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2010 J. Phys. A: Math. Theor. 43 205102

(http://iopscience.iop.org/1751-8121/43/20/205102)

IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **43** (2010) 205102 (7pp) doi:10.1088/1751-8113/43/20/205102

1D Cahn–Hilliard equation for 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

E-mail: simon.villain-guillot@u-bordeaux1.fr

Received 8 January 2010, in final form 16 March 2010
Published 29 April 2010
Online at stacks.iop.org/JPhysA/43/205102

Abstract
Formation of modulated phase patterns can be modelized by a modified Cahn–Hilliard equation which includes a non-local term preventing the formation of macroscopic domains. Using stationary solutions of the original Cahn–Hilliard equation as analytical ansatzs, we compute the thermodynamically stable period of a 1D modulated phase pattern. We find that the period scales like the power −1/3 of the strength of the long-range interaction.

PACS numbers: 47.54.Bd, 64.70.D−, 64.75.−g, 81.30.−t

1. Introduction

When a homogenous system is led suddenly into a linearly unstable configuration, it will spontaneously segregate into two different states which are more stable. These states are characterized by two distinct values of an order parameter. The leading instability selects a modulation of the initially uniform order parameter at a well-defined wavelength. This instability will grow exponentially and rapidly saturate because of nonlinearity. The resulting micro-segregated pattern is composed of well-defined interfaces (or interphases) delimiting monophasic domains containing the stable phases. These interfaces will then interact with each other and coalesce, during a much slower, self-inhibiting process, where the number of domains will reduce whereas their typical size will increase. The result of this so-called Ostwald ripening can be of two sorts, depending on the presence or absence of long-range interactions. Either the process continues until there remains a single interface separating two semi infinite domains, one for each new stable phase (macro-segregation), or, due to the long-range interactions, the coarsening is interrupted: the final pattern is micro-segregated with a spatially modulated order parameter of finite period [1]. The thermodynamical stability of such a modulated phase results from the competition between two types of interactions: a short-range interaction which tends to make the system locally homogeneous together, and a long-range one, or a non-local one, which allows domain walls, preventing the formation of

macroscopic domains when they are energetically disadvantageous (for recent application to proteins, see [2]). The aim of this paper is to use a family of exact solutions of the Ginzburg–Landau equation as an ansatz to look at the micro-segregation and to compute the period of these thermodynamically stable modulated patterns in the 1D case. In the first part, we will present briefly the Cahn–Hilliard model, mainly to fix the notation and to explain why this model predicts a complete coarsening ending with a single interface. In the second part, we will discuss the effect of adding long-range interactions within Oono's modified Cahn–Hillard dynamics. As a conclusion, we will compare with the results obtained with other models.

2. The simple Cahn–Hilliard model

2.1. Spinodal decomposition

The Cahn–Hilliard (or conservative time-dependant Ginzburg–Landau) equation is a modified diffusion equation which reads in its dimensionless form

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

The real order parameter Ψ can correspond to the fluctuation of density of a fluid around its mean value during a phase separation [3], to the dimensionless magnetization in a ferromagnet [4], or to the local concentration of one of the components of a binary solution (metal alloys [5, 6], polymers [7] or thin films of copolymers [8]). ε is the dimensionless control parameter of the system; in the systems cited above, it is the reduced temperature ($\varepsilon = \frac{T_c - T}{T_c}$ where T_c is the critical temperature of the phase transition). But the Cahn–Hilliard is a standard model which has applications to phase transition in liquid crystals [9], segregation of granular mixtures in a rotating drum [10] or formation of sand ripples [11]. A conservative noise can be added to account for thermal fluctuations [12, 13]; but in this paper, we will only consider the original noiseless (C-H) equation.

This partial differential equation 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 negative ε, there is only one homogenous extremum $\Psi = 0$ which is linearly stable (it is a minimum for $V(\Psi)$). When quenching from a negative control parameter ε to a positive one, the Landau potential $V(\Psi)$ exhibits now two wells and the system experiences a pitchfork bifurcation: the $\Psi = 0$ solution becomes an unstable maximum while two other symmetric stable minima appear $\Psi_b = \pm\frac{\sqrt{\varepsilon}}{2}$.

The stability of the homogeneous solution $\Psi = 0$ was studied by Cahn and Hilliard [5] considering Ψ as a sum of Fourier modes:

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

where ϕ_q is the Fourier coefficient at $t = 0$. By linearizing equation (1) around $\Psi = 0$ (i.e. neglecting the nonlinear term Ψ^3), they obtained for the growth factor $\sigma(q)$:

$$\sigma(q) = \left(\frac{\varepsilon}{2} - q^2\right) q^2. \tag{3}$$

This result shows immediately that $\Psi = 0$ is linearly stable for $\varepsilon < 0$, as all fluctuations are damped. In contrast, for positive ε, a band of Fourier modes are unstable since $\sigma(q) > 0$ for $0 < q < \sqrt{\varepsilon/2}$. The ignition of the instability will be characterized by the most unstable mode $q_{C\text{-}H} = \sqrt{\varepsilon}/2$. This first step of the dynamics is called spinodal decomposition. It will end when the profile Ψ will reach a stationary solution of (1) of period $\lambda_{C\text{-}H} = 4\pi\varepsilon^{-\frac{1}{2}}$.

If we look for symmetric solutions of the one-dimensional (G-L) equation

$$\frac{-\varepsilon}{2}\Psi + 2\Psi^3 - \frac{\partial^2\Psi}{\partial x^2} = 0 \tag{4}$$

satisfying $\langle\Psi\rangle = 0$, there exists, for $\varepsilon > 0$, a whole family of solutions

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

where $\mathrm{Sn}(x, k)$ is the Jacobian elliptic function sine-amplitude, or cnoidal mode. This family of so-called soliton-lattice solutions [14] is parametrized by ε and by the Jacobian modulus or 'segregation parameter' $k \in [0, 1]$. These solutions satisfy equation (4) or equivalently, if integrated over x:

$$\left(\frac{\partial}{\partial x}\Psi_{k,\varepsilon}\right)^2 = \Psi_{k,\varepsilon}^4 - \frac{\varepsilon}{2}\Psi_{k,\varepsilon}^2 + \frac{k^2}{\xi^4}. \tag{6}$$

They describe periodic patterns of period

$$\lambda = 4K(k)\xi, \qquad \text{where} \quad K(k) = \int_0^{\frac{\pi}{2}} \frac{\mathrm{d}t}{\sqrt{1-k^2\sin^2 t}} \tag{7}$$

is the complete Jacobian elliptic integral of the first kind. Together with k, $K(k)$ 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.

This family of solutions interpolates between the sinusoidal function (when $k = 0$), which corresponds to the distribution of the order parameter shortly after the quench, and the periodic step function (when k is closed to 1), more appropriate to describe the strong segregation regime as we will see below, both for a single interface and for a modulated phase system in the low-temperature region.

Equation (7) and the relation $\xi = \Delta^{-1}$ enable one to rewrite this family as

$$\Psi_{k,\lambda}(x) = \frac{4K(k)k}{\lambda}\,\mathrm{Sn}\left(\frac{4K(k)}{\lambda}x, k\right). \tag{8}$$

2.2. *Ostwald ripening*

Among this family of stationary solutions, the thermodynamically stable solution will minimize the energy density. Using equation (6), together with $\int_0^K \mathrm{Sn}^2(x,k)\,\mathrm{d}x = \frac{K-E}{k^2}$ and $\int_0^K \mathrm{Sn}^4(x,k)\,\mathrm{d}x = \frac{2+k^2}{3k^4}K - 2E\frac{1+k^2}{3k^4}$, we can write when $\varepsilon > 0$

$$F_{GL}(k,\lambda) = \frac{1}{\lambda}\int_0^\lambda \frac{1}{2}(\partial_x\Psi(x))^2 - \frac{\varepsilon}{4}\Psi^2(x) + \frac{1}{2}\Psi^4(x)\,\mathrm{d}x \tag{9}$$

$$= \left(\frac{4K}{\lambda}\right)^2\left[\frac{-\varepsilon}{4}\left(1-\frac{E}{K}\right) + \left(\frac{1+2k^2}{6} - \frac{E}{6K}(1+k^2)\right)\left(\frac{4K}{\lambda}\right)^2\right]. \tag{10}$$

So $\mathrm{F}(k = cste, \lambda)$ is minimum when

$$\varepsilon = \left(\frac{8K}{\lambda_k}\right)^2\left(\frac{1+k^2}{3} + \frac{k^2}{3\left(1-\frac{E}{K}\right)}\right), \tag{11}$$

whereas using equations (5) and (7), we find that the three parameters λ, k and ε are related to each other through the state equation

$$\varepsilon = \frac{1+k^2}{2}\left(\frac{8K(k)}{\lambda}\right)^2, \tag{12}$$

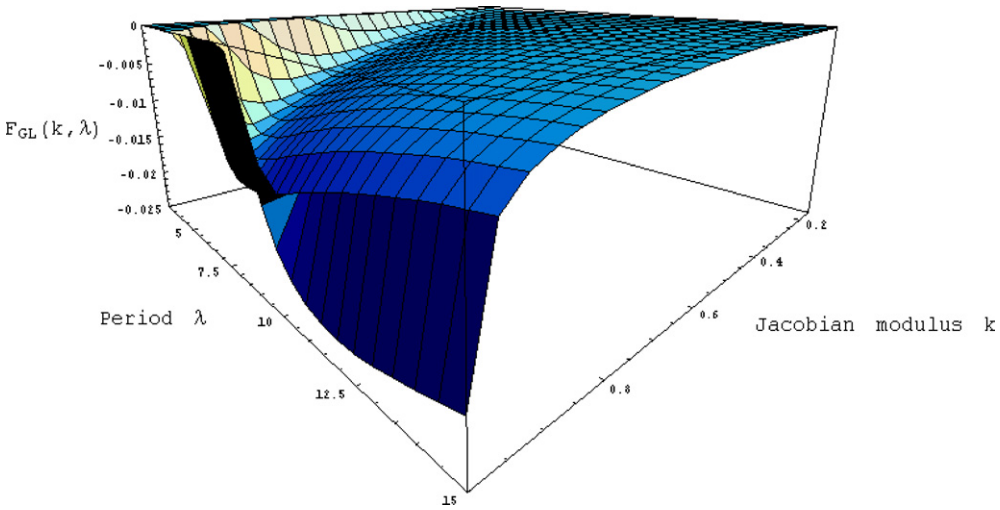

Figure 1. Plot of F(k, λ). One sees that in the (k, λ) space, the partial derivatives $(\frac{\partial F}{\partial k})_\lambda$ and $(\frac{\partial F}{\partial \lambda})_k$ never vanish simultaneously. As a consequence, there is no global minimum except for $k \to 1$ and $\lambda \to \infty$, i.e. for complete phase segregation.

(This figure is in colour only in the electronic version)

which is the constraint for which F($k, \lambda = cste$) is minimum. Thus, as nowhere in the (k, λ) space $\left(\frac{\partial F}{\partial k}\right)_\lambda$ and $\left(\frac{\partial F}{\partial \lambda}\right)_k$ vanish simultaneously, there is no global minimum, except for $k \to 1$ and $\lambda \to \infty$, i.e for complete phase segregation (see figure 1). Therefore, after saturation of the spinodal decomposition, the stationary state composed of domains of size $L_{C\text{-}H} = 2\pi\varepsilon^{-\frac{1}{2}}$, which ends the first step of the dynamics, is unstable with respect to period doubling: coarsening will drive the system from a micro-segregated pattern of a typical period $\lambda_{C\text{-}H}$ to a single-interface pattern. Minimization of the interfacial energy is the only motor of the process of Ostwald ripening [13, 15].

3. Case of the modulated phase systems: Oono's model

If we now want to treat the effect of a long-range interaction, or a non-local one, which is known to be responsible for the stabilization of the modulated phase (or spatially modulated order parameter [1]), we can no longer use a simple Ginzburg–Landau approach where the interactions are described by local terms, such as $(\nabla\Psi)^2$ and $(\nabla^2\Psi)^2$ like in the Swift–Hohenberg model. Indeed, because of the truncation in the gradient expansion [16, 17], below a certain temperature, the macroscopic or global segregation into two semi-infinite regions (one unique interface) will always be energetically favored compared to the microphase separation [16, 18]. In contrast, a correct description of the strong segregation limit which fully takes into account the long-range interactions shows that the modulated phase structure remains the thermodynamical stable phase even far below Tc [19] (in the case of Langmuir monolayer, an infinite number of domains have to be taken into account [20]).

An alternative approach has been proposed by Oono [21]. It relies on the study of dynamics of the phase transition. He considered a free energy density already proposed by Leibler [22]:

$$F(\Psi) = F_{\mathrm{GL}} + F_{\mathrm{int}} = \frac{1}{2}(\nabla\Psi(r))^2 - \frac{\varepsilon}{4}\Psi^2(r) + \frac{1}{2}\Psi^4(r) + \int \Psi(r')g(r', r)\Psi(r)\,\mathrm{d}r' \qquad (13)$$

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

$$\frac{\partial \Psi}{\partial t} = \nabla_r^2 \left(\frac{\delta F(\Psi)}{\delta \Psi} \right) = \nabla_r^2 \left(-\frac{\varepsilon}{2}\Psi + 2\Psi^3 - \nabla^2\Psi + \int \Psi(r')g(r', r)\,\mathrm{d}r' \right). \tag{14}$$

If one recalls that the Green's function associated with the Laplacian operator ∇_r^2 is $\frac{-1}{4\pi|r'-r|}$ in 3D, and $|x' - x|/2$ in 1D, the preceding equation then transforms into

$$\nabla_r^2 \int \Psi(r')g(r', r)\,\mathrm{d}r' = \int \Psi(r')\nabla_r^2 g(r', r)\,\mathrm{d}r' = -\beta^2 \int \Psi(r')\delta(r', r)\,\mathrm{d}r' = -\beta^2\Psi(r) \tag{15}$$

which leads to the following modified Cahn–Hilliard dynamics, which is often used for numerical simulations:

$$\frac{\partial \Psi}{\partial t} = \left(\nabla^2 \frac{\delta F_{GL}(\Psi)}{\delta \Psi} \right) - \beta^2\Psi = \nabla^2 \left(\frac{-\varepsilon}{2}\Psi + 2\Psi^3 - \nabla^2\Psi \right) - \beta^2\Psi. \tag{16}$$

One sees that all the long-range interactions are now in the last term $-\beta^2\Psi$: if Ψ is constant over a macroscopic domain such that the first part of the right-hand side vanishes, this last term will try to pinch or split this domain into two. It thus always prevents the formation of infinite homogeneous domains and favors the modulation even for large ε (i.e. T much lower than T_c), as we will also show below. Note that even with the addition of this new term to the usual Cahn–Hilliard equation, the dynamics remains in the class of the conservative models, as it derives from a conservation equation.

If we look at the linear stability analysis of the homogenous solution $\Psi = 0$, considering again Ψ as a sum of Fourier modes, we find almost the same results as in the original work of Cahn and Hilliard, except that the amplification factor $\sigma(\mathbf{q})$ now becomes

$$\sigma(\mathbf{q}) = \left(\frac{\varepsilon}{2} - \mathbf{q}^2 \right) \mathbf{q}^2 - \beta^2. \tag{17}$$

This shows immediately that $\Psi = 0$ is linearly instable if $\beta < \varepsilon/4$ (as $\sigma(\mathbf{q}) > 0$), with a band of unstable Fourier modes $\frac{\varepsilon}{4} - \sqrt{\left(\frac{\varepsilon}{4}\right)^2 - \beta^2} < \mathbf{q}^2 < \frac{\varepsilon}{4} + \sqrt{\left(\frac{\varepsilon}{4}\right)^2 - \beta^2}$. The most unstable mode remains $q_{C\text{-}H} = 0.5\,\varepsilon^{\frac{1}{2}}$ independently of β. Therefore, during the initial stage of the dynamics (the spinodal decomposition), the homogeneous domains appear with a size $L_{C\text{-}H} = 2\pi\varepsilon^{-\frac{1}{2}}$, as in the usual Cahn–Hilliard dynamics.

The stationary state composed of domains of size $L_{C\text{-}H}$ which ends the spinodal decomposition is still unstable with respect to period doubling [13, 15], leading again to the process of Ostwald ripening. But one sees that, contrary to the simple Cahn–Hilliard case where this process continues until a complete phase segregation is reached, the long wavelength modulations are now stable for $\mathbf{q}^2 < \frac{\varepsilon}{4} - \sqrt{\left(\frac{\varepsilon}{4}\right)^2 - \beta^2}$: because the interaction is long range, no matter how small β is, there will always be a finite region around $q = 0$ where $\sigma(\mathbf{q}) < 0$. This explains qualitatively why, for any finite value of β, the dynamics will end in a micro segregated regime, or modulated phase, as it is observed numerically and as we will now discuss quantitatively.

In $D = 1$, this long-range interaction term can be rewritten as [23]

$$F_{\text{int}} = \frac{-\beta^2}{\lambda} \int_0^{\frac{\lambda}{2}} \int_0^{\frac{\lambda}{2}} \Psi(x')|x' - x|\Psi(x)\,\mathrm{d}x\,\mathrm{d}x'. \tag{18}$$

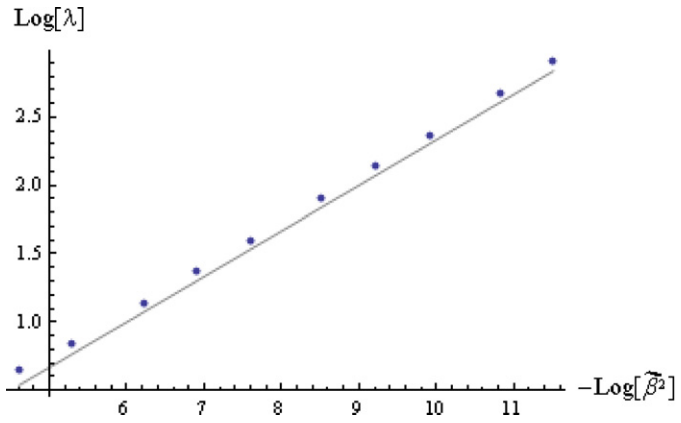

Figure 2. Graph of λ, the period of the modulated phase, as a function of the strength of the long-range interaction. This period is obtained by numerical minimization in k of the total energy density $F_{\rm GL}(k) + F_{\rm int}(k, \beta^2)$. One sees that the resulting points scale like $(\widetilde{\beta}^2)^{-1/3}$.

If we look for a solution in the ansatz family $\Psi_{k,\lambda}(x)$ (8), we then obtain

$$F_{\rm int} = \frac{-\beta^2}{\lambda} \int_0^{\frac{\lambda}{2}} \int_0^{\frac{\lambda}{2}} k^2 \left(\frac{4K}{\lambda}\right)^2 |x' - x| \,\mathrm{Sn}\left(\frac{4K(k)}{\lambda}x, k\right) \mathrm{Sn}\left(\frac{4K(k)}{\lambda}x', k\right) \mathrm{d}x \,\mathrm{d}x' \tag{19}$$

$$= \frac{-k^2\beta^2}{4K} \int_0^{2K} \int_0^{2K} |\widetilde{x}' - \widetilde{x}| \,\mathrm{Sn}(\widetilde{x}, k) \,\mathrm{Sn}(\widetilde{x}', k) \,\mathrm{d}\widetilde{x} \,\mathrm{d}\widetilde{x}'. \tag{20}$$

This contribution is thus independent of λ and depends only on k. Therefore, the minimization of the free energy with respect to λ takes place only on $F_{\rm GL}$ and gives, as in equation (10),

$$\lambda_k = 8K\varepsilon^{-\frac{1}{2}} \sqrt{\frac{1+k^2}{3} + \frac{k^2}{3\left(1 - \frac{E}{K}\right)}}.$$

The resulting $F_{\rm GL}$ scales as ε^2. Taking into account $F_{\rm int}$, we only have to minimize with respect to k the function $F_{\rm GL}(k) + F_{\rm int}(k)$, which can be done numerically for different values of $\widetilde{\beta} = \beta/\varepsilon$. Contrary to the simple case depicted in figure 1, the minimum in energy is now no longer for the value $k = 1$, i.e. the period of the pattern remains finite. As plotted in figure 2, the resulting $\lambda(\widetilde{\beta}^2)$ scales like $(\widetilde{\beta}^2)^{-1/3}$.

4. Conclusion

This result shows that the dynamics proposed by Oono is not in the class considered by Politi and Misbah in their study of interrupted coarsening [24], as the minimum of the total free energy is not associated with the maximum of the amplitude of the modulation. Indeed, even if Oono's equation is singular at $\widetilde{\beta} = 0$, taking the family $\Psi_{k,\lambda}(x)$ as an ansatz leads to a good description of the 1D profile. Numerically (especially for small $\widetilde{\beta}$) we find that the solution is close to $\Psi_{k,\lambda_k}(x)$, with k given by the minimization of $F_{\rm GL}(k, \lambda_k) + F_{\rm int}(k)$. Nevertheless, if one looks carefully, the domains are no longer homogeneous but present a small concavity. The interface profile is no longer monotonous, leading to a breakdown of Politi and Misbah analysis which would have predicted a scaling of λ in $\ln(1/\widetilde{\beta})$ [25]. Moreover, if we impose boundary conditions (i.e. if we artificially impose a fixed periodicity as it is the case in a numerical

experience), this concavity becomes more and more pronounced when $\widetilde{\beta}$ grows, and which eventually leads to a non-physical domain splitting ($\lambda \to \lambda/2$) if the imposed periodicity is too wide, i.e. closer to $2\lambda(\widetilde{\beta}^2)$ than $\lambda(\widetilde{\beta}^2)$. Such a splitting in a numerical experience (the inverse of the period doubling) enables one to reduce the total energy by approaching a period closer to the optimal one $\lambda(\widetilde{\beta}^2)$.

Contrary to a gradient expansion approximation [16, 18] where, far enough from the critical point, a global phase segregation is favored, we find here that the modulated phase remains energetically favored even for large values of ε/β.

Acknowledgments

I wish to thank the Laboratorio de Matera Fuera del Equilibrio in Santiago de Chili for his invitation and the Fondation Sciences Mathématiques de Paris for support during the semester 'Singularities' organized by L Saint-Raymond, C Josserand and J Eggers in Centre Emile Borel, Institut Henri Poincaré, where part of this work has been done.

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