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

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Abstract

Formation of modulated phase patterns can be modeled 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

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When a homogenous system is led suddenly into a linearly unstable configuration, it will spontaneously segregate into two different states, more stable, characterized by two distinct values of an order parameter. The leading instability selects a modulation of the order parameter at a well defined wave length. This instability will grow exponentially and, due to nonlinearity, rapidly saturate. The resulting micro-segregated pattern is composed of well defined interfaces (or interphases) 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 will reduce whereas their typical size increase. The result of this so-called Ostwald ripening can be of two sorts, depending on the presence of long range interaction or not. Either the process goes until 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. The aim of this letter is to use a family of exact solutions of 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.

The Cahn-Hilliard (or Conservative Time Dependant Ginzburg Landau) equation is a modified diffusion equation [2] which reads in its dimensionless form:

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

The real order parameter Ψ can correspond 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. This equation has also been retrieved by Langer [3] from microscopic considerations. A conservative noise can be added to account for thermal fluctuations [4] ; but in this article, we will only consider the original 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 negative 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 negative control parameter ε to a positive one : the $\Psi = 0$ solution becomes unstable ; two other symmetric stable solutions appear $\Psi_b = \pm \frac{\sqrt{\varepsilon}}{2}$.

If we look for symmetric solutions satisfying $\langle \Psi \rangle = 0$, there exists, for $\varepsilon > 0$, a whole family of solution of the one dimensional (G-L) equation [5] :

$$\frac{-\varepsilon}{2}\Psi + 2\Psi^3 - \nabla^2\Psi = 0 \quad (1)$$

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

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

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 satisfy equation (1) and its integrated version writes :

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

They describe periodic patterns of period

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

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 .

This family of solutions interpolates between the sinusoidal function (when $k = 0$), corresponding to the distribution of the order parameter near the critical temperature [6], and the periodic step function (when $k = 1$), more appropriate to describe to the strong segregation of the modulated phase in the low temperature region [7].

The equation (4) and the relation $\xi = \Delta^{-1}$, enable to rewrite this family as :

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

Moreover, using equations (2) and (4), we find that λ , k and ε are related to one another through the state equation

$$\varepsilon = 2(1+k^2) \left(\frac{4K(k)}{\lambda}\right)^2. \quad (5)$$

This implicit equation tells us that if we impose the temperature ε , then λ and k are linked together. As a consequence, the amplitude of the modulation, or the energy per unit length are functions of only one variable, k or λ .

For this family of solution, using equation (3), together with $\int_0^K \text{Sn}^2(x, k)dx = \frac{K-E}{k^2}$ and $\int_0^K \text{Sn}^4(x, k)dx = \frac{2+k^2}{3k^4}K - 2E\frac{1+k^2}{3k^4}$, we find for the energy density when $\varepsilon > 0$

$$\begin{aligned} F_{GL}(k, \lambda) &= \frac{1}{\lambda} \int_0^\lambda \frac{1}{2} (\nabla \Psi(r))^2 - \frac{\varepsilon}{4} \Psi^2(r) + \frac{1}{2} \Psi^4(r) dr = \\ &= \left(\frac{4K}{\lambda}\right)^2 \left[\frac{-\varepsilon}{4} \left(1 - \frac{E}{K}\right) + \left(\frac{1+2k^2}{6} - \frac{E}{6K}(1+k^2)\right) \left(\frac{4K}{\lambda}\right)^2 \right] \end{aligned} \quad (6)$$

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

$$\left(\frac{\lambda_k}{4K}\right)^2 = \frac{4}{\varepsilon} \left(\frac{1+k^2}{3} + \frac{k^2}{3(1-\frac{E}{K})}\right),$$

whereas $F(k, \lambda = cste)$ is minimum for equation (5) 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 $k \rightarrow 1$ and $\lambda \rightarrow \infty$, i.e for complete phase segregation, (see Figure 1).

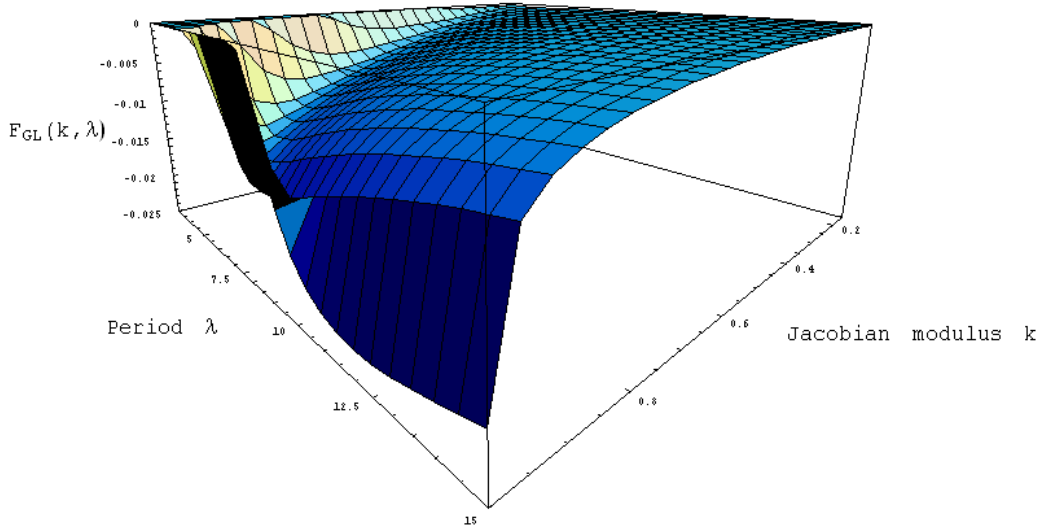


Fig. 1. Plot of $F(k, \lambda)$. One sees that in the (k, λ) space, the partial derivatives $\left(\frac{\partial F}{\partial k}\right)_\lambda$ and $\left(\frac{\partial F}{\partial \lambda}\right)_k$ never vanish simultaneously. As a consequence, there is no global minimum except for $k \rightarrow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

If we now want to treat the effect of a long-range interaction, or a non-local one, responsible of the stabilization of the modulated phase, we could start from a Ginzburg-Landau approach where the interactions are describe by local term, such as gradient expansion with $(\nabla\Psi)^2$ and $(\nabla^2\Psi)^2$ like in the Swift Hohenberg model. It then as been shown that below a certain temperature, the macroscopic or global segregation into two semi infinite region (one unique interface) will always be energetically favored compared to the microphase separation [8, 9]. The reason a Ginzburg-Landau type of expansion fails to describe correctly the strong segregation limit is due to the truncation in the gradient expansion [9, 10] : such an approximation is unable to take into account the long range interaction between more and more lamellae (in the case of Langmuir monolayer, an infinite number of domains have to be taken into account[11]). As it has been shown that the modulated phase structure remains the thermodynamical stable phase even far below T_c [7], an effective description using a simple GL equation cannot be used anymore.

An alternative approach has been proposed by Oono [13]. It relies on the study of dynamics of the phase transition. Following the description of Leibler [12], Oono has obtained the following modified Cahn-Hilliard dynamics, which is often use for numerical simulations:

$$\frac{\partial\Psi}{\partial t} = (\nabla^2 \frac{\delta F_{GL}(\Psi)}{\delta\Psi}) - \beta^2\Psi = \nabla^2(\frac{-\varepsilon}{2}\Psi + 2\Psi^3 - \nabla^2\Psi) - \beta^2\Psi. \quad (7)$$

$-\beta^2\Psi$ models in the Cahn-Hilliard equation the long-range interactions, which prevent the formation of macroscopic domains and thus favors the modulation : if Ψ is constant over a macroscopic domain, the first part of the right hand side might vanish, but the second part will lead to a dynamics of pinching or splitting of the homogeneous domain. 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.

Let's consider a free energy density written as :

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

where the long range interaction are described by $g(r',r) = \frac{\beta^2}{4\pi|r'-r|}$ in $D=3$, or $-\beta^2|x'-x|$ in $D=1$ [12]. 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 :

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

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

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

which leads to equation (7). Note that even with the new term added to the usual Cahn-Hilliard dynamics, this equation remains in the class of the conservative models, as it derives from a conservation equation. For simplicity, we will assume in the following that $\varepsilon = 1$. If we look at the linear stability analysis of the homogenous solution $\Psi = 0$, considering Ψ as a sum of Fourier modes:

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

where $\Psi_{\mathbf{q}}$ is the Fourier coefficient at $t = 0$, we found almost the same results as in the original work of Cahn and Hilliard, except that the amplification factor $\sigma(\mathbf{q})$ now writes :

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

This shows immediately that $\Psi = 0$ is linearly instable ($\sigma(\mathbf{q}) > 0$) if $\beta < 0.25$, with a band of unstable Fourier modes $1 - \sqrt{1 - 16\beta^2} < 4q^2 < 1 + \sqrt{1 - 16\beta^2}$. The most unstable mode remains $q_{C-H} = 0.5$ independently of β . Therefore, during the initial stage of the dynamics (the spinodal decomposition), the homogeneous domains appear with a size close to $L_{C-H} = 2\pi$, as in the usual Cahn-Hilliard dynamics.

The stationary state composed of domains of size L_{C-H} which ends the spinodal decomposition is unstable with respect to period doubling [3]. This leads to the process of Ostwald ripening. But one sees that, contrary to the simple Cahn-Hilliard case where this process goes until complete phase segregation, the long wave length modulations are now stable for $4q^2 < 1 - \sqrt{1 - 16\beta^2}$: because the interaction is long range, no matter how small β , there will always be a finite region around $q = 0$ where $\sigma(\mathbf{q}) < 0$. So a modulated phase should always end the dynamics. 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 now discuss quantitatively. In D=1, this long range interaction term can be rewritten [14]

$$F_{int} = \frac{-\beta^2}{\lambda} \int_0^{\frac{\lambda}{2}} \int_0^{\frac{\lambda}{2}} \Psi(r') |r' - r| \Psi(r) dr dr' ,$$

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

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

So it turns that this contribution is independent of λ and depends only of k . Thus, the minimization of the free energy with respect to λ takes place only on F_{GL} and gives $\lambda_k = 8K \sqrt{\frac{1+k^2}{3} + \frac{k^2}{3(1-\frac{E}{K})}}$ as in equation (6). Taking into account F_{int} , we only have to minimize with respect to k the function $F_{GL}(k) + F_{int}(k)$, which can be done numerically for different values of β . One sees in Figure 2 that the resulting $\lambda(\beta^2)$ scales like $(\beta^2)^{-1/3}$.

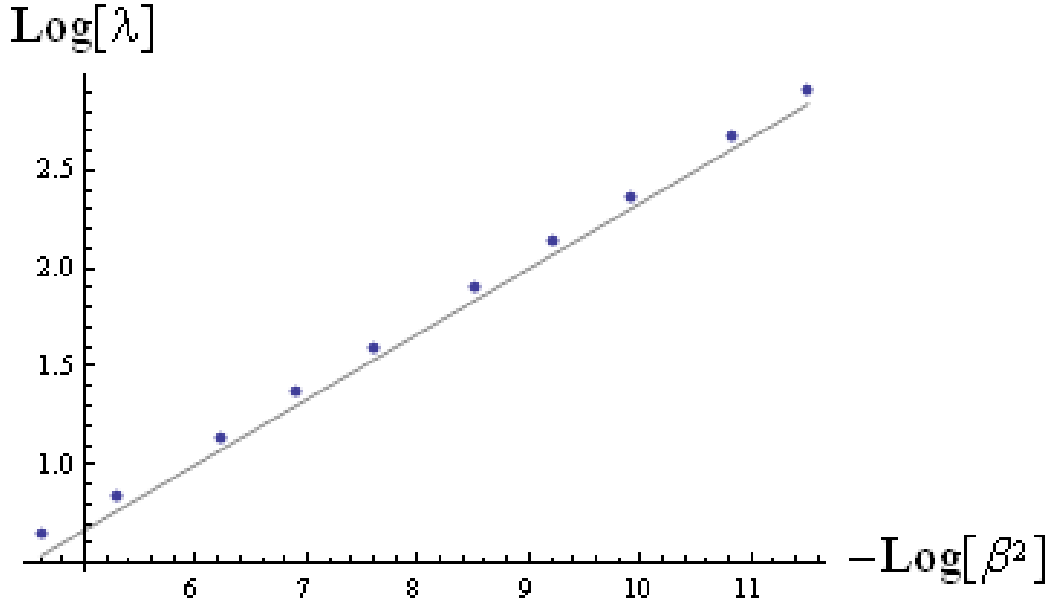


Fig. 2. Graph of λ , the period of the modulated phase, as a function of the strength of the long range interaction. This period is obtained by numerical minimization in k of the total energy density $F_{GL}(k) + F_{int}(k, \beta^2)$. One sees that the resulting points scale like $(\beta^2)^{-1/3}$.

Even if the Oono equation is singular in $\beta = 0$, taking the family $\Psi_{k,\lambda}(x)$ as an ansatz leads to a good description of the 1D profile. Numerically (especially for small β) we find that the solution is close to $\Psi_{k,\lambda_k}(x)$, with k given by the minimization of $F_{GL}(k, \lambda_k) + F_{int}(k)$. Nevertheless, if one looks carefully, the domains are not homogeneous anymore but present a small concavity. If we impose boundary conditions (i.e. if we impose a fixed periodicity), this concavity becomes more and more pronounced when β grows, and with eventually leads to a non physical domain splitting ($\lambda \rightarrow \lambda/2$)

Contrary to a gradient expansion approximation [8, 9] where, far enough from the critical point, the macroscopic phase segregation is favored, we find here that the modulated phase remains energetically favored even for large values of ε/β^2 .

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