SPONTANEOUS PROPAGATION OF SELF-ASSEMBLY IN A CONTINUUM MEDIUM

Wei Lu [a] & Zhouzhou Zhao
Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, 48109, USA

Summary We report a mechanism that self-assembly propagates spontaneously in a continuum medium, enabling the delivery of local order information to distance. In a large stable system a locally self-assembled structure as a precursor destabilizes its surrounding areas through an elastic dipole interaction. The newly formed structures inherit the same order information from the precursor and further activate the self-assembly of their neighbors. This process causes spatial extension of self-assembly and replication of the order, producing extremely long-range ordered superlattice without defects.

INTRODUCTION

Depending on the building blocks, self-assembly systems can be categorized into two types: discrete and continuum. A discrete system utilizes pre-fabricated building blocks such as nanoparticles and nanorods. These components, with fixed sizes and shapes, aggregate into ordered crystal-like structures. In contrast, a continuum system exploits the spontaneous formation of nanoscale domains. The domain size and shape are not pre-fabricated, but emerge during the self-assembly process. A continuum system offers several advantages. For instance, domains and their patterns self-assemble simultaneously, so that there is no need to pre-synthesize the building blocks. A significant degree of process flexibility and control can be achieved. The approach may be applied to diverse systems, such as microphase separation of block-copolymers, spinodal decomposition of binary monolayers and ordered pattern of organic molecules. While self-assembly holds great potential for nanofabrication, people have yet to find a general and intrinsic approach to effectively control defects. Homogenous development of self-assembly in a system is the origin of defects, which are prone to appear when multiple grains emerging at different locations meet. Top-down approach has been investigated to help reduce defect formation by regulating the orientations of grains though physical masks or templates of external fields. Here we show that extremely long-range ordered nanostructures can form without any external assistance by spontaneous propagation of self-assembly. The question we aim to address is: can self-assembly propagate? Is it possible for a system to self-assemble locally to form a regular domain pattern, and then replicate this pattern spontaneously to distance? We envision a mechanism as below. Consider a homogeneous system stable against small perturbation so that self-assembly does not occur spontaneously. Upon activation of self-assembly in a local region, the formed ordered pattern may produce sufficient destabilizing effect through long-range elastic interaction to trigger self-assembly in its immediate surrounding areas. The newly formed structures inherit the same order information and further destabilize their neighbours. The chain reaction may propel the propagation of self-assembly into distance and generate an extreme long-range order.

MODEL

Many self-assembly systems demonstrate similar domain patterns, suggesting a possible universal theoretical framework. Here we consider a representative system with dipole-type interaction, which can physically originate from elastic as well as electrostatic or magnetic interactions. Experiments have shown periodic dots or other regular domain patterns due to phase separation, with domain size in the range of 1-100nm. Consider a thin film of two atomic species A and B. Define $C(\mathbf{x})$ as the position dependent concentration fraction, C=0 for pure A and C=1 for pure B. A homogeneous film may phase separate to form A-rich and B-rich domains. The free energy involves short-range atomic interaction and long-range interaction between domains. The reduction of the free energy drives diffusion and leads to pattern formation. Take elastic dipole interaction induced by surface stress as an example, the normalized diffusion equation is

$$\frac{\partial C}{\partial t}=\nabla^2\left[\frac{df}{dC}-2\nabla^2 C+QI\right] \tag{1}$$

Here Q is a dimensionless number scales with the ratio of interface width and domain size. I is an area integration over the substrate surface characterizing the long-range elastic interaction, namely

$$I=-\frac{1}{\pi}\iint\frac{(x-\xi)\dfrac{\partial C}{\partial \xi}+(y-\eta)\dfrac{\partial C}{\partial \eta}}{\left[(x-\xi)^2+(y-\eta)^2\right]^{3/2}}d\xi d\eta \tag{2}$$

The condition of self-assembly can be obtained from linear stability analysis. Assume a regular solution $f(C)=C\ln C+(1-C)\ln(1-C)+\Omega C(1-C)$, where Ω is a dimensionless number measuring the bond strength relative to the thermal energy. The curve $f(C)$ is convex and prefers a homogenous film when Ω<2. Consider a perturbation

[a] Corresponding author. Email: weilu@umich.edu.

$C(x,t) = C_0 + q(t)\sin(kx)$, where C_0 is the average concentration. The solution of Eq. (1) is $q = q_0 e^{\alpha t}$, where q_0 is the initial amplitude and $\alpha = k^2[-1/[C_0(1-C_0)] + 2\Omega - 2k^2 + 2Qk]$. With $\alpha \le 0$ for all k, the perturbation amplitude q decays with time so that a homogeneous film is stable against small perturbation. This condition corresponds to $C_0 \le C_L$ or a symmetric case of $C_0 \ge C_H$, where $C_L = (1-\sqrt{1-s})/2$, $C_H = (1+\sqrt{1-s})/2$, and $s = 8/(Q^2 + 4\Omega)$. Self-assembly occurs for $C_L < C_0 < C_H$. With Ω=1.3 and Q=1.8 we have C_L=0.386 and C_H=0.614.

RESULTS

Unlike common study of self-assembly, here we focus on the stable regime $C_0 \le C_L$. Figure 1 demonstrates how self-assembly can propagate under such a condition. We performed fully non-linear simulation of Eq. (1) in Fourier space. The initial condition was set to fluctuate randomly within 0.001 from an average. We took Ω=1.3 and Q=1.8. The film was initially homogeneous with an average concentration of C_0=0.38 (below C_L), which was stable against small perturbation. We introduced a small initiation zone at the left edge by increasing its local concentration to 0.42 (above C_L) for self-assembly to occur. The width of the zone is roughly the diameter of a self-assembled dot. In experiments we envision that this process can be achieved by local mass deposition. Upon pattern formation, the nearby homogeneous region was disturbed and became unstable. Self-assembly propagated and generated a uniform lattice of dots in the entire film without any defects. To eliminate the boundary effect, the presented results were cropped from a larger calculation cell of 2048×48. We placed the initiation zone in the middle of the stripe so that self-assembly actually propagated symmetrically toward two sides. The right 512×48 was shown in Fig.1.

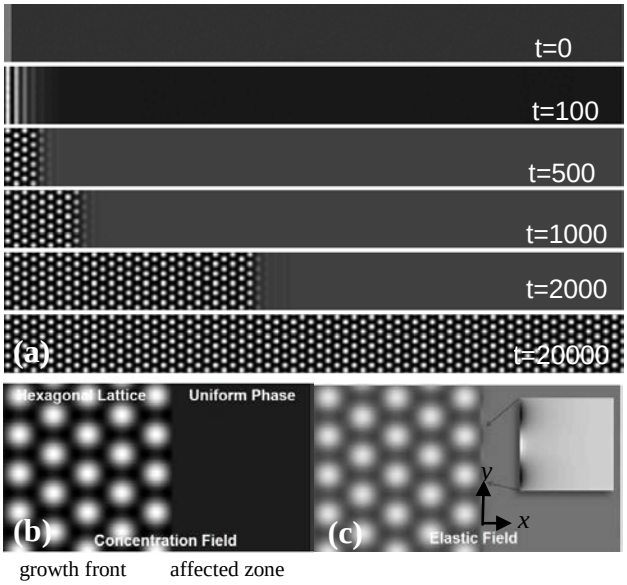

Fig. 1 Spontaneous propagation of self-assembly. (a) The propagation was initiated by a local deposition at the left edge. The locally self-assembled structure as a precursor destabilized its initially stable surrounding areas. The newly formed structures inherited the same order information from the precursor and further activated the self-assembly of their neighbors. This process caused spatial extension of self-assembly and replication of the order, producing a long-range ordered superlattice without defects. (b) Magnified concentration field. (c) The corresponding I field is in phase with the pattern. Q=1.8, Ω=1.3.

While we started self-assembly in a small initiation zone by giving it a concentration higher than C_L, this amount had negligible effect on the average concentration of the entire film. Thus the propagation was not due to the diffusion of higher concentration. We believe that the self-sustained propagation relies on the interaction between the ordered structure in the propagation front and the homogenous region immediately ahead of it, which we call affected zone. Equation (2) shows that the I term is negligible when the film is homogeneous with small random noise. In contrast, the self-assembled pattern in the propagation front induces a dipole-type I field that is in phase with the pattern and extends into the affected zone, as shown in Fig. 1. We find that the ordered pattern in the growth front helps to eliminate the energy battier in the affected zone. Our calculation shows that the hexagonal pattern has lower energy than a homogenous film when the concentration is higher than a critical value, C_D. The range between C_D and C_L creates a special bistable state, where a homogenous film is stable against small perturbation yet the hexagonal pattern has lower energy. The concentration C_0 in Fig. 1 falls in this bistable state. As illustrated in Fig. 2, self-assembly from a homogenous film (H) to the dot pattern (D) will reduce the free energy by Δg_{H-D}, but it needs help to first overcome an energy battier, Δg_b. The ordered pattern in the growth front helps to eliminate the energy battier in the affected zone by the I field.

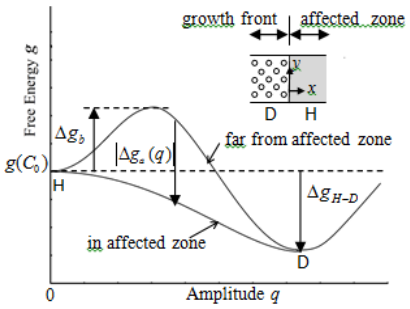

Fig. 2 The ordered pattern in the growth front removes the energy barrier, Δg_b, in the affected zone, causing an autocatalytic process H→D.

CONCLUSIONS

We proposed a mechanism that self-assembly can propagate spontaneously and deliver ordering information to distance. This mechanism utilizes the ordered pattern in the growth front to trigger self-assembly in the affected zone through long-range interaction such as elasticity. We showed that the propagation can produce extremely long-range ordered superlattice.