

Electronic Supplementary Information for *Soft Matter* manuscript: Frustrated phases under three-dimensional confinement simulated by a set of coupled Cahn-Hilliard equations

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1 Simulation parameters

Table 1. shows simulation parameters of figure 1 in the main text.

Subfigure	σ	α	τ_u	τ_v	Size	x_{len}
(b1)	180	0.04	1.0	100.0	128	2.0
(b2)	160	0.4	1.0	100.0	128	1.0
(b3)	100	0.1	1.0	100.0	128	2.0
(b4)	160	0.08	1.0	1.0	64	1.5

Table 1: Simulation parameters of Fig. 1

2 Details of theoretical model

Here we summarize the theoretical basis of the Cahn-Hilliard equation. In a blend of AB-diblock copolymer, the state of the system is defined by an order parameter, v , as a measure of the fraction of component A and B in the blend. Thus, v acquires values from the interval $[-1, 1]$ with ending points corresponding to A and B. The dynamics of the state of the above system evolves to minimize the value of an energy functional like in the following expression:

$$F_\epsilon(v) = \int_{\Omega} \left\{ \frac{\epsilon^2}{2} |\nabla v|^2 + W(v) \right\} dr \quad (1)$$

In eq. 1, the first term accounts for the interaction between neighboring positions and the second term is a double well potential to represent two different possible states, -1 or $+1$, in a phase transition. Ω is a smooth bounded domain in \mathbb{R}^N . Here we focus on three-dimensional confinement and thus $N = 3$.

The Euler-Lagrange equation associated to this energy functional is the Allan-Cahn equation:

$$\tau v_t = -\frac{\delta F}{\delta v} \quad (2)$$

$$= \epsilon^2 \Delta v + (1 - v)(1 + v)v \quad (3)$$

In eq. 3, parameter ϵ is proportional to the thickness of the propagating front. The Allan-Cahn equation is not conservative in the sense that all material is converted to -1 or $+1$. In order to have two different phases coexisting –for instance two different kinds of polymers– we request conservation of volume as:

$$\bar{v} = \frac{1}{|\Omega|} \int_{\Omega} v dr = \text{constant}, \quad (4)$$

where \bar{v} is the mass ratio between two polymers.

We also want to incorporate long-range interactions, and to do this we need a non-local term in the energy functional, like [1, 2, 3]:

$$F_{\epsilon, \sigma}(v) = \int_{\Omega} \left\{ \frac{\epsilon^2}{2} |\nabla v|^2 + W(v) + \frac{\sigma}{2} \left| (-\Delta)^{-1/2} (v - \bar{v}) \right|^2 \right\} dr \quad (5)$$

The associated Euler-Lagrange equation to the functional in eq. 5 is the Cahn-Hilliard equation:

$$\tau v_t = \Delta \left(\frac{\delta F}{\delta v} \right) \quad (6)$$

$$= -\Delta \left\{ \epsilon^2 \Delta v + (1 - v)(1 + v)v \right\} - \sigma (v - \bar{v}) \quad (7)$$

In eq. 7 we have parameter σ which is related to the bonding between block A and block B in the copolymer. If $\sigma = 0$ then there is no bonding, which means that there is not non-local term and in such case the first term in the energy functional will minimize the free energy simply by separating macrophases into domains -1 and $+1$. If $\sigma \neq 0$ then we have microphases within the copolymer and different morphologies will arise.

We propose a mixed system in which one component has $\sigma = 0$ and the other component has $\sigma \neq 0$. The first component plays the role of an auxiliary order parameter which separates two regions, which we call homopolymer and copolymer domains, and the second component undergoes microphase separation within the copolymer domain.

2.0.1 Free energy and Euler-Lagrange equations of the mixed system.

A mixed system has two order parameters u and v corresponding to $\sigma = 0$ and $\sigma \neq 0$, respectively. The energy functional for the mixed system is as follows:

$$F_{\epsilon,\sigma}(u, v) = \int_{\Omega} \left\{ \frac{\epsilon_u^2}{2} |\nabla u|^2 + \frac{\epsilon_v^2}{2} |\nabla v|^2 + W(u, v) + \frac{\sigma}{2} \left| (-\Delta)^{-1/2} (v - \bar{v}) \right|^2 \right\} dr, \quad (8)$$

where

$$W(u, v) = \frac{(u^2 - 1)^2}{4} + \frac{(v^2 - 1)^2}{4} + \alpha uv + \beta uv^2 + \gamma u^2 v^2 \quad (9)$$

Again \bar{v} is the mass ratio between two polymers and now the double-well potential in eq. 9 has two dimensions and coupling parameters α , β and γ . We set $\gamma = 0.0$. Notice the functional in eq. 8 is basically the resultant of combining two systems, each one with order parameter u and v .

In this scheme u describes the system with $\sigma = 0$, which undergoes macrophase separation into fully separate domains. If the system represents a blend of homopolymer and copolymer components, then u describes macrophase separation into homopolymer and copolymer domains. u takes values within the interval $[-1, +1]$ and for a homopolymer-copolymer blend, the ending points correspond to the homopolymer rich domain and the copolymer rich domain. Similarly, order parameter v describes the microphase separation within the copolymer domain and it also acquires values within the interval $[-1, +1]$. To set an example, if we assume that the copolymer component is constituted by hydrophilic block A and hydrophobic block B, then the ending points of the interval correspond to the hydrophilic rich domain and the hydrophobic rich domain.

The associated Euler-Lagrange system of equations corresponding to the mixed system are two coupled Cahn-Hilliard equations, as follows:

$$\tau_u u_t = \Delta \left(\frac{\delta F}{\delta u} \right) \quad (10)$$

$$= -\Delta \left\{ \epsilon_u^2 \Delta u + (1-u)(1+u)u - \alpha v - \beta \frac{v^2}{2} \right\} \quad (11)$$

$$\tau_v v_t = \Delta \left(\frac{\delta F}{\delta v} \right) \quad (12)$$

$$= -\Delta \left\{ \epsilon_v^2 \Delta v + (1-v)(1+v)v - \alpha u - 2\beta uv \right\} - \sigma(v - \bar{v}) \quad (13)$$

Equations 11 and 13 constitute a mixture of two systems: one with $\sigma = 0$ and the other with $\sigma \neq 0$. The former represents the separation into two domains or macrophases and the boundary between these two domains roughly plays the role of a confinement space containing the other system inside. The latter system with $\sigma \neq 0$ can evolve to form microphases in the copolymer domain.

References

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