



HAL
open science

1D Cahn-Hilliard dynamics : coarsening and interrupted coarsening

Simon Villain-Guillot

► **To cite this version:**

Simon Villain-Guillot. 1D Cahn-Hilliard dynamics: coarsening and interrupted coarsening. J. A. Tenreiro Machado, Dumitru Baleanu, Albert C J Luo. Discontinuity and Complexity in Nonlinear Physical Systems, Springer, pp.153, 2014, Nonlinear Systems and Complexity (Springer), 978-3-319-01410-4. hal-00933636

HAL Id: hal-00933636

<https://hal.science/hal-00933636v1>

Submitted on 20 Jan 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1D Cahn-Hilliard dynamics : coarsening and interrupted coarsening

Simon Villain-Guillot

*Laboratoire Onde et Matière d'Aquitaine, Université Bordeaux I
351, cours de la Libération 33405 Talence Cedex, France and
Email: simon.villain-guillot@u-bordeaux1.fr*

Abstract

Many systems exhibit a phase where the order parameter is spatially modulated. These patterns can be the result of a frustration caused by the competition between interaction forces with opposite effects.

In all models with local interactions, these ordered phases disappear in the strong segregation regime (low temperature). It is expected however that these phases should persist in the case of long range interactions, which can't be correctly described by a Ginzburg-Landau type model with only a finite number of spatial derivatives of the order parameter.

An alternative approach is to study the dynamics of the phase transition or pattern formation. While, in the usual process of Ostwald ripening, succession of doubling of the domain size leads to a total segregation, or macro-segregation, C. Misbah and P. Politi have shown that long-range interactions could cause an interruption of this coalescence process, stabilizing a pattern which then remains in a micro-structured state or super-crystal. We show that this is the case for a modified Cahn-Hilliard dynamics due to Oono which includes a non local term and which is particularly well suited to describe systems with a modulated phase.

I. INTRODUCTION

Many systems exhibit phases where the order parameter is spatially modulated and forms a pattern [1]. These phases are the result of a frustration caused by the competition between interaction forces with opposite effects.

For example, in a blend of polymers, the difference of interaction energies between homo and hetero polymers generates locally a repulsion between heteropolymers which leads to a macroscopic segregation. But for diblock co-polymers which are built with two heteropolymers A and B which are attached to each other by a chemical bond, such a macroscopic global phase separation is prohibited. They form a disordered phase at high temperature (when the entropic effects prevail), but below a critical temperature, whereas energetic considerations should lead to segregation, this chemical binding prevents separation between A and B heteropolymers over a long distance : the two components A and B self-organized in patterns or domains of finite size (mainly lamellar or hexagonal) in order to minimize nevertheless contacts between heteropolymers en thus the energy of interaction. The relative density in heteropolymers is thus spatially periodically modulated. This spontaneous microstructuration could be helpfull to design a new generation of solar cells based on organic semi-conductors[2].

In all models with local interactions, these ordered phases disappear in the strong segregation regime (low temperature). It is expected, however, that these phases should persist in the case of long-range interactions, which can't be correctly described by a Ginzburg-Landau type model with only a finite number of spatial derivatives of an order parameter (which can be defined in our preceding example from the relative density in the two components A and B).

An alternative approach is to study the dynamics of phase transition. While, in the usual process of Ostwald ripening, succession of coarsening events with doubling of the domain size leads to a total segregation, or macro-segregation, C. Misbah and P. Politi [3] have shown that long-range interactions could cause an interruption of this coalescence process, stabilizing a pattern that remains consequently in a micro-structured pattern or super-crystal.

We show here that this is the case for the equation of Oono[4], which is particularly well suited to describe the dynamics of systems with a modulated phase.

II. DYNAMICS OF PHASE TRANSITIONS

A. Time-Dependent Ginzburg Landau equation

1. Derivation of the model

Different equations can be used to describe the dynamics of a phase transition depending on, for example, if the order parameter is a scalar or a vector, and whether it is conserved by the dynamics or not (for a review see [6, 7]).

As at equilibrium, this order parameter must minimize a free energy, the dynamics out of equilibrium must then involve deviation from this stable order parameter value or function, just like in a simple mechanical system. The simplest dynamics based on Ginzburg-Landau free energy for a scalar order parameter is the TDGL (Time-Dependent Ginzburg Landau or model A in Hohenberg and Halperin classification[6]) which writes

$$\frac{\partial u}{\partial t}(\mathbf{r}, t) = -\frac{\delta F_{GL}}{\delta u} = \nabla^2 u - \frac{\varepsilon}{2}u - 2u^3 \quad (1)$$

In this equation, $u(\mathbf{r}, t)$ is a macroscopic order parameter which is a coarse grained of a microscopic order parameter in a small volume around the position \mathbf{r} . And ε is the dimensionless control parameter, usually the reduce temperature $\varepsilon = \frac{T-T_c}{T_c}$ where T_c is the critical temperature of the phase transition. This partial differential equation is invariant by the transformations $u \rightarrow -u$ and $x_i \rightarrow -x_i + a_i$. F_{GL} is the Ginzburg-Landau free energy local density or Lyapounov functional in the context of dynamical systems :

$$F_{GL} = \frac{1}{2} \left((\nabla u)^2 + \frac{\varepsilon}{2}u^2 + u^4 \right)$$

The non-local term $(\nabla u)^2$ prevents discontinuity or roughness of the order parameter and assigns energetic overcost to its variations in proportion with their sharpness. When looking at the temporal evolution of the free energy $\int F_{GL}(r, t)dr$:

$$\frac{d}{dt} \int F_{GL}dr = \int \frac{\delta F_{GL}}{\delta u} \cdot \frac{\partial u}{\partial t} dr = \int \frac{\delta F_{GL}}{\delta u} \cdot \left(-\frac{\delta F_{GL}}{\delta u} \right) dr = - \int \left(\frac{\delta F_{GL}}{\delta u} \right)^2 dr < 0$$

One notices from equation 1 that the dynamics will induce a change of $u(\mathbf{r})$ as long as it hasn't reached a minimum of the free energy density F_{GL} . If one looks for homogeneous states (where the order parameter is independent of the spatial coordinates) to be stationary states of this equation, they will be the extrema of the Landau potential $V(u) = \frac{\varepsilon}{2}u^2 + u^4$

FIG. 1: Landau potential as a function of u , the amplitude of the order parameter. We have plotted the profil of this potential above and below the pitchfork bifurcation at $\varepsilon=0$.

For $\varepsilon > 0$, the potential is a convex function and there is only one minimum, $u = 0$.

For $\varepsilon < 0$, the Landau potential is a concave function around $u = 0$, which is now a maximum ; two other solutions have now appeared as minimum of the potential, symmetric one each other.

which is plotted in Fig. 1 for the two possible signs of the control parameter. For $\varepsilon > 0$, the only extremum is $u = 0$, so there is only one homogenous solution, which is stable, being a minimum of the Landau potential (which is a convex function as long as $\varepsilon > 0$). When $\varepsilon < 0$, this potential is now concave in a neighborhood of $u = 0$, which is now a maximum and thus is now linearly instable. Two other symmetric solutions $u = \pm \frac{\sqrt{-\varepsilon}}{2}$ have now appeared due to this pitchfork bifurcation. They are the new stable homogeneous solutions and correspond to a minimum of the potential $V_{\min} = -\varepsilon^2/32$.

2. Linear stability analysis

Linear stability analysis consists in computing the growth rate of small fluctuations of a solution. When linearizing equation (1) around $u = 0$ (i.e. when neglecting the nonlinear term u^3) one gets

$$\frac{\partial u}{\partial t}(\mathbf{r}, t) = -\frac{\varepsilon}{2}u + \nabla^2 u$$

Considering this equation in the Fourier space we can decompose u in Fourier series in the case of a finite size problem or Fourier transform in the infinite case :

$$u(\mathbf{r}, t) = \sum_{\mathbf{q}} u_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r} + \sigma t} \quad (2)$$

where $u_{\mathbf{q}}$ is the amplitude of the Fourier mode at $t = 0$. For example, it can be the thermal fluctuations proportional to T . This mode decomposition enables to compute the q -dependence of the amplification factor $\sigma(q)$ (or growth rate or imaginary part of $k = q - i\sigma$) :

$$\sigma(\mathbf{q}) = -(q^2 + \frac{\varepsilon}{2}) \quad (3)$$

$\sigma(\mathbf{q})$ is negative for $\varepsilon > 0$, and thus the homogeneous solution $u = 0$ is unstable with respect to fluctuations of the order parameter. The whole band $0 < q < \sqrt{(-\varepsilon/2)}$ is linearly unstable as $\sigma(\mathbf{q}) > 0$ (see Fig. 2)

FIG. 2: Amplification factor $\sigma(q)$ computed via linear stability analysis of the time-dependent Ginzburg-Landau equation (TDGL). It is positive (growth of the modulations) for all the modes $q < \sqrt{\frac{-\varepsilon}{2}}$.

3. *Symmetry breaking and conservation law*

The linear stability analysis enables to conclude that the most instable mode is for $q = 0$: it is thus a long wave instability, which will give rise to large homogeneous domains and imply spontaneous symmetry breaking. This is the case, for example, in magnetic systems.

But if there is a conservation law, as for example a conservation of mass, such an instantaneous symmetry breaking is prohibited : the matter, or the different species diffuse with a finite characteristic time. Hillert [8], Cahn and Hilliard [9] have proposed a model to describe segregation in a binary mixture. This equation, later on denoted C-H for Cahn-Hilliard, corresponds to model B in the Hohenberg and Halperin classification[6]. Cahn-Hilliard dynamics is the minimal equation describing phase transition for a conserved scalar order parameter. As this conservation law prevents global symmetry breaking, it will generate numerous domains and interfaces separating them. This dynamic governs a whole class of first order phase transition like the Fréedericksz transition in liquid crystals [10], segregation of granular media in a rotating drum[11], or formation of ripple due to hydrodynamic oscillations [13, 14].

B. Model B or Cahn-Hilliard equation

1. Derivation of the model

Cahn-Hilliard dynamics is a modified diffusion equation for a scalar order parameter u , which writes :

$$\frac{\partial u}{\partial t}(\mathbf{r}, t) = \nabla^2 \left(\frac{\varepsilon}{2} u + 2u^3 - \nabla^2 u \right) = \nabla^2 \left(\frac{\delta F}{\delta u} \right) \quad (4)$$

In the original work of Cahn and Hilliard, $u(\mathbf{r}, t)$ represents the concentration of one of the components of a binary alloy. But it can also be the fluctuation of density of a fluid around its mean value, or concentration of one chemical component of a binary mixture, or the height of a copolymer layer[15]..

As in model A, this equation is invariant by the transformations $u \rightarrow -u$ and $x_i \rightarrow -x_i + a_i$ and when looking at the time evolution of the local quantity $F(t)$, we still have :

$$\frac{dF}{dt} = \frac{\delta F}{\delta \Phi u} \cdot \frac{\partial u}{\partial t} = \frac{\delta F}{\delta u} \cdot \nabla^2 \left(\frac{\delta F}{\delta u} \right) = - \left(\nabla \frac{\delta F}{\delta u} \right)^2 < 0$$

In order to derive a conservative dynamics, such that $\int \Phi(x, t) dx = cste$, one can start from a detail balance [16], or from a conservation equation for the order parameter Φ .

$$\frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{j}$$

where \mathbf{j} is a matter current associated with u . This current is related to the gradient of the chemical potential μ via the Hartley-Fick law : $\mathbf{j} = -\nabla \mu$. And this chemical potential is itself related to the functional derivative of the free energy $\mu = \frac{\delta F}{\delta \Phi}$. This phenomenological approach enables to recover the C-H equation(eq 4).

If one looks globally at the quantity $\int u(x, t) dx = \langle u \rangle$, the Cahn-Hilliard gives

$$\frac{d \langle u \rangle}{dt} = \int \frac{\partial u}{\partial t}(x, t) dx = \int \nabla^2 \left(\frac{\delta F}{\delta u}(x, t) \right) dx = \left[- \left(\nabla \frac{\delta F}{\delta u} \right) \right]$$

So, apart from boundary terms, the order parameter is indeed a conserved quantity.

2. Linear stability analysis

FIG. 3: Amplification factor $\sigma(q)$ computed from the linear stability analysis of Cahn and Hilliard equation

Stationary states of the (C-H) are again the extrema of the Landau potential $V(u) = \frac{\varepsilon}{2}u^2 + u^4$. And after a quench, the system undergoes a first order phase transition associated with the pitchfork bifurcation from the $u = 0$ solution to the symmetric solutions $u = \pm\frac{\sqrt{-\varepsilon}}{2}$. But due to the conservation law, the dynamics is different as Cahn and Hilliard have shown via the linear stability analysis of equation (4) around $u = 0$.

$$\frac{\partial u}{\partial t}(\mathbf{r}, t) = \nabla^2 \frac{\varepsilon}{2} u - \nabla^4 u \quad (5)$$

one gets for the amplification factor in the Fourier space $\sigma(q)$:

$$\sigma(\mathbf{q}) = -(q^2 + \frac{\varepsilon}{2})q^2 \quad (6)$$

So, as $\sigma(\mathbf{q})$ is negative for $\varepsilon > 0$, the $u = 0$ solution is stable with respect to small fluctuations of the order parameter. For negative ε , Fig 3 shows a band of instable Fourier modes, as $\sigma(\mathbf{q}) > 0$ for $0 < q < \sqrt{(-\varepsilon/2)}$. Moreover, linear stability analysis of C-H predicts that the most instable mode is not anymore for $q = 0$ but for $q_{C-H} = \sqrt{-\varepsilon}/2$ (for which $\sigma_{\max} = \frac{\varepsilon^2}{16}$). This wave number of maximum amplification factor will dominate the first stage of the dynamics which is called the spinodal decomposition; this explains in particular why the homogeneous domains appear at length scales close to $L = \lambda_{C-H}/2 = \pi/q_{C-H}$, half the wave length associated with the instability. For longer times, interfaces separating each

domain interact through Ostwald ripening or coarsening, causing $\langle L \rangle$ to change slowly toward higher values.

III. CAHN-HILLIARD EQUATION

A. On the periodic solutions of Cahn-Hilliard equation

When the equation is studied for a constant negative ε , via a rescaling of u (as $\sqrt{-\varepsilon}u$), position \mathbf{r} (as $\mathbf{r}/\sqrt{-\varepsilon}$) and time (as $t/|\varepsilon|^2$), we observe that we could restrict the dynamics to the case $\varepsilon = -1$. So later on, we will study the equation

$$\frac{\partial u}{\partial t}(\mathbf{r}, t) = \nabla^2 \left(-\frac{1}{2}u + 2u^3 - \nabla^2 u \right) \quad (7)$$

In 1D, a family of stationary solution of this nonlinear dynamics is the so-called interface-lattice solutions (or soliton-lattice), which writes :

$$U_{k,\varepsilon}(x) = k\Delta \text{Sn}\left(\frac{x}{\xi}, k\right) \text{ with } \xi = \Delta^{-1} = \sqrt{2(k^2 + 1)} \quad (8)$$

where $\text{Sn}(x, k)$ is the Jacobian elliptic function sine-amplitude, or cnoidal mode. This family of solutions is parametrized by the Jacobian modulus $k \in [0, 1]$, or "segregation parameter". These solutions describe periodic patterns of period

$$\lambda = 4K(k)\xi, \text{ where } K(k) = \int_0^{\frac{\pi}{2}} \frac{dt}{\sqrt{1 - k^2 \sin^2 t}} \quad (9)$$

is the complete Jacobian elliptic integral of the first kind. $K(k)$ together with k , characterize the segregation, defined as the ratio between the size of the homogeneous domains, $L = \lambda/2$, and the width of the interface separating them, 2ξ . The equation (9) and the relation $\xi = \Delta^{-1}$ enable to rewrite this family as :

$$U_{k,\lambda}(x) = \frac{4K(k) \cdot k}{\lambda} \text{Sn}\left(\frac{4K(k)}{\lambda}x, k\right). \quad (10)$$

and using equations (8) and (9), we find that for a stationary solution, λ , and k have to be related one another through the following implicit equation (or the state equation) :

$$\lambda^2 = 2(1 + k^2) (4K(k))^2. \quad (11)$$

Using equations (10) we can compute the free energy per unit length

$$F_{GL}(k, \lambda) =$$

$$\left(\frac{4K}{\lambda}\right)^2 \left[\frac{-\varepsilon}{4} \left(1 - \frac{E}{K}\right) + \left(\frac{1+2k^2}{6} - \frac{E}{6K}(1+k^2) \right) \left(\frac{4K}{\lambda}\right)^2 \right]$$

where $E(k)$ is the complete Jacobian elliptic integral of the second kind. The absolute minimum for $F_{GL}(k, \lambda)$ is for $k = 1$ and $\lambda = \infty$, i.e. for complete segregation with a single interface.

B. Stationary States of the Cahn-Hilliard Dynamics

The dynamics starts initially with $k = 0$, for which $U(x)$ describes a sinusoidal modulation of almost vanishing amplitude around the high temperature homogenous stationary solution $u = 0$

$$U_{k \rightarrow 0, \varepsilon}(x) = k \sqrt{\frac{1}{2}} \sin\left(\sqrt{\frac{1}{2}}x\right) \quad (12)$$

$$= k \frac{2\pi}{\lambda_{C-H}} \sin\left(\frac{2\pi}{\lambda_{C-H}}x\right) = k q_{C-H} \sin(qx)$$

The spinodal decomposition dynamics will saturate and reach a stationary state which is a periodic pattern with a finite domain length (weak segregation regime) for which $\lambda = \lambda_{C-H}$, and $k = k_0^s = 0.687$ so as to satisfy (11), i.e k is solution of the implicit equation :

$$2(1 + k_0^{s2})K(k_0^s)^2 = -\frac{\varepsilon_0 \lambda_{C-H}^2}{16} = \pi^2 . \quad (13)$$

The amplitude of the modulation is then $k_0^s \Delta_0^s = 0.400 \sqrt{-\varepsilon_0}$, which is different from u_b .

Using linear stability analysis, Langer has shown that the stationary profile thus obtained, $u_0(x) = U_{k_0^s, \lambda_{C-H}}(x)$, is destroyed by stochastic thermal fluctuations [16]. He has identified the most unstable mode as an "antiferro" mode, leading to an infinite cascade of period doubling [17]. Disorder of the pattern is also a cause of Ostwald ripening : if the periodicity of the interface-lattice is broken, either when the distance between these interfaces or when the bulk value in the different domains become non-constant, coarsening is triggered by diffusion of matter between neighboring domains : big domains will then absorb smaller ones [18].

C. Coarsening

When considering the C-H equation 4 as a diffusion equation, P. Politi and C. Misbah have shown that there should be coarsening as long as $d\nu/d\lambda$ is positive, where ν is the amplitude of the modulation and λ its [3]. As in Cahn-Hilliard dynamics

$$\nu = k\Delta = k\sqrt{\frac{-\varepsilon}{2(k^2 + 1)}} \quad \text{and} \quad \lambda = 4K(k)\xi = 4K(k)\sqrt{\frac{2(k^2 + 1)}{-\varepsilon}}$$

are two growing functions of the parameter k , this diffusion coefficient will always remain positive and coarsening will proceed until $\lambda \rightarrow \infty$ (as in Fig. 4 left).

FIG. 4: Left : evolution of the amplitude of the modulation of the stationary states as a function of the period, in the cases of a Cahn-Hilliard dynamics. As $d\nu/d\lambda$ is always positive, the pattern will ripen until all the interfaces disappear but one (note that as $d\nu/d\lambda \rightarrow 0$, there is a slowing down of the coarsening process). Right, a model where $d\nu/d\lambda$ changes sign : the coarsening will then be interrupted.

When looking at Figure (1), one can see that the bulk energy is decreasing when the amplitude varies from $\nu = 0$ to $\nu = \pm\frac{\sqrt{-\varepsilon}}{2}$, that is, when the segregation increase. Meanwhile, the interfacial energy is proportional to the period, we finally get that the total energy decreases when the period of the stationary solutions gets longer and longer. But for other dynamics (as in Fig. 4 right), $d\nu/d\lambda$ can change of sign as we will see in the following : segregation then remains partial. P. Politi et C. Misbah speak then of interrupted coarsening.

IV. OONO'S MODEL

A. Derivation of the model

We would like to work out the period of modulated phase systems for which there is a competition between two types of interactions: a short-range interaction which tends to

make the system more homogeneous together with a long-range one, or a non-local one, which prefers proliferation of domain walls. This competition results in a microphase separation with a preferred mesoscopic length scale. These systems forming a super-crystal can be studied using a modified Landau-Ginzburg approach, derived from Cahn-Hilliard equation and of practical use for numerical simulations [4]:

$$\frac{\partial u}{\partial t} = \left(\nabla^2 \frac{\delta F_{GL}(u)}{\delta u} \right) - \beta^2 u = \nabla^2 \left(\frac{-1}{2} u + 2u^3 - \nabla^2 u \right) - \left(\frac{\beta}{4} \right)^2 u. \quad (14)$$

The $-\beta^2 u$ term models in the Cahn-Hilliard equation the long-range interactions, which prevents the formation of macroscopic domains and favors the modulation. We will see that the inclusion of such a term, following Oono, enables to describe the behavior of modulated systems at T much lower than T_c . If we suppose, for example, that in a 3D problem, the long-range interaction decreases like $\frac{1}{r}$, the full free energy density writes

$$\begin{aligned} F(u) &= F_{GL} + F_{int} \\ &= \frac{1}{2} (\nabla u(r))^2 + \frac{-1}{4} u^2(r) + \frac{1}{2} u^4(r) + \int u(r') g(r', r) u(r) dr', \end{aligned} \quad (15)$$

where $g(r', r) = 4\pi \frac{(\frac{\beta}{4})^2}{|r'-r|}$ in D=3, or $|x' - x|$ in D=1. The long-range interaction $g(r', r)$ corresponds to a repulsive interaction when $u(r')$ and $u(r)$ are of the same sign : thus it favors the formation of interphases. If we want to study the dynamic of this phase separation, we use the Cahn-Hilliard equation :

$$\begin{aligned} \frac{\partial u}{\partial t} &= \nabla_r^2 \left(\frac{\delta F(u)}{\delta u} \right) \\ &= \nabla_r^2 \left(\frac{-1}{2} u + 2u^3 - \nabla^2 u + \int u(r') g(r', r) dr' \right). \end{aligned} \quad (16)$$

If one recalls that $\frac{-1}{|r'-r|}$ is the Green's function associated with the Laplacian operator ∇_r^2 in 3D, the preceding equation then transforms into

$$\begin{aligned} \nabla_r^2 \left(\int u(r') g(r', r) dr' \right) &= \int u(r') \nabla_r^2 g(r', r) dr' \\ &= - \left(\frac{\beta}{4} \right)^2 \int u(r') \delta(r', r) dr' = - \left(\frac{\beta}{4} \right)^2 u(r). \end{aligned} \quad (17)$$

which leads to equation (14). Note that, even with the new term added by Oono to the usual Cahn-Hilliard dynamics, this equation remains in the class of the conservative models, as it derives from a equation of conservation. Note also that the free energy F_{int} is infinite if $u(r)$ is of the same sign in a macroscopic domain.

B. Linear stability analysis for Oono's model

If we look at the linear stability analysis of the homogenous solution $u = 0$, we found almost the same results as in the original work of Cahn and Hilliard, except that the amplification factor $\sigma(\mathbf{q})$ now write:

$$\sigma(\mathbf{q}) = \left(\frac{1}{2} - \mathbf{q}^2\right)\mathbf{q}^2 - \left(\frac{\beta}{4}\right)^2$$

This shows immediately that $u = 0$ is linearly unstable if $\beta < 1$, with a band of unstable Fourier modes $0.5\sqrt{1 - \sqrt{1 - \beta^2}} < q < 0.5\sqrt{1 + \sqrt{1 - \beta^2}}$ (for which $\sigma(\mathbf{q}) > 0$). The most unstable mode is for $q_{C-H} = 0.5$ like in the simplest Cahn-Hilliard model(4). Therefore, during the initial stage of the dynamics, the spinodal decomposition the homogeneous domains appear at length scales close to $L = 2\pi$, as in the usual Cahn Hilliard dynamics. But one sees that, contrary to the simple Cahn-Hilliard case, the long wave length modulations are now stable as $\sigma(\mathbf{q}) < 0$ for $q < 0.5\sqrt{1 - \sqrt{1 - \beta^2}}$. This explains qualitatively why, for any finite value of β , the dynamics will end in a micro segregated regime, as it is observed numerically and as we will discuss quantitatively below.

It has been noticed in different models [20] that, if the interaction responsible of the modulation is local (i.e. described in the free energy by local terms only, like $-(\nabla u)^2$ in the Swift Hohenberg model), then for low temperature or small β , the macrosegregated regime (one unique interface) will be energetically favored compared to the microphase separation.

However, in this model by Oono, because the interaction is long range (i.e. non-local), no matter how small is β , there will always be a finite region around $q = 0$ where $\sigma(\mathbf{q}) < 0$. Indeed, $\sigma(\mathbf{0}) = -\left(\frac{\beta}{4}\right)^2$. Consequently, a modulated phase should always end the dynamics[21].

C. Direct minimization of the free energy

For D=1, the contribution of the long-range interaction to the free energy per unit length is [22]

$$\mathcal{F}_{int} = \frac{1}{\lambda} \int_0^\lambda F_{int} dr = \frac{-\beta^2}{2\lambda} \int_0^{\frac{\lambda}{2}} \int_0^{\frac{\lambda}{2}} \Psi(r') |r' - r| \Psi(r) dr dr'.$$

When using as ansatz the family of interface-lattice solutions $U_{k,\lambda}(x)$, we then obtain

$$\begin{aligned}\mathcal{F}_{int} &= \frac{-\beta^2}{2\lambda} \int_0^{\frac{\lambda}{2}} \int_0^{\frac{\lambda}{2}} k^2 \left(\frac{4K}{\lambda}\right)^2 |r' - r| \operatorname{Sn}\left(\frac{4K(k)}{\lambda}r, k\right) \operatorname{Sn}\left(\frac{4K(k)}{\lambda}r', k\right) dr dr' \\ &= \frac{\pi}{K} \frac{-\beta^2}{8} \int_0^{2K} \int_0^{2K} k^2 |x' - x| \operatorname{Sn}(x, k) \operatorname{Sn}(x', k) dx dx'.\end{aligned}$$

Thus, this contribution is independent of λ and the only minimization is with respect to k . Consequently, the minimization with respect to λ concerns only F_{GL} and enables to find λ as a function of k : $\lambda(k) = 8K \sqrt{\frac{1+k^2}{3} + \frac{k^2}{3(1-\frac{E}{K})}}$. And the minimization of the free energy $F_{GL}(k, \lambda(k)) + F_{int}(k)$ is simply with respect to a single variable k , which can be done numerically for different values of the interaction strength β^2 .

Figure 5 presents $\lambda(\beta^2)$ which scales like $(\beta^2)^{1/3}$.

FIG. 5: Graph of the stable period $\lambda(\beta^2)$ computed by minimizing the free energy $F_{GL}(k, \lambda(k)) + F_{int}(k, \beta^2)$ with respect to k . The result scales like $(\beta^2)^{1/3}$.

D. Stationary microsegregated patterns

The family (10) is not anymore an exact stationary solution of the dynamics (14) because of its last term. Nevertheless, it is a good candidate for an approximate solution (especially in the case of small β) and thus can be used as a tool for calculation using a solvability condition or Fredholm's alternative.

Indeed, we can write deviation from a given periodic stationary profile of period λ as $u(x, t) = u_0(\phi(x, t)) + \varepsilon u_1(\phi(x, t)) + \dots$ where ε is a small parameter and u_0 is a periodic

function of the phase $\phi(x, t)$. For a steady state solution $\phi(x, t) = qx$ with $q = 2\pi/\lambda$. In the general case $\phi(x, t) = q(X, T)x$ where $X = \epsilon x$ and $T = \epsilon^2 t$ i.e. $q = \frac{\partial \phi}{\partial x}$ is now a slowly varying function of x and t .

$$\begin{aligned}\frac{\partial u}{\partial t} &= \frac{\partial u}{\partial \phi} \frac{\partial \phi}{\partial t} = \frac{\partial u}{\partial \phi} \frac{\partial \phi}{\partial T} \frac{dT}{dt} = \epsilon^2 \frac{\partial \phi}{\partial T} \frac{\partial u}{\partial \phi} \\ \frac{\partial u}{\partial x} &= \frac{\partial u}{\partial \phi} \frac{\partial \phi}{\partial x} = \frac{\partial u}{\partial \phi} \left(q + \frac{\partial \phi}{\partial X} \frac{dX}{dx} \right) = q \frac{\partial u}{\partial \phi} + \epsilon \frac{\partial u}{\partial X}\end{aligned}$$

If we denote $\Psi(X, T) = \epsilon \phi(x, t)$, then the local wave number is $q(X, T) = \frac{\partial \phi}{\partial x} = \frac{\partial \Psi}{\partial X}$ and

$$\begin{aligned}\frac{\partial}{\partial t} &= \epsilon \partial_T \Psi \partial_\phi \\ \frac{\partial}{\partial x} &= q \partial_\phi + \epsilon \frac{\partial q}{\partial X} \partial_q = q \partial_\phi + \epsilon \frac{\partial^2 \Psi}{\partial X^2} \partial_q\end{aligned}$$

$$\begin{aligned}\frac{\partial^2}{\partial x^2} &= q \frac{\partial}{\partial \phi} (q \partial_\phi + \epsilon \partial_{XX}^2 \Psi \partial_q) + \epsilon \partial_{XX}^2 \partial_q (q \partial_\phi + \epsilon \partial_{XX}^2 \Psi \partial_q) \\ \frac{\partial^2}{\partial x^2} &= q^2 \partial_{\phi\phi} + \epsilon \partial_{XX}^2 \Psi \partial_\phi + 2\epsilon \partial_{XX}^2 \Psi q \partial_q \partial_\phi \\ \frac{\partial^2}{\partial x^2} &= q^2 \partial_{\phi\phi} + \partial_{XX}^2 \Psi (1 + 2q \partial_q) \partial_\phi\end{aligned}$$

where we have kept only the first order terms in ϵ .

If we consider a stationary profile u_0 which satisfies (zero order equation):

$$q^2 \frac{\partial^2}{\partial \phi^2} \left(\frac{-1}{2} u_0 + 2u_0^3 - q^2 \frac{\partial^2}{\partial \phi^2} u_0 \right) - \left(\frac{\beta}{4} \right)^2 u_0 = 0$$

$$\text{i.e. } \frac{\partial}{\partial \phi} \left(\frac{-1}{2} u_0 + 2u_0^3 - q^2 \frac{\partial^2}{\partial \phi^2} u_0 \right) = \left(\frac{\beta}{4} \right)^2 w \text{ where } \partial_\phi w = q^{-2} u_0 \quad (18)$$

Oono's equation (14) becomes then at order one in ϵ

$$\epsilon \partial_T \Psi \partial_\phi u_0 = \epsilon \mathcal{N}_0(u_1) + \epsilon \mathcal{N}_1(u_0) \text{ where}$$

$$\begin{aligned}\mathcal{N}_0(u_1) &= q^2 \frac{\partial^2}{\partial \phi^2} \left(\frac{-1}{2} u_1 + 6u_0^2 u_1 - q^2 \frac{\partial^2}{\partial \phi^2} u_1 \right) - \left(\frac{\beta}{4} \right)^2 u_1 \\ &= q^2 \frac{\partial^2}{\partial \phi^2} \mathcal{L}(u_1) - \left(\frac{\beta}{4} \right)^2 u_1 \text{ and}\end{aligned}$$

$$\begin{aligned}
\mathcal{N}_1(u_0) &= \partial_{XX}^2 \Psi (1 + 2q\partial_q) \partial_\phi \left(\frac{-1}{2} u_0 + 2u_0^3 - q^2 \frac{\partial^2}{\partial \phi^2} u_0 \right) \\
&\quad - q^2 \frac{\partial^2}{\partial \phi^2} (\partial_{XX}^2 \Psi (1 + 2q\partial_q) \partial_\phi u_0) \\
&= \left(\frac{\beta}{4} \right)^2 \partial_{XX}^2 \Psi (1 + 2q\partial_q) w - q^2 \frac{\partial^2}{\partial \phi^2} (\partial_{XX}^2 \Psi (1 + 2q\partial_q) \partial_\phi u_0)
\end{aligned}$$

where we have used $\partial_\phi w = q^{-2} u_0$ and equation (18) to simplify $\mathcal{N}_1(u_0)$. So Oono's equation (14) writes

$$\begin{aligned}
&\epsilon \partial_T \Psi \partial_\phi u_0 - \left(\frac{\beta}{4} \right)^2 \partial_{XX}^2 \Psi (1 + 2q\partial_q) w \tag{19} \\
&+ q^2 \partial_{XX}^2 \Psi \frac{\partial^2}{\partial \phi^2} ((1 + 2q\partial_q) \partial_\phi u_0) = q^2 \frac{\partial^2}{\partial \phi^2} \mathcal{L}(u_1) - \left(\frac{\beta}{4} \right)^2 u_1
\end{aligned}$$

E. Stability of stationary microsegregated patterns

A necessary condition for a solution to exist is that the left-hand side of the system is orthogonal to the kernel of the adjoint operator $\mathcal{N}_0^\dagger = \left(q^2 \partial_{\phi\phi} \mathcal{L} - \left(\frac{\beta}{4} \right)^2 Id \right)^\dagger$; if $v \in \text{Ker} \left(q^2 \partial_{\phi\phi} \mathcal{L} - \left(\frac{\beta}{4} \right)^2 Id \right)^\dagger$ then the solvability condition (or Fredholm alternative) writes:

$$\langle v | \partial_T \Psi \partial_\phi u_0 - \mathcal{N}_1(u_0) \rangle = \langle v | \mathcal{N}_0(u_1) \rangle = 0$$

As for any v we have

$$\begin{aligned}
&\langle v | q^2 \frac{\partial^2}{\partial \phi^2} \left(\frac{-1}{2} u_1 + 6u_0^2 u_1 - q^2 \frac{\partial^2}{\partial \phi^2} u_1 \right) - \left(\frac{\beta}{4} \right)^2 u_1 \rangle \\
&= \langle q^2 \frac{\partial^2}{\partial \phi^2} v | \frac{-1}{2} + 6u_0^2 - q^2 \frac{\partial^2}{\partial \phi^2} \rangle u_1 \rangle - \left(\frac{\beta}{4} \right)^2 \langle v | u_1 \rangle \\
&= \langle q^2 \left(\frac{-1}{2} + 6u_0^2 - q^2 \frac{\partial^2}{\partial \phi^2} \right) \partial_{\phi\phi} v | u_1 \rangle - \left(\frac{\beta}{4} \right)^2 \langle v | u_1 \rangle
\end{aligned}$$

this adjoint operator writes :

$$\mathcal{N}_0^\dagger = \left(q^2 \partial_{\phi\phi} \mathcal{L} - \left(\frac{\beta}{4} \right)^2 Id \right)^\dagger = q^2 \left(\frac{-1}{2} + 6u_0^2 - q^2 \frac{\partial^2}{\partial \phi^2} \right) \partial_{\phi\phi} - \left(\frac{\beta}{4} \right)^2$$

If $v \in \text{Ker} \mathcal{N}_0^\dagger$, we can define \tilde{u} such that $q^2 \partial_{\phi\phi} v = \tilde{u}$ and which satisfies

$$q^2 \frac{\partial^2}{\partial \phi^2} \left(\frac{-1}{2} \tilde{u} + 6u_0^2 \tilde{u} - q^2 \frac{\partial^2}{\partial \phi^2} \tilde{u} \right) = q^2 \left(\frac{\beta}{4} \right)^2 \partial_{\phi\phi} v = \left(\frac{\beta}{4} \right)^2 \tilde{u}. \tag{20}$$

So \tilde{u} is solution of $\frac{-1}{2} \tilde{u} + 6u_0^2 \tilde{u} - q^2 \frac{\partial^2}{\partial \phi^2} \tilde{u} = \left(\frac{\beta}{4} \right)^2 v$.

Using equation (18), we thus find that v defined by

$$q^2 \partial_{\phi\phi} v (= \tilde{u}) = \partial_{\phi} u_0 \text{ is an element of } \text{Ker} \left(q^2 \partial_{\phi\phi} \mathcal{L} - \left(\frac{\beta}{4} \right)^2 Id \right)^{\dagger}.$$

As a consequence, the diffusion equation writes

$$\epsilon \partial_T \Psi = \frac{-q^2 \langle v | \frac{\partial^2}{\partial \phi^2} ((1 + 2q\partial_q) \partial_{\phi} u_0) \rangle + \langle v | \left(\frac{\beta}{4} \right)^2 (1 + 2q\partial_q) w \rangle}{\langle v | \partial_{\phi} u_0 \rangle} \partial_{XX}^2 \Psi$$

As $q^2 \partial_{\phi} w = u_0$ and $q^2 \partial_{\phi\phi} v = \partial_{\phi} u_0$ we get the equality

$$v = w.$$

$$\begin{aligned} \text{So } \langle v | \partial_{\phi} u_0 \rangle &= - \langle \partial_{\phi} v | u_0 \rangle = - \langle \partial_{\phi} w | u_0 \rangle \\ &= -q^{-2} \langle u_0 | u_0 \rangle \end{aligned}$$

and consequently equation (19) is a diffusion equation

$$\begin{aligned} \epsilon \partial_T \Psi &= D \partial_{XX}^2 \Psi \\ \epsilon \partial_T \Psi &= q^2 \frac{\partial_q \langle q (\partial_{\phi} u_0)^2 \rangle - \left(\frac{\beta}{4} \right)^2 \partial_q \langle q w^2 \rangle}{\langle u_0^2 \rangle} \partial_{XX}^2 \Psi \end{aligned}$$

V. CONCLUSION

As long as the diffusion coefficient is negative (due to the $\langle \partial_k u_0 | ((1 + 2q\partial_q) \partial_{\phi} u_0) \rangle = \partial_q \langle q (\partial_{\phi} u_0)^2 \rangle$ term), the coarsening process goes on, in order to minimize interfacial energy. But, due to its second part in β^2 , the diffusion coefficient will vanishe and thus the coarsening will be interrupted at a finite length scale.

Acknowledgment

The authors would like to thank Dr. Chaouqi Misbah (LIPhy, Grenoble) for fruitful discussions and an invitation in Grenoble where part of this work was done.

-
- [1] "Domain Shapes and Patterns: The Phenomenology of Modulated Phases" M. Seul and D. Andelman, Science 267, 476 (1995).

- [2] "Semiconducting Block Copolymers for Self-Assembled Photovoltaic Devices" G. Hadziioannou, *MRS Bulletin* 27, 456 (2002).
- [3] "When does coarsening occur in the dynamics of one-dimensional fronts?" P. Politi and C. Misbah, *Phys. Rev. Lett.* 92, 090601 (2004).
- [4] "Computationally efficient modeling of ordering of quenched phases" Y. Oono and S. Puri, *Phys. Rev. Lett.* 58, 836 (1987)
- [5] "Computationally efficient modeling of block copolymer and Benard pattern formations" Y. Oono and Y. Shiwa, *Mod. Phys. Lett. B* 1, 49 (1987).
- [6] "Theory of dynamical critical phenomena" P.C. Hohenberg et B.I. Halperin, *Rev. Mod. Phys.* 49, 435 (1977). See also "Pattern formation out of equilibrium" M.C. Cross et P.C. Hohenberg, *Rev. Mod. Phys.* 65, 851 (1993).
- [7] J.D. Gunton, M. San Miguel et P.S. Sahni, in *Phase Transition et Critical Phenomena*, edited by C. Domb et J.L. Lebowitz (Academic, London, 1983), Vol. 8, p. 267.
- [8] "A Solid Solution Model for Inhomogeneous Systems" M. Hillert, *Acta Met.* 9, 525 (1961).
- [9] "Free Energy of a Nonuniform System. I. Interfacial Free Energy" J.W. Cahn et J.E. Hilliard, *J. Chem. Phys.* 28, 258 (1958). "Phase Separation by Spinodal Decomposition in Isotropic Systems" *J. Chem. Phys.* 42, 93 (1965).
- [10] "Interface dynamics in Liquid crystals" C. Chevillard, M. Clerc, P. Coulet et J.M. Gilli, *Eur. Phys. J. E* 1, 179 (2000).
- [11] "Mixxing of solids" Y. Oyama, *Bull. Inst. Phys. Chem. Res. Rep.* 5, 600 (1939). English translation S. S. Weidenbaum, 1958, *Adv. Chem. Eng.* 2, 211 (1958).
- [12] "Segregation of Granular Mixtures in a Rotating Drum" S. Puri et H. Hayakawa, *Advances in Complex Systems*, Vol. 4, No. 4 (2001) 469-479 .
- [13] "Sand ripples in an oscillating annular sand–water cell " M.A. Scherer, F. Melo et M. Marder, *Phys. Fluids* 11, 58 (1999).
- [14] "Dynamical evolution of sand ripples under water" A. Stegner et J.E. Wesfreid, *Phys. Rev. E* 60, R3487 (1999).
- [15] "Early Stage of Spinodal Decomposition in 2D" S. Joly, A. Raquois, F. Paris, B. Hamdoun, L. Auvray, D. Ausserre et Y. Gallot, *Phys. Rev. Lett.* 77, 4394 (1996).
- [16] "Theory of spinodal decomposition in alloys" J.S. Langer, *Annals of Physics* 65, 53 (1971).
- [17] "Coalescence in the 1D Cahn–Hilliard model" S. Villain-Guillot , *J. Phys. A: Math. Gen.* 37,

6929 (2004).

- [18] "Bubbles interaction in Cahn-Hilliard equation" Calisto, H., Clerc, M.G., Rojas R. & Tirapegui, E., *Phys. Rev. Lett.* **85**, 3805 (2000).
- [19] "Coarsening dynamics of the one-dimensional Cahn-Hilliard model" Argentina, M., Clerc, M.G., Rojas, R. & Tirapegui, E., *Phys. Rev. E* **71**, 046210 (2005).
- [20] "Generalized Ginzburg-Landau theory for nonuniform FFLO superconductors" A.I Buzdin and H. Kachkachi, *Phys. Lett. A* **225** 341 (1997).
- [21] "Phase transitions in Langmuir monolayers of polar molecules" D. Andelman, F. Brochard and J.-F. Joanny, *J. Chem. Phys.* **86**, 3673, (1987).
- [22] "Dynamics of phase separation in block copolymer melts" F. Liu and N. Goldenfeld, *Phys. Rev. A* **39**, 4805 (1989).