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Instabilities and pattern formation in a generalized Cahn-Hilliard model with 2+1 components

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Abstract

The dynamics of phase separation of co-polymers is investigated theoretically in the case where the bridging between the heteropolymers is realized by a surfactant. The Cahn-Hilliard-Oono equation which describes the dynamics of the polymers is here coupled with a diffusion equation for the surfactant which has an affinity for the interfacial region of the polymer blend. As a result, we find a dual localization of the interfaces of the different species. We investigate in particular, in detail the onset of the phase transition dynamics associated with these coupled diffusion equations, both analytically and numerically.

I. INTRODUCTION

Self-organization in soft condensed matter systems can lead to new promising idea for smart technologies [[1]]. Modulated phases systems can for instance be a solution for easily building 2 or 3D spatial patterns in a reproducible manner. The di-block copolymers are good examples of such micro-structured systems and are therefore widely studied, especially for their 2D lamellar phase which can be used to print and flexible films. It has been proposed to apply this spontaneous micro-structuration property to design a new class of flexible photo-voltaic devices using semi-conducting di-block copolymers. Alternatively, small length ad-hoc diblock copolymers could be engineered such to act as surfactant to bridge together longer semi-conducting polymers, with the desired complementary properties in order to produce a junction.

Di-block copolymers are composed of two different semi-flexible chains linked together. Contrary to the case of heterogeneous polymers mixtures which tend to segregate at low enough T or high enough Flory parameter, the chemical bridging characteristic of di-block copolymers prevents a global phase separation (also called strong segregation). The usual repulsion between hetero-polymers and the attraction due to the permanent link (or to the semi-permanent link created by the surfactant with affinity for both heterogeneous polymers) are two antagonist tendencies which generate a geometric frustration and result in the formation of periodic structures, or micro-structured patterns [2]. This bridging, which can be a permanent link when induced by a covalent bounding, or a semi-permanent link created by a surfactant with affinity for both heterogeneous polymers, results in an effective long range attraction.

The dynamics of self-structuration of this class of systems can be model using a modified Cahn-Hilliard equation with additional terms that model this homogenizing long range interaction term. Like the standard Cahn-Hilliard dynamics, which describes the spinodal decomposition in the usual segregation within binary alloys of hetero-polymers mixtures[3], theses modified versions remain in the class of conservative dynamics (also called model B) [4]. Oono [5] proposed to add to the Cahn-Hilliard dynamics a term derived from the long-range interaction energy proposed by Leibler [6],[7]. The resulting time dependent equation is well adapted for numerical studies but also for analytical treatment in 1D, using exact results from the standard Cahn-Hilliard dynamics[8], [9], [10]. The phase diagram

obtained with these dynamics shows stationary patterns with a well-defined periodicity for the modulation of the order parameter [11].

In this letter, we propose to adapt the standard Cahn-Hilliard-Oono's dynamics to model a new class of copolymer where the link between the two heteropolymers is not anymore permanent.

This bound can be thought as a surface active agent engineered to have affinity for the two specific polymers it is designed to glue and therefore to favour the colocation of heteropolymers and thus

micro-segregation, by favourably locates itself at the interfaces between heteropolymer bulk regions. It can for example be a small length macromolecule, even a copolymer, with two different specific affinities on each end branches. As this additional ingredient in the polymers blend can diffuse, its coarse grained density $d(x, t)$ will also be space dependent (and time dependent during the transient regime of the dynamics toward stationary pattern formation), with a spacial average value d_0 . In order to take into account of this new degree of freedom, we propose to modify the Cahn-Hilliard conservative dynamics by coupling it to a diffusion equation for the surfactant.

Our model is then based on the following properties :

- the strength of the link between heteropolymers, denoted $\alpha(d)$, depends locally on the density of surfactant. In the following, we will take a linear dependence $\alpha(d) = \alpha d(x, t)$.
- the surfactant can diffuse through the polymer blend, with a preference toward the well-mixed regions ($u = 0$) where it can link to both heteropolymers. This favours interfaces by lowering their energetic cost.

The dynamics can therefore be modelled by two coupled equations, the first one being the Oono's extension of the Cahn-Hilliard conservative equation :

$$\frac{\partial u}{\partial t} = \nabla^2(-u + u^3 - \nabla^2 u) - \alpha du \quad (1)$$

The order parameter $u(x, t)$ represents the coarse grained fluctuations of one of the component of the polymer blend. Because we restrict our study to the symmetric case, this order parameter verifies $\langle u(x) \rangle = 0$. The first part of the right hand side derives from the usual

Ginzburg-Landau free energy

$$F_{G-L} = \int \left(-\frac{u^2(x)}{2} + \frac{u^4(x)}{4} + \frac{1}{2} (\nabla u(x))^2 \right) dx$$

Below the critical temperature (negative sign of the first coefficient), the sole Ginzburg-Landau free energy drives the order parameter u to non zero value (inverse diffusion), close to the bulk values ± 1 which minimize the free energy density $-\frac{u^2(x)}{2} + \frac{u^4(x)}{4}$. Derived by Oono from Leibler's free energy using a conservative dynamics, the last term of the dynamics describes the effect of the long range interaction which is to prevent the formation of large size domains when α is positive. It forces the order parameter to be on the average of zero value on macroscopic scale (homogenization by regular diffusion). But we take its amplitude proportional to the local density of the surface active agent $d(x, t)$. This auxiliary order parameter being a positive quantity, this dynamical equation, including its last term, is on the overall conservative if initially $\langle u(x) \rangle = 0$. But the competition between the antagonist effect of the two parts of the right hand side leads to the formation of a spatially modulated phase [[2]]. The relative strength of the two competing effects is determined on the average by the value of α .

In this article, the strength of this long range interaction force can vary locally, according to the local density of surface active agent, or surfactant. The consequence of this new degree of freedom is to locally reduce the energetic cost of interfaces. The density of surfactant itself obeys a diffusion equation

$$\frac{\partial d}{\partial t} = D \nabla^2 d + \frac{\alpha}{2} \nabla^2 (u^2) \quad (2)$$

We have chosen the simplest form for a diffusion equation coupled to the Oono's version of the Cahn-Hilliard dynamics. The last term of the right hand side favours the localization of the surface active agents in the u -interfacial region (where $u^2(x)$ is small and convex) in between the homogeneous domains (where $u^2(x) \simeq 1$). In other terms, it tends to expel the surfactant from homogeneous polymer domains, driving thus the surfactant to be mainly at the interfaces. This additional diffusion term, proportional to $\frac{\alpha}{2}$, is the counterpart in the d -diffusion equation of the Oono's term in the d -diffusion equation 1. It couples the order parameter $u(x, t)$ with the surfactant concentration $d(x, t)$, acting like an effective potential (which is taken to be symmetric in $u \leftrightarrow -u$). The first term of the right hand side is the usual self diffusion term, where D is the positive coefficient of diffusion of the surfactant within the

polymers melt. It tends to homogenize the surfactant distribution and prevents singularities in the d -profile, which would otherwise appear collocated at every u -inter-phase, if the d -dynamics were solely governed by the symmetric effective $u^2(x)$ potential.

Note that this dynamics is also conservative for the order parameter $d(x, t) : \forall t, \langle d(x) \rangle = d_0$ (which can be verified numerically). It can be seen as a modified diffusion equation where the diffusion coefficient varies due to the local variation of polymer density. Note also that conservative noise terms can be added to both equations.

II. LINEAR STABILITY IN THE ONE DIMENSIONAL CASE

We have limited our study to small values of α , because in Oono's version of the Cahn-Hilliard dynamics (when $d(x, t) = 1$), there is a linear instability for values of α between 0 (simple C-H limit) and $1/4$ (Swift-Hohenberg limit[11]).

Indeed, when looking at the linear stability around the homogeneous solution $u = 0$, by analysing the behaviour of the different Fourier modes $u_{\mathbf{q}}$:

$$u(\mathbf{r}, t) = u_{\mathbf{q}} \sin(\mathbf{q} \cdot \mathbf{r}) e^{\sigma(\mathbf{q})t},$$

we recover that the amplification factor associated with linearized version of equation (1) is close to Cahn and Hilliard original stability analysis,

$$\sigma(\mathbf{q}) = (1 - \mathbf{q}^2)\mathbf{q}^2 - \alpha$$

Thus, if $\alpha < \alpha_c = 1/4$, some Fourier modes are linearly unstable as $\sigma(\mathbf{q}) > 0$ in the band $0.5\sqrt{1 - \sqrt{1 - 4\alpha}} < q < 0.5\sqrt{1 + \sqrt{1 - 4\alpha}}$. The most unstable mode remains $q_{C-H} = 0.5$ independently of α .

The spatial variation of the strength of the long range interaction doesn't change this linear stability analysis around the homogeneous solution $u_0 = 0$, which now gives the growth factor $\sigma(q) = q^2 - q^4 - \alpha d_0$ where $d_0 = \langle d \rangle$. The maximum growth rate is still for $q_{C-H}^2 = 1/2$, associated to a growth factor $\sigma_{C-H} = 1/4 - \alpha d_0$ which is positive if $\alpha d_0 < 1/4$.

The second equation could a priori give rise to a different growth rate and a different spatial characteristic wavelength. The linearization of the second equation is done around an homogeneous order parameter $d_0 = \langle d \rangle$, with additional fluctuations of low amplitudes $u_1(t) = u_1 e^{\sigma_{C-H} t}$ and $d_1(t)$ such that

$$\begin{aligned}
u(x, t) &= u_1 e^{\sigma_{C-H} t} \sin(q_{C-H} x) \\
d(x, t) &= d_0 + d_1(t) \sin(q' x + \phi)
\end{aligned}$$

Replacing $d(x, t)$ and $u(x, t)$ in equation 2 and keeping only the lowest order terms, we obtain

$$\begin{aligned}
\frac{\partial}{\partial t} d_1(t) \sin(q' x + \phi) &= -q'^2 D d_1(t) \sin(q' x + \phi) + \frac{\alpha}{2} u_1^2 e^{2\sigma_{C-H} t} \nabla^2 \sin^2(q_{C-H} x) \\
&= -q'^2 D d_1(t) \sin(q' x + \phi) + \alpha q_{C-H}^2 u_1^2 e^{2\sigma_{C-H} t} \cos(2q_{C-H} x)
\end{aligned} \tag{3}$$

Multiplying both sides by $\sin(q' x + \phi)$, and averaging over $2\pi/q$, allows only one possible value $q' = 2q_{C-H}$ for a positive value of the right hand side of the preceding equation, so 3 reads

$$\begin{aligned}
\frac{\partial}{\partial t} d_1(t) &= (-4D d_1(t) + \alpha u_1^2 \sin(\phi) e^{2\sigma_{C-H} t}) q_{C-H}^2 \quad \text{which is maximum for } \phi = \frac{\pi}{2} \\
\text{so } d(x, t) &= d_0 + d_1(t) \cos(2q_{C-H} x) \\
\text{with } d_1(t) &= \frac{\alpha u_1^2}{4D + 2\sigma_{C-H}/q_{C-H}^2} (e^{2\sigma_{C-H} t} - e^{-4Dq_{C-H}^2 t}) + d_1(t=0) e^{-4Dq_{C-H}^2 t}
\end{aligned}$$

The dynamics at the onset of the instability of the order parameter profile $d(x, t)$ representing the surfactant density is dominated by the first part of the solution, $\alpha \frac{(u_1 e^{\sigma_{C-H} t})^2}{4D + 2\sigma_{C-H}/q_{C-H}^2}$. Thus the dynamics of $d(x, t)$ is entirely driven by the instability of the order parameter $u(x, t)$, which acts as a source term (or more precisely, because of the phase $\phi = \frac{\pi}{2}$, $u^2(x, t)$ is a sink term). The amplitude d_1 of the modulation of $d(x, t)$ will grow exponentially with the growth factor $2\sigma_{C-H}$ and will follows the dynamics of u^2 , even if $d_1(t=0) = 0$ (the amplitude of the initial fluctuation of $d(x, t)$ is irrelevant). The two profiles are developing their respective modulated patterns in such a way that $d(x)$ is maximum when $u(x) = 0$, i.e. the anti-nodes of $d(x)$ are at the interfaces (or nodes) of the u -homogeneous domains.

III. NUMERICAL STUDY OF THE COUPLED DYNAMIC IN IN THE ONE DI-

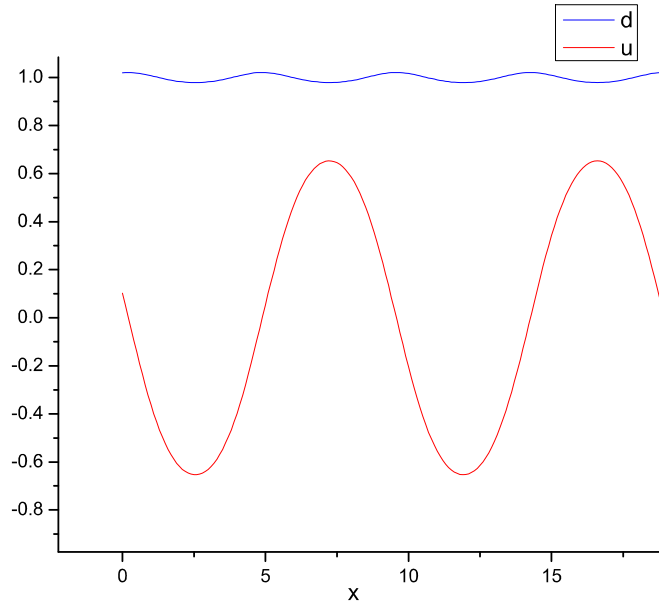


FIG. 1:

MENSIONNAL CASE

We have consider a 1D system of length $L \gg \lambda_{CH} = 2\pi\sqrt{2}$, with an initial completely disordered order parameter $u(x, t = 0)$, of zero mean value (high temperature phase), and a surfactant distribution $d(x, t = 0)$ with fluctuation around a mean value $d_0 = 1$. As predicted by the linear stability analysis, the early stage of the dynamics of $d(x, t)$ follows that of $u(x, t)$: islands of non-zero values of u push the surfactant away towards the interfaces, as a direct effect of the term $\alpha \nabla^2 u^2$. The usual diffusion term $D \nabla^2 d(x, t)$ tends to homogenize the distribution of $d(x, t)$ and prevents its singularities.

The Figures 1.a) and 1.b) show final profiles $u(x)$ and $d(x)$, for different values of D and fixed value of α . These simulations confirm that the dynamics is indeed conservative, for both $u(x, t)$ and $d(x, t)$. They also enlight that the diffusion coefficient D controls the amplitude of the final distribution of d . When D is large enough (Figure 1.a), the diffusion of d homogenizes the surfactant density ($d \simeq 1$) in the melt of polymers, and the dynamics is then similar to Oono's dynamics. Otherwise, for small values of D (Figure 1.b), the distribution of d becomes less homogenous. This may causes different regions to have locally different values of $\alpha \times d$ (i.e. local effective " α " values). Within domains, the

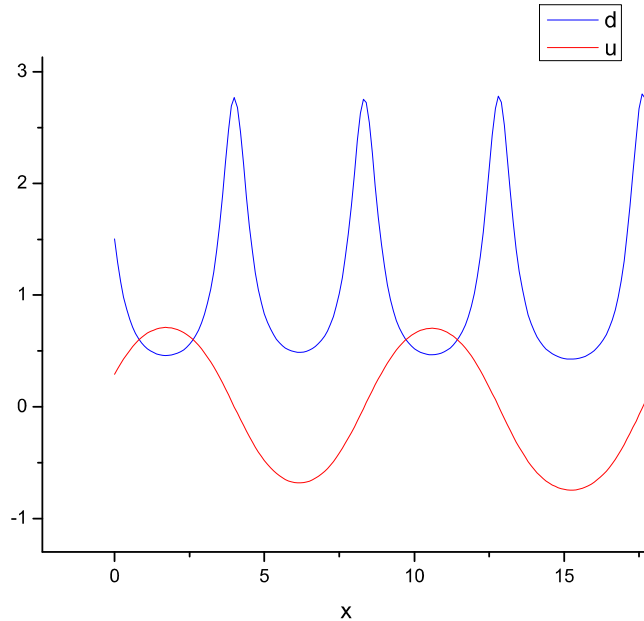


FIG. 2: The right image shows the spatial profiles of the order parameters u and d , respectively in red and blue, for $\alpha = 0.1$, and $D = 1.0$ for the Figure a) and $D = 0.001$ for the Figure b). We didn't use any stability criteria but we consider solutions that are stable after long time simulation, usually $6 \cdot 10^6$ iterations with time steps changing dynamically between 0.0001 and 0.1.

effective value of the long range interaction is lower than its average value, removing thus partially the frustration. On the contrary, the value of this interaction is higher near the u -inter-phase where it is energetically less costly. As can be seen on the Figure 1.b), the effective local value of $\alpha \times d$ could then be close or even higher than $\alpha_c = 1/4$, the critical value of the simple Oono's dynamics. Thus, we could wonder if the interruption of the coarsening dynamics wouldn't therefore take place earlier, than in the Oono's model.

IV. CONCLUSION

The dynamics of phase separation of co-polymers is investigated theoretically in the case where the bridging between the heteropolymers is realized by a surfactant. The Cahn-Hilliard-Oono equation is here coupled with a diffusion equation for the surfactant. Due to its affinity for the interfacial region of the polymer blend, this surfactant will migrate mostly

in the interfacial region of the polymer blend, where the segregation is the weakest, in order to lower the energetic cost of the periodic interfaces. We have investigated in particular the coupled instabilities of the distributions of the polymer and the surfactant concentrations.

V. ANNEXE

Oono's original derivation starts from the free energy proposed by Leibler [6] for the long range interaction term (and treated for the strong segregation case by Ohta and Kawasaki [7]):

$$\int \int u(x')g(x',x)u(x)dx'dx \quad \text{with } \nabla^2 g(x',x) = -\alpha\delta(x',x)$$

The simplest extension of this dynamics would be either to have d -dependence of the α term.

$$\nabla^2 g(x',x) = -\alpha d(x,t)\delta(x',x)$$

Or we could have chosen a kernel that could be written $d(x',t)g(x',x)d(x,t)$ in order to keep a symmetric form in $x \leftrightarrow x'$. But whether it is a linear or quadratic d -dependence, this would lead to the same behaviour at first order, as $\langle d(x) \rangle = d_0$ is finite. And such a symmetric expression of the kernel would also lead to an additional non-local term in the dynamics

$$\begin{aligned} & \nabla^2 \left(\frac{\delta}{\delta u(x)} \int u(x')d(x')g(x',x)d(x)u(x)dx' \right) = \nabla^2 \int u(x')d(x')g(x',x)d(x)dx' \\ & = \int (u(x')d(x')g(x',x)\nabla^2 d(x) + u(x')d(x')\nabla^2 g(x',x)d(x))dx' = \int u(x')d(x')g(x',x)\nabla_x^2 d(x)dx' - \alpha u(x)d(x,t) \end{aligned}$$

This non-locality is also present if we attempt to derive the additional diffusion equation from the variation of the free energy with respect to $d(x)$:

$$\begin{aligned} & \nabla_x^2 \left(\frac{\delta}{\delta d(x)} \int u(x')d(x',t)g(x',x)d(x,t)u(x)dx' \right) = \nabla_x^2 \int u(x')d(x',t)g(x',x)u(x)dx' \\ & = \int u(x')d(x',t)(g(x',x)\nabla_x^2 u(x) + \nabla_x^2 g(x',x)u(x))dx' = \int u(x')d(x',t)g(x',x)\nabla_x^2 u(x)dx' - \alpha u^2(x,t)d(x,t) \end{aligned}$$

Note also that the first term obtained is not conservative. The proposed empirical coupled dynamical equations avoid the non-locality and are conservative for the order parameters, $u(x,t)$ and $d(x,t)$.

If we choose the d -dependence of the α term, we have to make the approximation

$\nabla_x^2(\frac{\delta}{\delta d(x)} \int u(x')g(x', x)u(x)dx' \simeq \frac{\alpha}{2}\nabla^2 u^2$ which is conservative. Again, at first order, it would be equivalent to $\frac{\alpha}{2}\nabla^2(u^2(x)d(x))$ as $\langle d(x) \rangle = d_0$ is finite.

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