

while close enough to equilibrium where the condition $\mu_{\mathbf{i}} \cong 0$ holds, we can define a local mobility; the one which can be introduced in the generalised Cahn-Hilliard equation describing the kinetics of the system. To first order in the chemical potential,

$$M_{loc}(p_{\mathbf{i}}) = w_0 \frac{e^{-z\varepsilon/2kT}}{kT} (1 - p_{\mathbf{i}})^2 \tag{7}$$

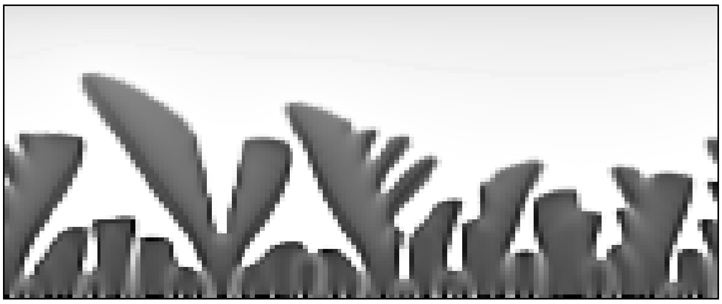
Eq.7 is equivalent to eq.6 in a homogeneous system at equilibrium.

Dendritic growth and interface dynamics

After a quench in the unstable region of the phase diagram (which is here the phase diagram of a simple binary system in a mean field approximation), we observe phase separation, while in the metastable region, a supercritical germ of one phase (α, with $p_A > p_B$) imbedded in a supersaturated bath of the other phase (β, with $p_B > p_A$) grows. In the linear approximation, the concentration p^β just in front of the growing interface is such that,

$$\frac{p^\beta - p^\beta_{eq}}{\Delta p} = d(\theta)\, K + \beta_0(\theta)\, v \,. \tag{8}$$

where $p_{eq}{}^\beta$ is the bulk equilibrium value of the β phase, Δp the equilibrium miscibility gap, d(θ) the orientation dependent capillary length, K the total curvature, v the normal velocity of the interface, and $\beta_o(\theta)$ the orientation dependent kinetic coefficient.



If the initial conditions correspond to a rough surface where the first layer is formed of randomly occupied sites, the growth presents chaotic structures shown in the opposite figure. No other noise is added. The directions of easier growth is along the (11) directions.

Fig.1. Growth from a rough interface on a 150×80 square lattice at $T = 0.1T_c$; the concentration far from the substrate is fixed at $p_\infty = 0.02$

Numerical simulations of eqns 2 and 4 lead to structures shown in figures 1, 2a and 2b. In figure 2 the effect of the lattice anisotropy is reflected in the fourfold symmetry of the patterns.

In the numerical experiments a germ is placed in the center of a 200×200 square lattice and the concentration is maintained fixed $p_\infty = 0.02$ on a large circle, the temperature is fixed at $T = 0.1T_c$. In figure 2a, no noise is added, while a conservative Langevin noise term is superposed to the kinetic equation in figure 2b. Sidebranches develop from the tips of the four branches, as expected.

We have studied with some details the characteristics of the interface. An example of the shape of a plane interface moving at velocity $v = a\, w_o \tilde{v}$ is shown in figure 3. To find the interface profile we have solved the continuous approximation of eqns 2 and 4. The following results have been obtained [9]: In the lowest order approximation, the equilibrium (planar) profile takes the form,

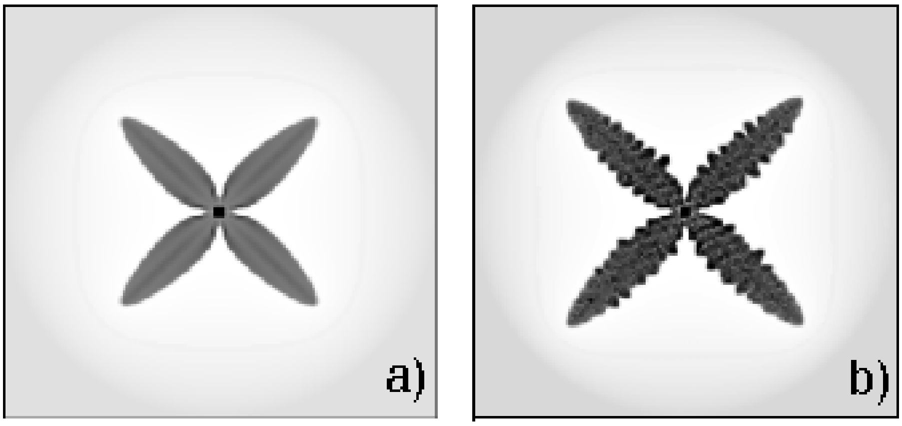


Fig. 2. a) Fourfold "snowflake" grown on a 200×200 square lattice at $T = 0.1T_c$; concentration is fixed at $p_\infty = 0.02$ on a large circle. b) the same conditions but now a conservative Langevin noise has been added: sidebranches develop.

$$p_0(x) = \frac{1}{2} - \frac{\Delta p}{2} \tanh\left(\frac{x}{2\xi_0}\right), \tag{9}$$

where Δp is the miscibility gap, and $\xi_o = a\sqrt{\varepsilon\,\chi_{eq}}$ the interface thickness. $\chi_{eq} = \chi(p_{eq})$, where $\chi(p)$ is the susceptibility defined by,

$$\chi(p) = \frac{p\,(1-p)}{kT - z\varepsilon\, p\,(1-p)},$$

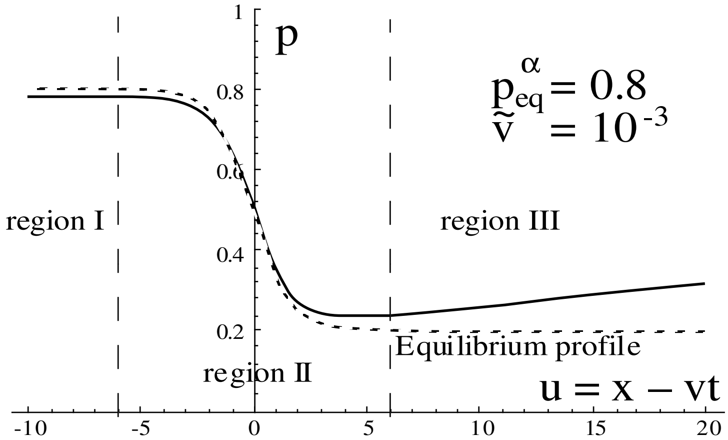
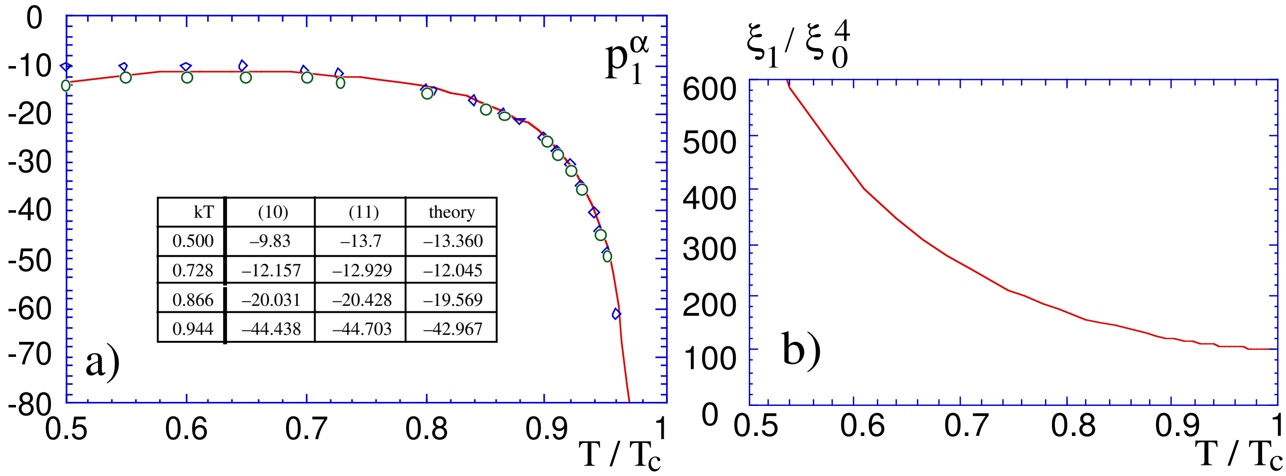


Fig.3. Stationary interface shape for $T = 0.86T_c$ and dimensionless velocity $\tilde{v} = 10^{-3}$, obtained from the continuum treatment. The broken line is the equilibrium profile.



kT	(10)	(11)	theory
0.500	–9.83	–13.7	–13.360
0.728	–12.157	–12.929	–12.045
0.866	–20.031	–20.428	–19.569
0.944	–44.438	–44.703	–42.967

Fig.4 Parameters of the moving interface : a) Solute trapping $\tilde{v}\, p^{\alpha}_1$, the solid line is the continuum approximation, symbols are values of numerical simulations. Diamonds, (10) direction, circles (11) direction.

Inset : table with some numerical values of p_1^{α}. b) Correction $\tilde{v}\,\xi_1$ to the interface thickness.

When the interface moves at velocity v, the profile is deformed and for a planar interface we find that, in the moving frame (u = x–vt) the new profile is essentially of the form,

$$p(u) = \frac{1}{2} - \frac{\Delta p}{2}\tanh\frac{u}{2\left(\xi_0 + \tilde{v}\,\xi_1\right)} + \tilde{v}\,p_1^{\alpha} + \tilde{v}\;g(u)\,. \qquad (10)$$

We see that

i) a constant term p_1^{α} is present which corresponds to “solute trapping” . This is the fact that during the interface motion, B particles (or vacancies) initially in the β phase (regions III) are trapped in region I before reaching their equilibrium and cannot diffuse fast enough to return to the β phase. The solute trapping correction is shown in figure 4a.

ii) the thickness of the interface increases ($\xi = \xi_o + \tilde{v}\,\xi_1$), and figure 4b shows the behaviour of ξ_1.

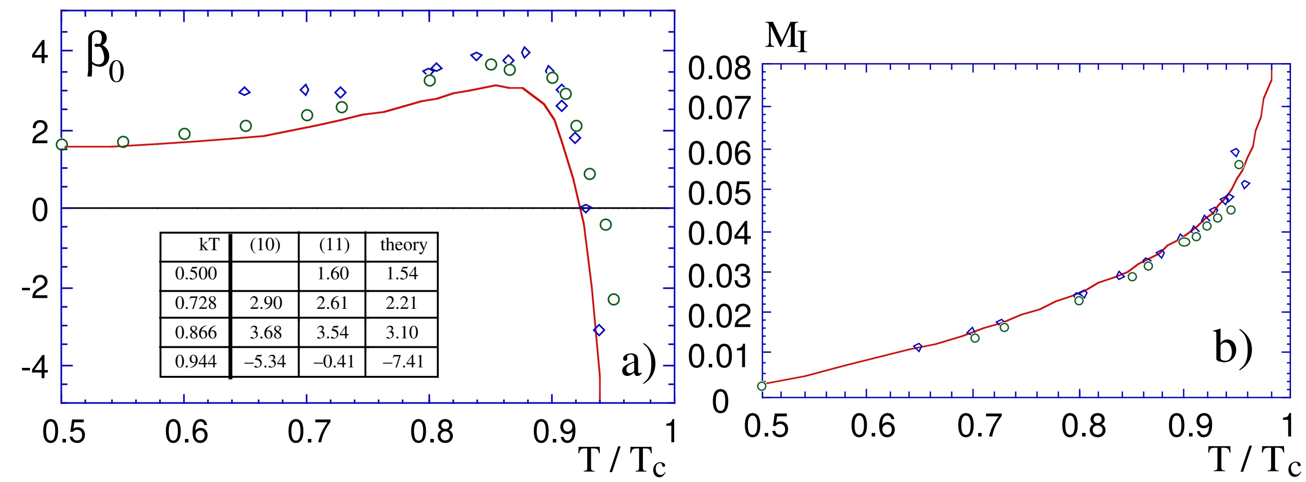
We have determined analytically the critical behaviour of ξ_1 and obtained a $\xi_o^{\,4}$ divergence close to T_c:

$$\xi_1 \propto C\,\xi_0^{\,4}\,, \qquad (11)$$

The last term, g(u) corresponds to the concentration gradient in region III, which fixes the current at a given distance from the interface. Finally from the kinetic equations we can determine the kinetic coefficient β_o (eq. 8). The graph of β_o is represented in figure 5a, while its analytic expression is,

$$\beta_0 = \frac{8kT\,\xi_0^{\,3}\,\Delta p\, e^{-\frac{z\varepsilon}{2kT}}}{\varepsilon\, a^3\,(1+\Delta p)^2}\left(\frac{T_c}{T} + \frac{1}{1-\Delta p}\right) + \frac{p_1^{\alpha}}{\Delta p}\,. \qquad (12)$$

Note that β_o does not depend on the orientation in the continuum model.



kT	(10)	(11)	theory
0.500		1.60	1.54
0.728	2.90	2.61	2.21
0.866	3.68	3.54	3.10
0.944	–5.34	–0.41	–7.41

Fig.5 Symbols as in fig.4. a) Kinetic coefficient β_o; b) Interface mobility M_I.

An interface mobility M_I can be defined by $\tilde{v} = M_I\,\Delta\mu$ where $\Delta\mu$ is the chemical potential difference between the two sides of the interface. Its graph is represented in figure 5b. Explicitely [6],

$$M_I = \chi_{eq}/\left(\Delta p\;\beta_0 - p_1^{\alpha}\right). \qquad (13)$$

The Gibbs-Thomson effect due to the interface curvature K which is characterised by the parameter d(θ) in eq.8 can also be easily determined,

$$d(\theta) = \frac{a^2\,\chi_{eq}\,\sigma_0}{(\Delta p)^2}\left(1 - 15\alpha_S\cos 4\theta\right). \qquad (14)$$

σ_o is the average surface tension and α_S the anisotropy of the surface tension.

Surface modes in an ABv model

A second example of the present approach [10] is devoted to spinodal decomposition of a droplet of an unstable ABv mixture of concentrations $p^A = p^B = 0.46464$ in the numerical simulation, immersed in a vapor of concentration $p^A = p^B = 0.03536$ and a fixed temperature such that $\beta\,\varepsilon_{AA}=2$. In addition we choose a completely symmetrical phase diagram, by taking $\varepsilon_{AA}=\varepsilon_{BB}=2\varepsilon_{AB}$.

In ABv systems eqns 4 and 5 now become

$$j^{\alpha}_{\mathbf{ik}} = - M^{\alpha}_{\mathbf{ik}}\,(\mu^{\alpha}_{\mathbf{k}} - \mu^{\alpha}_{\mathbf{i}}) \tag{15}$$

where the mobility of species α (=A, B or v) is given by,

$$M^{\alpha}_{\mathbf{ik}} = (1-p^{A}_{\mathbf{i}}-p^{B}_{\mathbf{i}})(1-p^{A}_{\mathbf{k}}-p^{B}_{\mathbf{k}})(e^{\beta\mu^{\alpha}_{\mathbf{k}}} - e^{\beta\mu^{\alpha}_{\mathbf{i}}})/(\mu^{\alpha}_{\mathbf{k}} - \mu^{\alpha}_{\mathbf{i}}) \tag{16}$$

and the local chemical potential of species α by

$$\mu^{\alpha}_{\mathbf{k}} = - \varepsilon_{\alpha A} \sum_{\mathbf{a}} \left(p^{A}_{\mathbf{k+a}} - p^{A}_{\mathbf{k}}\right) - \varepsilon_{\alpha B} \sum_{\mathbf{a}} \left(p^{B}_{\mathbf{k+a}} - p^{B}_{\mathbf{k}}\right) - z\,\varepsilon_{\alpha A}\, p^{A}_{\mathbf{k}} - z\,\varepsilon_{\alpha B}\, p^{B}_{\mathbf{k}} + kT \log \frac{p^{\alpha}_{\mathbf{k}}}{1 - p^{A}_{\mathbf{a}} - p^{B}_{\mathbf{a}}}\,. \tag{17}$$

The chemical potential, and the pressure (negative of the grand potential) are equal in the two phases with the present choice of concentrations and temperature. A small amplitude noise is added and the mean field equations integrated numerically. Phase separation first develops at the surface and propagates into the bulk of the droplet with a checkerboard structure. This is shown in figure 6a.

The charateristics of surface modes may be determined using a linear stability analysis. In the example in figure 6a, for instance we found a wavelength of the mode parallel to the surface $\lambda_y \cong 16$, while the mode normal to the surface was $\lambda_x \cong 6$, with a velocity $v \cong 5\times10^{-4}$, all in good agreement with the numerial simulations.

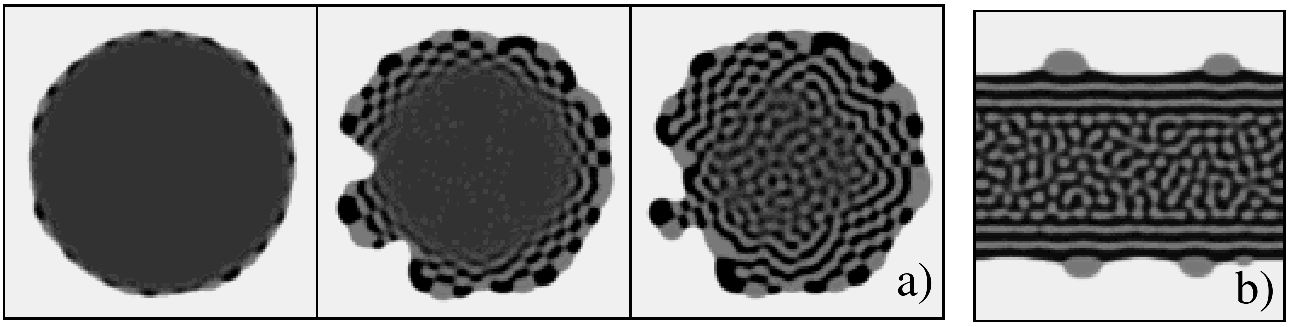


Fig. 6 a) Snapshot pictures at t = 22400, 56900, and 79400 (from left to right) of a decomposing droplet on a 128×128 lattice. White: vapor, black: A-rich, light grey: B-rich phase, dark grey: mixture. Parameter values as given in the text. b) Stripe of unstable material with asymmetric initial concentrations ($p^A = 0.56007$, $p^B = 0.37338$) at $\beta\varepsilon_{AA} = 2$ on a 128×128 lattice with periodic boundary conditions; $t = 89400\ w_o^{-1}$.

The choice of an off critical composition (60:40) is shown in the stripe sample presented in figure 6b. The surface modes still expand, but the first layer is now destabilised and droplets form at the surface which coarsen very rapidly.

Finally we are interested in the parameters which fix the thickness of the surface layer. Its propagation stops when the bulk decomposition reaches the nonlinear regime. The development of the spinodal decomposition in the bulk depends on the initial noise; considering that the growth is exponential before the non linear regime is reached, and comparing the propagation of the bulk and surface modes, we find for the thickness,

$$d = v\,(1/\omega_b - 1/\omega_s)\,\ln(\delta/\delta_o) \tag{18}$$

where ω_b and ω_s are the growth rates of the fastest growing bulk and surface modes, δ_o the initial noise strength and δ some threshold where nonlinear effects start to limit the growth.

We thank W. Dieterich, H.P. Fischer, V. Fleury, M. Kolb, P. Maass and O. Penrose for very interesting discussions. M.P. benefitted from a grant by the Ministère de l'Enseignement Supérieur et de la Recherche (MESR). Laboratoire de Physique de la Matière Condensée is URA 1254 to CNRS.

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Corresp. author : e-mail : jean-francois.gouyet@polytechnique.fr