

1D Cahn-Hilliard equation : Ostwald ripening and modulated phase systems

Simon Villain-Guillot

*Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux I,
351 cours de la Libération 33405 Talence Cedex, France **

Abstract

Using an approximate analytical solution of the Cahn-Hilliard equation describing the coalescence during a first order phase transition, we compute the characteristic time for one step of period doubling in Langer's self similar scenario for Ostwald ripening. As an application, we compute the thermodynamically stable period of a 1D modulated phase pattern.

*Electronic address: s.villain@cpmoh.u-bordeaux1.fr

I. INTRODUCTION

When a homogenous system departs suddenly from equilibrium, it will spontaneously segregate into two different states, thermodynamically more stable.

This process can either initiate via a nucleation process, where an energy barrier has to be crossed, or via a spinodal decomposition when the system is led into a linearly unstable configuration. In this latter case, the leading instability selects a modulation of the order parameter at a well defined length scale. This instability will grow and, due to nonlinearity, saturates. The resulting micro-segregated pattern is composed of well defined interfaces delimiting monophasic domains containing one of the two stable phases. These interfaces will then interact with each other and coalesce, during a much slower, self-inhibiting process, where the number of domains diminishes whereas their typical size increases, ending with the formation of either a micro-segregated complex pattern [1], or a single interface separating two semi infinite domains, one for each new stable phase (macro-segregation).

Hillert[2], Cahn and Hilliard[3] have proposed a model equation describing the segregation for a binary mixture. This model, known as the Cahn-Hilliard equation (C-H later on), belongs to the Model B class in Hohenberg and Halperin's classification [4]. It is a standard model for phase transition with conserved quantities and has applications to phase transition in alloys [2], binary mixtures[5], vapor condensation [6] and liquid crystals[7], segregation of granular mixtures in a rotating drum[8], or formation of sand ripples [9, 10].

In this article, by spinodal decomposition, we refer to the first stage of the dynamics only, while coarsening or Ostwald ripening will denote the second stage. Although this coarsening dynamics is in fact already present, its influence can be neglected during the first stage of the process.

An important activity has been devoted to the description of the dynamics of phase transition, using experiments, numerical simulations [11] or scaling methods [12]. The late stage of the dynamics, where the Ostwald ripening dominates, exhibits "dynamical scaling" : the dynamics presents a self-similar evolution where time enters only through a length scale $L(t)$, associated with a typical length of the domains. This scaling argument gives the law $L(t) \sim t^{1/3}$ for spatial dimensions greater than one and a logarithmic behavior in $D=1$.

This last stage, as observed in two-dimensional demixion of copolymers[13] and as suggested initially by Langer[14], can be described as a process of synchronous fusion and evaporation of domains, spatially alternated. It corresponds to the evolution that breaks the least the symmetries of the pattern. This observation motivated our work and the aim of this article is to make use of a one dimensional ansatz to describe quantitatively the ideal coalescence process. This ansatz is in the form of a one parameter family of symmetric profiles which interpolates between two stationary states composed of homogeneous domains of length λ and 2λ . It allows in 1D to describe a self similar sequence of coalescence and evaporation of domains (or of their dual counterparts, the interfaces), starting from the periodic micro-segregated state which ends the spinodal decomposition dynamics, and leading continuously to either a single interface, or a stable 1D modulated phase.

The paper is organized as followed: part 2 will focus on the first part of the dynamics, i.e. spinodal decomposition. We will reproduce briefly the original derivation by Cahn and Hilliard, restricting ourselves to the one dimensional case, mainly to fix the notations (part 2.1). In part 2.2, a family of symmetric solutions of the Ginzburg-Landau equation will be used to study the non linear part of dynamics and in part 2.3 we will identify all the intermediate symmetric stationary states of the (C-H) dynamics. Then in part 3, we will turn to Ostwald ripening : in part 3.1, a non-symmetric family of solutions of the (G-L) equation is used to construct a continuous interpolation between two consecutive symmetric stationary states. After a study of the energy landscape associated with this ansatz (part 3.2), we will compute in part 3.3 the characteristic time associated with one step of coalescence : we will recover the 1D logarithmic law. Before concluding, as an application in part 4, our ansatz will be used, in the case of micro-segregation, to compute the period of the final thermodynamically stable modulated pattern.

II. THE CAHN-HILLIARD MODEL

A. Linear stability Analysis

The Cahn-Hilliard (or Conservative Time Dependant Ginzburg Landau) equation is a modified diffusion equation for the scalar order parameter Ψ , which reads in its dimensionless form:

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

The real order parameter can correspond to the dimensionless magnetization in Ising ferromagnet, to the fluctuation of density of a fluid around its mean value during a phase separation or to the local concentration of one of the components of a binary solution. ε is the dimensionless control parameter of the system ; it is often identified to the reduced temperature ($\varepsilon = \frac{T-T_c}{T_c}$ where T_c is the critical temperature of the first order phase transition). This equation, first derived by Cahn and Hilliard, has also been retrieved by Langer[14] from microscopic considerations. A conservative noise can be added to account for thermal fluctuations [15], but in this article, we will only consider the noiseless (C-H) equation.

It admits homogeneous stationary solutions which are extrema of the symmetric Landau potential $V(\Psi) = \frac{\varepsilon}{4}\Psi^2 + \frac{1}{2}\Psi^4$. For positive ε , there is only one homogenous solution $\Psi = 0$ which is linearly stable. A pitchfork bifurcation can be experienced when quenching the system from a positive reduced temperature ε to a negative one : the $\Psi = 0$ solution becomes unstable ; two other symmetric stable solutions appear $\Psi = \pm \frac{\sqrt{-\varepsilon}}{2}$.

Spinodal decomposition is the dynamics resulting of such a quench. Cahn and Hilliard have studied the early times of this dynamics by linearizing equation (1) around $\Psi = 0$ (i.e. neglecting the non linear term Ψ^3). Considering Ψ as a sum of Fourier modes:

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

where $\Psi_{\mathbf{q}}$ is the Fourier coefficient at $t = 0$, they obtained for the amplification factor $\sigma(\mathbf{q})$:

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

This shows immediately that $\Psi = 0$ is linearly stable for $\varepsilon > 0$ while a band of Fourier modes are unstable for negative ε , since $\sigma(\mathbf{q}) > 0$ for $0 < q < \sqrt{(-\varepsilon/2)}$. Moreover, the

most unstable mode is for $q_{C-H} = \sqrt{-\varepsilon}/2$. This wave number of maximum amplification factor will dominate the first stage of the dynamics; 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, causing $\langle L \rangle$ to change slowly toward higher values [11, 16]

We will now use known results on non-homogeneous solutions of the (G-L) equation to study both the saturation of the spinodal decomposition and the coalescence.

B. Stationary States of the Cahn-Hilliard Dynamics : Symmetric Soliton Lattice Solutions

For $\varepsilon < 0$, there exists a whole family of solution of the one dimensional (G-L) equation :

$$\frac{\varepsilon}{2}\Psi + 2\Psi^3 - \nabla^2\Psi = 0 \quad (4)$$

These solutions, the so-called soliton-lattice solutions, are :

$$\Psi_{k,\varepsilon}(x) = k\Delta\text{Sn}\left(\frac{x}{\xi}, k\right) \text{ with } \xi = \Delta^{-1} = \sqrt{2\frac{k^2+1}{-\varepsilon}} \quad (5)$$

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

$$\lambda = 4K(k)\xi, \text{ where } K(k) = \int_0^{\frac{\pi}{2}} \frac{dt}{\sqrt{1 - k^2 \sin^2 t}} \quad (6)$$

is the complete Jacobian elliptic integral of the first kind. Together with k , it characterizes 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 (6) and the relation $\xi = \Delta^{-1}$, enable to rewrite this family as :

$$\Psi_{k,\lambda}(x) = \frac{4K(k) \cdot k}{\lambda} \text{Sn}\left(\frac{4K(k)}{\lambda}x, k\right). \quad (7)$$

As for $k = 1$, $\text{Sn}(x, 1) = \tanh(x)$, we recover the usual solution

$$\Psi_{1,\varepsilon}(x) = \frac{\sqrt{|\varepsilon|}}{2} \tanh\left(\frac{\sqrt{|\varepsilon|}}{2}x\right). \quad (8)$$

associated with a single interface (or soliton) of width $2/\sqrt{|\varepsilon|}$ that connected the two homogenous phases $\Psi = \pm \frac{\sqrt{-\varepsilon}}{2}$. Because $K(1)$ diverges, it corresponds to a strong, or macroscopic, segregation. In the opposite limit (weak segregation regime), $\Psi_{k,\varepsilon}(x)$ describes a sinusoidal modulation

$$\Psi_{k \rightarrow 0, \varepsilon}(x) = k \sqrt{\frac{|\varepsilon|}{2}} \sin\left(\sqrt{\frac{|\varepsilon|}{2}} x\right) = k \frac{2\pi}{\lambda} \sin\left(\frac{2\pi}{\lambda} x\right) = kq \sin(qx) \quad (9)$$

It will correspond to the Fourier mode $q = \frac{2\pi}{\lambda} = \frac{\sqrt{|\varepsilon|}}{2}$ of the initial white noise, with vanishing amplitude $\Psi_{\mathbf{q}} = kq$. Since experiences, numerical simulations and linear stability analysis show that λ , the spatial period of the pattern is constant during the whole spinodal decomposition process, we choose λ to coincide with the most instable wave length obtain with the Cahn Hilliard linear approach, $\lambda = \lambda_{C-H} = \frac{4\pi}{\sqrt{-\varepsilon_0}}$, where ε_0 is the quench temperature. We then obtain a one parameter family of profiles $\Psi^*(x, k) = \Psi_{k, \lambda_{C-H}}(x)$ which describe very well both the linear growth and the saturation of the spinodal decomposition [17]. Thus, the dynamics is now reduced to the time evolution of the single free parameter: $k(t)$. Using equations (5) and (6), we find that λ , k and ε are related to one another through the state equation

$$\varepsilon(k) = -2(1 + k^2) \left(\frac{4K(k)}{\lambda} \right)^2. \quad (10)$$

This implicit equation tells us that if we impose $\lambda = \lambda_{C-H}$, the dynamics can be reduced to the evolution of $\varepsilon(t)$, interpreted as the fictitious temperature or “local temperature” associated with the segregation parameter $k(t)$ which characterizes the pattern. This temperature can be extracted from the profile at any time, using the correspondence between ε and k of equation (10). For instance, at $t = 0$, the amplitude is small and we find that $k(t = 0) = \frac{\Psi_{\mathbf{q}} \lambda_{C-H}}{2\pi} \rightarrow 0$ and thus $\varepsilon^*(0) = 8\pi^2/\lambda^2$, different *a priori* from ε_0 ($\varepsilon^*(0) = \frac{\varepsilon_0}{2}$ for $\lambda = \lambda_{C-H}$) : the system is initially out of equilibrium

Somehow, the dynamics of (C-H) can be projected at first order onto a dynamics along the sub-family $\Psi^*(x, k) = \Psi_{k, \lambda_{C-H}}(x)$, which can be considered as an attractor of the solutions, i.e. the density profile of the system will evolve with time, staying always close to a function $\Psi^*(x, k)$. Thus, using equation (4), the (C-H) dynamics reduces to equation :

$$\frac{\partial \Psi^*}{\partial t}(\mathbf{r}, t) = \frac{\partial \Psi^*}{\partial k}(\mathbf{r}, k(t)) \frac{dk}{dt} = \frac{(\varepsilon_0 - \varepsilon(k))}{2} \nabla^2 \Psi^*. \quad (11)$$

The non linearity has now disappeared into $\Psi^*(x, k)$. Using a solubility condition, it is possible to transform this equation into a differential equation for $k(t)$ and to compute the

full non linear part of this dynamics (i.e. the saturation of the spinodal decomposition), which leads the system in a well defined stationary state [17].

C. Saturations of the Spinodal Decomposition Dynamics

The spinodal decomposition dynamics will saturate when the fictitious temperature $\varepsilon(t)$ will reach the real thermodynamic one, i.e. the quench temperature ε_0 ; that is, using equation of state (10) for $\lambda = \lambda_{C-H}$, when $k = k_0^s = 0.687$ solution of the implicit equation :

$$2(1 + k_0^{s2})K(k_0^s)^2 = -\frac{\varepsilon_0 \lambda_{C-H}^2}{16} = \pi^2 . \quad (12)$$

Using linear stability analysis, Langer has shown that the stationary profile thus obtained, $\Psi^*(x, k_0^s) = \Psi_{k_0^s, \lambda_{C-H}}(x)$, is destroyed by stochastic thermal fluctuations. He has identified the most instable mode as an "antiferro" mode, leading to a period doubling. The result of this destabilization is another periodic profile of alternate interfaces of period $\lambda = 2\lambda_{C-H}$, where the length of the domains is : $L = \lambda/2 = \lambda_{C-H}$. This means that the new stationary profile is given by $\Psi_{k_1^s, 2\lambda_{C-H}}(x)$, where $k_1^s = 0.985$ is solution of the implicit relation

$$2(1 + k_1^{s2})K(k_1^s)^2 = \frac{-\varepsilon_0 (2\lambda_{C-H})^2}{16} = 4\pi^2 . \quad (13)$$

Again, this new stationary profile turns out to be linearly instable with respect to an "antiferro" perturbation of period $4\lambda_{C-H}$.

Thus these families of profiles and instabilities enable to describe the one dimensional coarsening as a cascade of doubling process. Each of these successive intermediate profiles can be described by an element of the above family of soliton lattice $\Psi_{k_n^s, 2^n \times \lambda_{C-H}}(x)$. The sequence of associated segregation parameters $\{k_n^s\}$, are determined by the implicit relations

$$2(1 + k_n^{s2})K(k_n^s)^2 = -\frac{\varepsilon_0 (2^n \lambda_{C-H})^2}{16} = \pi^2 2^{2n} . \quad (14)$$

We have found numerically for the first of them [18]

$k_0^s = 0.6869795924$
$k_1^s = 0.9851675587$
$k_2^s = 0.99997210165$
$k_3^s = 0.9999999999027$

(15)

We see that $\{k_n^s\}$ converges toward $k_\infty^s = 1$ (single interface case), while the amplitude of the modulation converges toward $\frac{\sqrt{|\varepsilon_0|}}{2}$. For large n , we can conclude from the implicit relation (14) that the ratio of the domain size to the interface width characterized by $K(k_n^s)$ behaves as $\pi 2^{n-1}$ and $(k_n^s)^2 = 1 - 16 \exp(-\pi 2^n)$. Each of the stationary profiles

$$\Psi_n(x) = \Psi_{k_n^s, 2^n \lambda_{C-H}}(x) = \frac{\sqrt{|\varepsilon_0|} k_n^s K(k_n^s)}{2^n \pi} \text{Sn}\left(\frac{\sqrt{|\varepsilon_0|} K(k_n^s)}{2^n \pi} x, k_n^s\right) = \frac{\sqrt{|\varepsilon_0|} k_n^s}{\sqrt{2(1+k_n^{s2})}} \text{Sn}\left(\frac{\sqrt{|\varepsilon_0|} x}{\sqrt{2(1+k_n^{s2})}}, k_n^s\right) \quad (16)$$

is identically destroyed by the Langer "antiferro" instability .

III. 1D OSTWALD RIPENING

A. Non-symmetric soliton lattice profile as an ansatz for the 1D coarsening process

In order to describe one step of the coalescence process, i.e. the dynamics that starts from $\Psi_n(x)$ and ends with the profile $\Psi_{n+1}(x)$, we will use another family of equilibrium profiles [19], of period 2λ , solutions of (G-L) equation, which write:

$$\widehat{\psi}(x, k) = \frac{K(k)}{\lambda} + \widehat{\psi}^*(x, k) = \frac{K(k)}{\lambda} \frac{1 - k' - (1 + k')\sqrt{1 - k'} \text{Sn}(2x, k)}{\sqrt{1 - k'} \text{Sn}(2x, k) - 1} \quad (17)$$

where $k^2 + k'^2 = 1$. Note that $\langle \widehat{\psi}(x, k) \rangle = 0$ whereas the family $\widehat{\psi}^*(x, k)$ is solution of :

$$\nabla^2 \widehat{\psi}^* = \varepsilon(k) \frac{\widehat{\psi}^*}{2} + 2\widehat{\psi}^{*3} + \mu(k) \quad (18)$$

with $\mu(a, k) = (k^2 - 1) \left(\frac{2K(k)}{\lambda}\right)^3$ and $\varepsilon(k) = (k^2 - 5) \left(\frac{2K(k)}{\lambda}\right)^2$ (we have $\varepsilon(k) > \varepsilon_0$).

Using Gauss' transformation (or descending Landen transformation [20]), we can relate the soliton lattice of spatial period 2λ (and of modulus k) to the soliton lattice of period λ (and of modulus $\mu = \frac{1-k'}{1+k'}$) as follows

$$\widehat{\psi}\left(x - \frac{\lambda}{2}, k\right) + \widehat{\psi}\left(x + \frac{\lambda}{2}, k\right) = \frac{4\mu K(\mu)}{\lambda} \text{Sn}\left((4x + \lambda) \frac{K(\mu)}{\lambda}, \mu\right) \quad (19)$$

$$\widehat{\psi}\left(x - \frac{\lambda}{4}, k\right) + \widehat{\psi}\left(x + \frac{\lambda}{4}, k\right) = \frac{4kK(k)}{2\lambda} \text{Sn}\left(4x \frac{K(k)}{2\lambda}, k\right) \quad (20)$$

Note that $K(k) = (1 + \mu) K(\mu)$. As if $k = k_{n+1}^s$, $\mu = k_n^s$, we see that both the initial state $\Psi_n(x) = \Psi_{k_n^s, 2^n \lambda_{C-H}}(x)$ and the final state $\Psi_{n+1}(x) = \Psi_{k_{n+1}^s, 2^{n+1} \lambda_{C-H}}(x)$ of a step of the coalescence process can be describe, modulo a phase shift, by the same function :

$$\Phi(x, k, \phi) = \widehat{\psi}\left(x - (1 - \phi/2) \frac{\lambda}{2}, k\right) + \widehat{\psi}\left(x + (1 - \phi/2) \frac{\lambda}{2}, k\right) \quad (21)$$

with $k = k_{n+1}^s$ and $\lambda = 2^n \lambda_{C-H}$ (see also Figure 1). Therefore we can describe the coalescence by a transformation at constant segregation parameter k , while the degree of freedom ϕ , associated with the relative phase between the two profiles, evolves in time from 0 to 1 (or -1) according to the C-H dynamics [22].

B. Energy Landscape

In order to prove the usefulness of this ansatz, we have plot the energy averaged over a period, $\mathcal{F}_{GL}(\phi) = \int F_{GL}(\Phi(x, k, \phi)) dx$, as a function of the parameter ϕ , keeping k constant. We see in Figure 2 that the value $\phi = 0$ corresponds to a local maximum of energy, while $\phi = 1$ (or -1) is a minimum. Note that there is no energy barrier in this particular energy landscape, in agreement with linear stability analysis.

Using the properties of the ansatz, we can extract $\phi(t)$ from a numerical simulation. Indeed

$$\begin{aligned}\Phi\left(\frac{\lambda}{2}, k, \phi\right) &= \widehat{\psi}\left(\phi\frac{\lambda}{4}, k\right) + \widehat{\psi}\left(\lambda - \phi\frac{\lambda}{4}, k\right) = 2\widehat{\psi}\left(\phi\frac{\lambda}{4}, k\right) \\ \Phi\left(-\frac{\lambda}{2}, k, \phi\right) &= \widehat{\psi}\left(\phi\frac{\lambda}{4} - \lambda, k\right) + \widehat{\psi}\left(-\phi\frac{\lambda}{4}, k\right) = 2\widehat{\psi}\left(-\phi\frac{\lambda}{4}, k\right)\end{aligned}\quad (22)$$

For $\phi = 0$, $\Phi(\frac{\lambda}{2}) = \Phi(-\frac{\lambda}{2}) = \frac{2K}{\lambda} (k' - 1)$ while $\Phi(\frac{\lambda}{2}) = -\Phi(-\frac{\lambda}{2}) = \frac{2Kk}{\lambda}$ for $\phi = 1$. A $k = k_{n+1}^s$ is known, from $A(t) \in [0, 1]$ defined as follows

$$2A(t) = 1 - \frac{\Phi(\frac{\lambda}{2}, k, \phi(t))}{\Phi(-\frac{\lambda}{2}, k, \phi(t))} = \frac{4k'Sn(\phi\frac{K(k)}{2}, k)}{\sqrt{1-k'} + 2k'Sn(\phi\frac{K(k)}{2}, k) - k\sqrt{1+k'}Sn^2(\phi\frac{K(k)}{2}, k)}, \quad (23)$$

one can extract ϕ :

$$\phi(t) = \frac{2}{K(k)} \int_0^{\frac{k'(A-1) + \sqrt{A^2 + k'^2 - 2Ak'^2}}{kA\sqrt{1+k'}}} \frac{da}{\sqrt{1-k^2a^2}\sqrt{1-a^2}}. \quad (24)$$

One sees in Figure3 that the dynamics is dominated by the time required to leave a stationary state. Moreover, the dynamics ends when ϕ reaches 1 : we then have $\Phi = \Psi_{n+1}$ for which $\frac{\varepsilon_0}{2}\Psi_{n+1} + 2\Psi_{n+1}^3 - \nabla^2\Psi_{n+1} = 0$.

C. Linear stability analysis

If we look at the time evolution of the profile $\Phi(x, k_{n+1}^s, \phi)$, starting from the region $\phi = 0$, we can transform the (C-H) equation into a phase field equation, replacing $\frac{\partial}{\partial t} \Phi(x, k_{n+1}^s, \phi)$

by $\frac{\partial}{\partial \phi} \Phi(x, k_{n+1}^s, \phi(t)) \times \frac{d\phi}{dt}$ (with k fixed). The dynamics will then be similar to spinodal decomposition (eq. (11)), for ϕ growing initially as $\exp(t/\tau_n)$ and saturating later at $\phi = 1$.

In Figure 4 is plotted $\frac{\partial \Phi}{\partial \phi}(x, k_{n+1}^s) = \frac{\lambda}{4} \tilde{\Psi}_L(x, k_{n+1}^s)$ for $\phi = 0$, which corresponds to the most unstable mode founded in Langer's linear stability analysis and is characterized by the alternated growth and decrease of domains ("antiferro" mode) :

$$\tilde{\Psi}_L(x, k) = \hat{\psi}'(x - (1 - \phi/2)\frac{\lambda}{2}, k) - \hat{\psi}'(x + (1 - \phi/2)\frac{\lambda}{2}, k) \quad (25)$$

where

$$\hat{\psi}'(x, k) = k' \sqrt{1 - k'} \left(\frac{2K(k)}{\lambda} \right)^2 \frac{Cn(2x \frac{K(k)}{\lambda}, k) Dn(2x \frac{K(k)}{\lambda}, k)}{\left(1 - \sqrt{1 - k'} Sn(2x \frac{K(k)}{\lambda}, k) \right)^2} \quad (26)$$

verifies

$$\nabla^2 \hat{\psi}'(x, k) = \varepsilon(k) \frac{\hat{\psi}'(k, x)}{2} + 6 \hat{\psi}^{*2} \hat{\psi}'(k, x). \quad (27)$$

In order to describe the evolution of the phase $\phi(t)$ we linearize the Cahn-Hilliard dynamics around $\Psi_n(x) = \Phi(x, k_{n+1}^s, \phi = 0)$ inserting $\Psi(x, t) = \Psi_n(x) + \frac{\partial \Phi}{\partial \phi} \phi(t) = \Psi_n(x) + \frac{\lambda}{4} \tilde{\Psi}_L(x, k_{n+1}^s) \phi(t)$ into (1). We then have the following dynamics

$$\tilde{\Psi}_L \cdot \frac{d\phi}{dt} = \phi(t) \frac{\partial^2}{\partial x^2} \left(\frac{\varepsilon_0}{2} \tilde{\Psi}_L + 6 \Psi_n^2 \tilde{\Psi}_L - \nabla^2 \tilde{\Psi}_L \right) = \phi(t) \frac{\partial^2}{\partial x^2} \mathcal{L}(\tilde{\Psi}_L). \quad (28)$$

where \mathcal{L} is the Lamé operator. Even if this operator doesn't have simple (algebraic) exact eigenfunction of period $2\lambda_{C-H}$ [21], $\tilde{\Psi}_L(x, k, \phi)$, for $\phi = 0$ and $k = k_{n+1}^s$, happens nevertheless to be a good approximation for the eigenfunction of lowest eigenvalue [22]. Due to the concavity of $\mathcal{F}_{GL}(\phi)$ around $\phi = 0$, (see Figure 2), this eigenvalue will be negative, triggering a linear destabilization of the pattern Ψ_n and an exponential amplification of the perturbation, i.e. an exponential growth of the translation ϕ with time.

Indeed, using equation (18) we get

$$\nabla^2 \tilde{\Psi}_L = \nabla^2 [\hat{\psi}'_+ - \hat{\psi}'_-] = \frac{\varepsilon(k)}{2} \tilde{\Psi}_L + 6(\hat{\psi}_+^{*2} \hat{\psi}'_+ - \hat{\psi}_-^{*2} \hat{\psi}'_-). \quad (29)$$

So

$$\begin{aligned} \frac{\varepsilon_0}{2} \tilde{\Psi}_L + 6 \Psi_n^2 \tilde{\Psi}_L - \nabla^2 \tilde{\Psi}_L &= \frac{\varepsilon_0 - \varepsilon(k)}{2} \tilde{\Psi}_L + 6 \left(\hat{\psi}_-^{*2} \hat{\psi}'_+ - \hat{\psi}_+^{*2} \hat{\psi}'_- \right) \\ &+ 6 \left[\left(\frac{2K(k)}{\lambda} \right)^2 + 2 \left(\frac{2K(k)}{\lambda} (\hat{\psi}_+^* + \hat{\psi}_-^*) + \hat{\psi}_+^* \hat{\psi}_-^* \right) \right] (\hat{\psi}'_+ - \hat{\psi}'_-). \end{aligned} \quad (30)$$

It turns out that for $\phi = 0$,

$$\frac{2K(k)}{\lambda} \left(\hat{\psi}_+^* + \hat{\psi}_-^* \right) + \hat{\psi}_+^* \hat{\psi}_-^* = (k'^2 - 4) \left(\frac{K(k)}{\lambda} \right)^2$$

together with

$$\hat{\psi}_-^{*2} \hat{\psi}_+' - \hat{\psi}_+^{*2} \hat{\psi}_-' \simeq \left(4 - k'^2 - 4k' \right) \left(\frac{K(k)}{\lambda} \right)^2 (\hat{\psi}_+' - \hat{\psi}_-').$$

So finally

$$\frac{\varepsilon_0}{2} \tilde{\Psi}_L + 6\Psi_{i0}^{*2} \tilde{\Psi}_L - \nabla^2 \tilde{\Psi}_L \simeq -6k' \left(\frac{2K(k)}{\lambda} \right)^2 \tilde{\Psi}_L. \quad (31)$$

As the period associated with k_{n+1}^s is 2λ , equation (10) gives $\left(\frac{2K(k)}{\lambda} \right)^2 = -\frac{\varepsilon_0}{2(1+k^2)}$ and thus equation (28) can now be written in a simpler form, similar to equation (11) :

$$\tilde{\Psi}_L \cdot \frac{d\phi}{dt} = \varepsilon_0 \frac{3k'}{1+k^2} \phi(t) \frac{\partial^2}{\partial x^2} \tilde{\Psi}_L. \quad (32)$$

We recover that $\tilde{\Psi}_L$ is an eigenstate of Lamé equation with a negative eigenvalue $\frac{-3k'|\varepsilon_0|}{2-k'^2}$. This eigenvalue goes to zero as the coalescence progresses towards higher segregation.

The characteristic time for one step of period doubling is thus $\tau_n \simeq \frac{2}{3\varepsilon_0^2} \frac{2-k'^2}{k'}$ (the extra $\varepsilon_0/2$ comes from $\frac{\partial^2}{\partial x^2} \tilde{\Psi}_L$). As for small k' , $k' \simeq 4 \exp(-K(k))$, we have the following relationship between τ_n^{-1} and the period of the profile :

$$\tau_n^{-1} \simeq \frac{3}{4} \varepsilon_0^2 k' = 3\varepsilon_0^2 \exp(-K(k)) = 3\varepsilon_0^2 \exp(-2^{n-1}\pi) = 3\varepsilon_0^2 \exp\left(-\frac{\pi\lambda}{2\lambda_{C-H}}\right). \quad (33)$$

As $\ln \tau_n$ goes like a power of n , we can conclude that in $D = 1$, the size of the domain will evolve for long t as $\frac{2}{\pi} \lambda_{C-H} \ln(3\varepsilon_0^2 t)$.

IV. APPLICATION : MODULATED PHASE SYSTEMS

We can use the preceding ansatz 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 length scale [1]. These systems can be study using a modified Landau-Ginzburg approach, derived from Cahn-Hilliard equation and often use for numerical simulations [23]:

$$\frac{\partial \Psi}{\partial t} = \left(\nabla^2 \frac{\delta F_{GL}(\Psi)}{\delta \Psi} \right) - \beta^2 \Psi = \nabla^2 \left(\frac{\varepsilon_0}{2} \Psi + 2\Psi^3 - \nabla^2 \Psi \right) - \beta^2 \Psi. \quad (34)$$

$-\beta^2\Psi$ models in the Cahn-Hilliard equation the long-range interactions, which prevents the formation of macroscopic domains and favors the modulation. We could have chosen other ways of representing this long-range interaction, but the inclusion of such a term, following Oono, enables to describe the behavior of modulated systems at T much lower than T_c , as we will show below. 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

$$F(\Psi) = F_{GL} + F_{int} = \frac{1}{2}(\nabla\Psi(r))^2 + \frac{\varepsilon}{4}\Psi^2(r) + \frac{1}{2}\Psi^4(r) + \int \Psi(r')g(r',r)\Psi(r)dr', \quad (35)$$

where $g(r',r) = \frac{\beta^2}{|r'-r|}$. The long range interaction $g(r',r)$ corresponds to a repulsive interaction when $\Psi(r')$ and $\Psi(r)$ 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 :

$$\frac{\partial\Psi}{\partial t} = \nabla_r^2 \left(\frac{\delta F(\Psi)}{\delta\Psi} \right) = \nabla_r^2 \left(\frac{\varepsilon_0}{2}\Psi + 2\Psi^3 - \nabla^2\Psi + \int \Psi(r')g(r',r)dr' \right). \quad (36)$$

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

$$\nabla_r^2 \left(\int \Psi(r')g(r',r)dr' \right) = \int \Psi(r')\nabla_r^2 g(r',r)dr' = -\beta^2 \int \Psi(r')\delta(r',r)dr' = -\beta^2\Psi(r). \quad (37)$$

which leads to equation (34). The family (16) is not anymore an exact stationary solution of this dynamics. Nevertheless, $\Psi_n(x, k_n, 2^n\lambda_{C-H})$ is an approximate solution and thus can be use as a tool for the calculation using a solubility condition (i.e. if we project the dynamics on $\chi \in Ker(\frac{\partial^2}{\partial x^2}\mathcal{L})$). There exists a new sequence $\{k_n^o\}$ which satisfies $(\varepsilon^*(k_n^o) - \varepsilon_0) < \chi \mid \partial_{x^2}\Psi_{k_n^o} > +\beta^2 < \chi \mid \Psi_{k_n^o} \geq 0$ and which will characterize the new family of approximate stationary configuration. When looking at the linear stability analysis of these solutions, equation (1) now writes

$$\tilde{\Psi}_L \cdot \frac{d\phi}{dt} = \phi(t) \left(\frac{3\varepsilon_0 k'}{2 - k'^2} \frac{\partial^2}{\partial x^2} \tilde{\Psi}_L - \beta^2 \tilde{\Psi}_L \right). \quad (38)$$

The profile will become stable when the eigenvalue of this modified Lamé's equation become negative, i.e. for $\tau_n^{-1} < \beta^2$. This will take place for $3\varepsilon_0^2 \exp(-\frac{\pi\lambda}{2\lambda_{C-H}}) \simeq \beta^2$. The dynamics of period doubling will thus end with a thermodynamically stable 1D microseparated phase of period $\lambda = \frac{8}{\sqrt{-\varepsilon_0}} \ln(\frac{3\varepsilon_0^2}{\beta^2})$

V. DISCUSSION ON THE HYPOTHESIS AND CONCLUSION

We have shown that the choice of two ansatzs within the soliton-lattice family allows a reliable description of the one dimensional dynamics of both spinodal decomposition and Ostwald ripening. Contrary to [11], our ansatz relies on the hypothesis that during the first stage of the dynamics, the periodicity of the order parameter remains constant, while during each steps of the coarsening process, it is the parameter k which remains constant. In a sense, there are adiabatic ansatzs : the generation of higher harmonics is governed solely by the time evolution of $k(t)$ during the non linear saturation of the spinodal decomposition and later on solely by $\phi(t)$ during the Ostwald ripening. The validity of the assumptions have been investigated in details and checked numerically [17].

Our analytic method rely on the assumption that at each step of the dynamics, the system can be characterized by a specific spatial period : we need therefore to discuss how this approach is relevant to the general case where noise is present. We have noted numerically that, for the spinodal decomposition, the average size of the modulation is λ_{C-H} , with a deviation of less than one percent from the value predicted by the linear theory. It does not mean that, in a real system, each domain has a length scale of $L = \lambda_{C-H}/2$, but that the distribution of the domains' length will be centered around L . The coalescence events can be neglected during the initial growth of the amplitude of the modulation : as all the eigenvalues of the Lamé operator (28) are then positive, the dynamics remains within the ansatz subfamily $\Psi^*(x, k)$. Only after this initial growth has saturated, turns negative the lowest eigenvalue ; the coalescence process then starts, and dominates the forthcoming dynamics.

We have computed in this article the characteristic time associated with one step of ideal coalescence. By ideal coalescence, we mean a process which breaks as few symmetries as possible. In a real system, because of initial fluctuations in the periodicity of the pattern selected just after the quench, this instability will concern only region of finite size, where it choose a certain sublattice, or a range for ϕ (for example, ϕ varies from 0 to 1), while it is the opposite choice in the neighboring region (ϕ varies from 0 to -1). The global symmetry is thus recover on the overall (as in an antiferromagnet). During each step of the process, the width of the domains will locally double; but for the system as a whole, due to non synchronization between regions, the average length scale will vary continuously.

We have also shown that in a modified version of the Cahn-Hilliard dynamics, which take into account long range interactions, the computation of this lowest eigenvalue enables to compute that the spatial period of the thermodynamically stable modulated phase will be $\lambda = \frac{8}{\sqrt{-\varepsilon_0}} \ln(\frac{\varepsilon_0^2}{2\beta^2})$.

The use of the solubility technics combined with the choice of an adiabatic ansatz might be generalized to the study of other non linear dynamics. For instance, spinodal decomposition in superfluid Helium or Bose condensate has been argued to be described by a cubic-quintic non linear equation[24] ; in this particular case, one needs to retrieve a relevant soliton-like family of solution along which to compute the adiabatic dynamics. The same difficulties would arise as well when the method will be adapted to higher space dimensions as there is no equivalent to soliton lattice in 2D; the ansatzs (16) and (21) could however be used in a numerical simulation as tools for following the dynamics.

It might also be possible to extend this approach to non symmetric profile like the ones introduced in different contexts[19, 25]. Or for the cases of special quenches which are time periodic [26] or spatially periodic [27].

I would like to thanks Christophe Josserand, Avadh Saxena and David Andelman for fruitful discussions and Turab Lookman for bringing to me ref [23].

-
- [1] M. Seul and D. Andelman, *Science* **267**, 476 (1995).
 - [2] M. Hillert, *Acta Met.* **9**, 525 (1961).
 - [3] J.W. Cahn and J.E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
 - [4] P.C. Hohenberg and B.I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977). See also M.C. Cross and P.C. Hohenberg, *Rev. Mod. Phys.* **65**, 851 (1993). For a review, see J.D. Gunton, M. San Miguel and P.S. Sahni, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J.L. Lebowitz (Academic, London, 1983), Vol. 8, p. 267.
 - [5] C. Wagner, *Z. Electrochem.* **65**, 581 (1961).
 - [6] J.S. Langer, in *Solids Far From Equilibrium*, edited by C. Godrèche (Cambridge University Press, Cambridge, England 1992), pp. 297-363.
 - [7] C. Chevallard, M. Clerc, P. Couillet and J.M. Gilli, *Eur. Phys. J. E* **1**, 179 (2000).
 - [8] Y. Oyama, *Bull. Inst. Phys. Chem. Res. Rep.* **5**, 600 (1939). S. Puri and H. Hayakawa,

- cond-mat/9901260 and *Advances in Complex Systems* **4**, 469 (2001).
- [9] M.A. Scherer, F. Melo and M. Marder, *Phys. Fluids* **11**, 58 (1999).
 - [10] A. Stegner and J.E. Wesfreid, *Phys. Rev. E* **60**, R3487 (1999).
 - [11] J.S. Langer, M. Bar-on and H.D. Miller, *Phys. Rev. A*, **11**, 1417 (1975). R. Mauri, R. Shinnar and G. Triantafyllou, *Phys. Rev. E* **53**, 2613 (1996).
 - [12] I.M. Lifshitz and V.V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961). For a review, see A.J. Bray, *Adv. Phys.* **43**, 357 (1994).
 - [13] S. Joly, A. Raquois, F. Paris, B. Hamdoun, L. Auvray, D. Ausserre and Y. Gallot, *Phys. Rev. Lett.* **77**, 4394 (1996).
 - [14] J.S. Langer, *Annals of Physics* **65**, 53 (1971).
 - [15] H.E. Cook, *Acta Met.* **18**, 297 (1970).
 - [16] T. Izumitani and T. Hashimoto, *J. Chem. Phys.*, **83**, 3694 (1985).
 - [17] S. Villain-Guillot and C. Josserand, *Phys. Rev. E* **66**, 036308 (2002).
 - [18] Note that if we had looked at the equation $\frac{\partial \Psi}{\partial t} = \nabla^2(\alpha \Psi + \beta \Psi^3 - \nabla^2 \Psi)$, the amplification factor would have been $\sigma(q) = -(q^2 + \alpha)q^2$ for which the most unstable mode is $\lambda_{C-H} = 2\sqrt{2}\pi/\sqrt{-\alpha}$. Meanwhile, the period of the static Ginzburg-Landau solution (5) would be $\xi = 2\beta^{-1}\Delta^{-1} = \sqrt{\frac{k^2+1}{-\alpha}}$ leading to the same implicit relation (10) and same sequence $\{k_n\}$.
 - [19] A. Novik-Cohen and L.A. Segel, *Physica D* **10**, 277 (1984).
 - [20] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
For a comparison between Landen transformation and relation (10) see [22] .
 - [21] F.M. Arscott, *Periodic Differential Equations* (Pergamon, Oxford, 1981).
 - [22] S. Villain-Guillot , *J. Phys. A: Math. Gen.* **37**, 6929 (2004)
 - [23] Y.Oono and S. Puri, *Phys. Rev. Lett.* **58**, 836 (1987); Y.Oono and Y. Shiwa, *Mod. Phys. Lett. B*, **1**, 49 (1987).
 - [24] C. Josserand and S. Rica, *Phys. Rev. Lett.* **78**, 1215 (1997).
 - [25] Y. Jiang, T. Lookman and A. Saxena, *Phys. Rev. E* **61**, R57 (2000).
 - [26] A. Onuki, *Progress of Theoretical Physics* **67** 1740 (1982)
 - [27] S. Buil, J. P. Delville, A. Ducasse, *Phys. Rev. Lett.* **82** 1895 (1999).

VI. FIGURES

Figure 1

Construction of the two first steady solutions of the (C-H) dynamics, using a superposition of the non-symmetric profile $\widehat{\psi}^*(k, x)$, itself stationary solution of the (C-H) equation. By changing the phase shift between the two profiles entering into the linear combination, one obtains two different symmetric profiles, of periods λ and segregation parameter $k_0^s=0.687$ (equation (19)) or of period 2λ and segregation parameter $k_1^s=0.985$ (equation (20)).

Figure 2

Profile of the free energy landscape during a coarsening process, $F(\phi)$. It starts at $\phi = 0$ for a configuration characterized by the segregation ratio $k_1^s=0.687$ for which the energy per unit length is $F(\phi) \simeq -0.135$; one sees that in this region, the free energy is a concave function of ϕ and thus, the associated pattern is linearly instable. The elementary step of the coarsening process ends for $\phi = 1$ associated with a pattern characterized by the segregation ratio $k_2^s=0.985$ for which the energy per unit length is $F(\phi) \simeq -0.45$. In the region $\phi = 1$, the free energy is a convex function of ϕ . Note that there is no energy barrier.

Figure 3

Parameter ϕ as a function of time. ϕ is extract from a numerical integration of the Cahn-Hilliard dynamics using relation (24) to relate at a given time the profile with the phase ϕ . It starts at $\phi = 0$ with an exponential growth and saturates at $\phi = 1$.

Figure 4

Langer's most instable perturbation mode of destabilization of the soliton lattice is identified with $\widetilde{\Psi}_L = \frac{\partial}{\partial \phi} \Phi(x, k, \phi)$ at $\phi = 0$. It is composed of two antisymmetric patterns, plotted in dotted (plain) line, evolving toward right (left) at velocity $+\frac{d\phi}{dt}$ ($-\frac{d\phi}{dt}$), causing an "antiferro" instability leading to a period doubling of the pattern. They are the spatial derivative of the initial non symmetric profile $\widehat{\psi}^*(x)$ which has been used to construct our ansatz in Figure 1.







