

Theory of lithographically-induced self-assembly

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Recent experiments show that, when a two-phase fluid confined between parallel substrates is subject to an electric field, one phase can self-assemble into a triangular lattice of islands in another phase. We describe a theory of the stability of the island lattice. It is well known that the total interface energy reduces when the island diameter increases. We show that, under certain conditions, the electrostatic free energy reduces when the island diameter decreases. The islands select the equilibrium diameter to minimize the combined interface energy and electrostatic energy. We describe the conditions for electrostatic field to stabilize the island lattice, and analyze an idealized model. The theory suggests considerable experimental control over stable island size. © 2001 American Institute of Physics. [DOI: 10.1063/1.1380728]

Chou and co-workers recently discovered a process in which a flat film self-assembled into a periodic array of islands.^{1,2} They first deposited a thin polymer film on a substrate, then placed another substrate (to be called the ceiling here) above the film, with a small air gap fixed by a spacer. When the system was heated in a uniform temperature field, the polymer flowed and broke into islands. The islands rose to bridge the substrate and the ceiling, formed a two-dimensional triangular lattice, and were fixed after cooling to room temperature. Image charges were implicated for driving the process. In a subsequent work, Schaffer *et al.*³ reported that only when a voltage was applied across the polymer melt did it break into islands. Islands reported so far have diameters of a few micrometers.

The process offers *guided self-assembly*. For the islands to form a periodic lattice, neither the substrate nor the ceiling needed to be patterned. However, when the ceiling height was patterned at a coarse scale by using lithography, the height pattern influenced the fine scale island pattern self-assembled by internal forces; the process was named “lithographically induced self-assembly” (LISA).^{1,2} One can envision extensions of the process. If the polymer wets preferentially to one of the two substrates, and breaks only under an external voltage, the polymer may flow back to a flat film upon reheating without voltage. The process thus offers *erasable self-assembly*. In principle, the electrodes can also be patterned and addressed at a coarse scale. After an island pattern has formed, upon reheating subject to a new voltage pattern, a different island pattern can form. Furthermore, both heat and voltage can be supplied by an array of atomic force microscope tips, similar to a data storage method developed recently.⁴ The process thus offers *programmable self-assembly*. The air gap between the polymer film and the ceiling can be replaced by another polymer. The two polymers are immiscible, and may flow into an ordered pattern subject to a voltage. Using lithography, one can fabricate a multicellular body with polymers and electrodes, and then switch on fine scale patterns within each cell. The process thus offers *three-dimensional self-assembly*.

Technological possibilities aside, LISA poses scientific questions even when the electrodes are flat and unpatterned. Why does the film break into islands? Why do islands have a uniform size? How small can the islands be? Why do islands order into a lattice? Can the process be used for materials other than polymers?

Hitherto only the first question has a clear answer. This has to do with the instability of a flat interface between two insulators, or between a conductor and an insulator, subject to an electric field normal to the interface.⁵ Even if no external voltage is applied, the contact potential between dissimilar materials can generate significant electric field over a small gap.⁶ The instability is usually understood in terms of a linear perturbation analysis, but can also be understood in terms of energetics, as follows. Consider a two-phase fluid lying between parallel electrodes under a constant voltage. For the time being, the two phases are perfect dielectrics with different permittivities. They can flow and change the configuration to reduce the combined interface energy and electrostatic energy. Figure 1 illustrates two configurations of the mixture: lamellar and columnar. In the lamellar configuration, with any vertical arrangement, the electric displacement is uniform in the two phases. In the columnar configuration, with any lateral arrangement, the electric field is uniform in the two phases. All lamellar configurations have the same electrostatic free energy, which is the highest

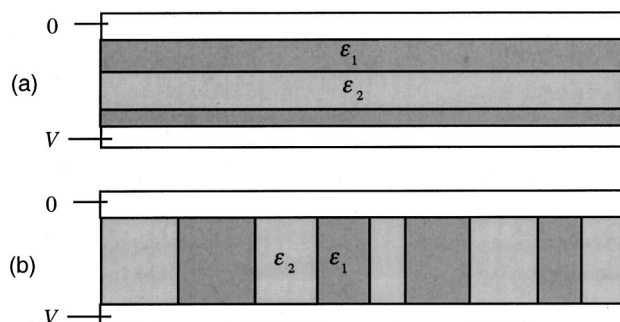


FIG. 1. A two-phase dielectric fluid lies between parallel electrodes, subject to a voltage. (a) shows a lamellar configuration and (b) shows a columnar configuration.

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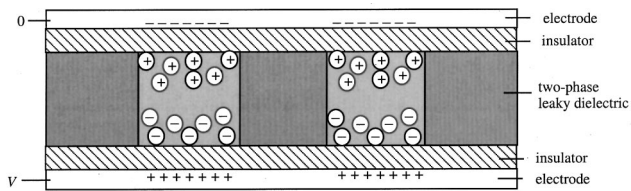


FIG. 2. This is a sketch of an idealized model. In the binary fluid, one phase contains mobile charges, and the other is a perfect dielectric. The junctions acquire diffused dipoles. Solid insulators may be coated on the electrodes to block electric current.

among all configurations of the mixture. All columnar configurations have the same electrostatic free energy, which is the lowest among all configurations of the mixture. Consequently, the voltage drives the fluid to flow from a lamellar to a columnar configuration, at a cost of adding some interface energy. The instability has been demonstrated in various systems.⁷

The instability, however, does not set a stable, uniform island size. Focus on the process in the columnar configuration, in which the two phases can change configuration by lateral flow. When the lateral feature size increases, the total interface energy reduces, but the electrostatic energy remains constant. Consequently, to reduce the combined energy, the binary fluid flows to coarsen. Some islands grow at the expense of others; time permitting, one single island will form. No stable, uniform island size is expected.

To form stable, uniform islands, the theory needs more ingredients. In essence, an electrostatic field must be made to drive phase refining, overcoming the coarsening driven by interface energy. This refining action can be acquired as follows. One phase may be a leaky dielectric⁸ containing mobile charges, either ionic or electronic, and the other phase may still be a perfect dielectric, or a dissimilar leaky dielectric (Fig. 2). To sustain a large voltage without electrolysis or excessive electric current, one may coat the two electrodes with solid insulators. When a voltage is applied between the electrodes, space charges of opposite signs pile up at junctions. The equilibrium distribution of the space charge is governed by the Poisson–Boltzmann equation.^{9,10} Each junction now acquires a diffused dipole. The dipoles interact through the intervening dielectrics, driving phase refining.

The density of the mobile charges in the leaky dielectrics must be controlled. In one limit, when the mobile charge density is so high that the Debye length approaches the atomic dimension, the binary fluid reaches the lowest electrostatic energy configuration when the conducting phase covers both the substrate and the ceiling, and forms bridges connecting them, leaving the insulating phase to carry no electric field. In this limit, islands are unstable.

We now analyze another limit, when the mobile charge density in the binary fluid is so low that both phases can be modeled as perfect dielectrics (Fig. 3). The general case of leaky dielectrics will be considered elsewhere. The substrate is coated with a solid dielectric of permittivity ϵ and thickness b . A binary dielectric fluid of permittivities ϵ_1 and ϵ_2 lies between the coated substrate and the ceiling. The electrodes are perfect conductors, separated by distance s , and subject to voltage V . The presence of the solid dielectric coating is significant. Unlike the structures in Fig. 1, in the

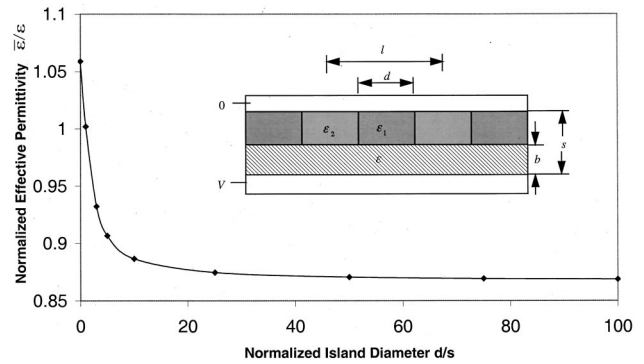


FIG. 3. One substrate is coated with an insulator, and the fluid consists of two perfect dielectrics. The effective permittivity is plotted as a function of the island diameter. The parameters used for the calculation are $B=C=0.5$, $\epsilon_1/\epsilon=2$ and $\epsilon_2/\epsilon=0.25$.

structure in Fig. 3, neither electric field nor electric displacement is uniform, and the electrostatic energy does change when the binary fluid changes configuration.

Under a constant voltage, the average electrostatic free energy (i.e., the total electrostatic free energy in the system divided by the volume occupied by all three dielectrics) is

$$G_e = -\frac{\bar{\epsilon}}{2} \left(\frac{V}{s} \right)^2, \quad (1)$$

where $\bar{\epsilon}$ is the effective permittivity. Subject to a constant voltage, the more permeable a configuration is, the lower the electrostatic free energy it contains. Assume that phase 1 forms a periodic lattice of cylindrical islands, each with diameter d . The effective permittivity takes the dimensionless form

$$\bar{\epsilon}/\epsilon = f(d/s, B, C, \epsilon_1/\epsilon, \epsilon_2/\epsilon), \quad (2)$$

where $B=b/s$, and C is the volume fraction of phase 1 in the binary mixture.

Analytic expressions are available at two limits: needles ($d/s \ll 1$) and diskettes ($d/s \gg 1$). For needles, phase 1 and 2 in parallel form a capacitor, and the coating forms another capacitor. The two capacitors then combine in series, giving the effective permittivity

$$\bar{\epsilon}_{\text{needle}} = \left[\frac{1-B}{C\epsilon_1 + (1-C)\epsilon_2} + \frac{B}{\epsilon} \right]^{-1}. \quad (3)$$

For diskettes, phase 1 and the coating in series form a capacitor, and phase 2 and the coating in series form another capacitor. The two capacitors then combine in parallel, giving the effective permittivity

$$\bar{\epsilon}_{\text{diskette}} = C \left(\frac{1-B}{\epsilon_1} + \frac{B}{\epsilon} \right)^{-1} + (1-C) \left(\frac{1-B}{\epsilon_2} + \frac{B}{\epsilon} \right)^{-1}. \quad (4)$$

The needle configuration is more permeable than the diskette configuration, $\bar{\epsilon}_{\text{needle}} \geq \bar{\epsilon}_{\text{diskette}}$. (The equality holds for trivial cases: $B=0$, $B=1$, $C=0$, $C=1$, or $\epsilon_1=\epsilon_2$.) When the binary fluid has a large dielectric contrast ($\epsilon_1/\epsilon=\infty$ and $\epsilon_2/\epsilon=0$), $\bar{\epsilon}_{\text{needle}}=\epsilon/B$ and $\bar{\epsilon}_{\text{diskette}}=\epsilon C/B$.

To deal with intermediate island diameters, we analyze an axisymmetric model. Say the islands form a triangular lattice. A unit cell is a hexagonal prism containing a single cylindrical island. We model the hexagon by a cylinder of

diameter l , setting $C=(d/l)^2$ to be the volume fraction of phase 1 in the binary fluid. Thus, l is an effective spacing between the neighboring islands. The electrostatic energy stored in an axisymmetric cell should not differ too much from that in a prismatic cell. The bottom and the top surfaces of the cylinder are prescribed with electric potential V and 0, respectively. The outer surface of the cylinder has zero radial electric displacement. We use a commercial finite element code, ABAQUS, to calculate the electric field, and then integrate the electric displacement at the bottom of the cylinder surface. Figure 3 shows the calculated effective permittivity as a function of the island diameter. The function decreases monotonically, approaching the analytic values at the two limits. As anticipated, the electrostatic free energy reduces when the island diameter decreases. That is, the voltage drives phase refining.

In the idealized model, the edge of the islands are taken to be vertical. Of all interfaces, only the one between phase 1 and 2 changes area when the islands change diameter. The interface energy divided by the total volume occupied by the three dielectrics is

$$G_i = 4\gamma(1-B)/d, \quad (5)$$

where γ is the tension of the interface between phase 1 and 2. The total interface energy reduces when the island diameter increases. That is, the interface energy drives phase coarsening.

The combined energy, $G = G_i + G_e$, takes the dimensionless form

$$\frac{G}{\varepsilon(V/s)^2} = \frac{4(1-B)C}{(d/s)\xi} - \frac{f}{2}. \quad (6)$$

The dimensionless parameter $\xi = (\varepsilon V^2)/(s\gamma)$ measures the relative importance of the electrostatic energy and the surface energy. Using representative values for various quantities, we estimate that the parameter falls in the range $\xi = 0.1-100$. Figure 4 plots the combined energy as a function of the island diameter. When ξ is small, the interface energy prevails, and the combined energy decreases monotonically as the island diameter increases, so that the islands coarsen indefinitely. When ξ is large, the combined energy reaches a minimum, selecting an equilibrium island diameter. The larger the value of ξ , the more significant the effect of voltage, and the smaller the stable islands.

The voltage is limited by the breakdown field E_B of one of the phases, so that $\xi \sim \varepsilon E_B^2 s / \gamma$. To stabilize small islands, one should choose binary dielectrics of large permittivities, high breakdown fields, and small interface tension. In particular, the polymer-polymer interface tension can easily be one order of magnitude smaller than air-polymer interface tension. The equilibrium island diameter also depends on

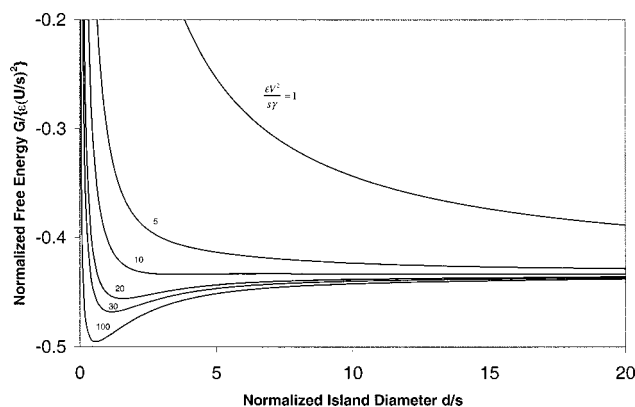


FIG. 4. The combined energy as a function of the island diameter at several levels of the dimensionless parameter $\xi = \varepsilon V^2 / s \gamma$ are shown.

various ratios entering Eq. (2), as well as the density of mobile charges. These effects will be reported elsewhere. No fundamental barrier seems to exist to prevent the stable island diameter from lowering by at least one order of magnitude from the experimental values reported in Refs. 1–3. Islands reported so far are of higher dielectric constant of the two phases, the other phase being air. The theory can also be used to explore whether islands of lower dielectric constant can form, or alternating stripes of the two phases can form. Furthermore, in a similar spirit, we have developed a theory on stabilizing semiconductor islands using elastic energy, referred to as the height constrained Stranski–Krastanov growth.¹¹ We anxiously await quantitative experiments suggested by the theory.

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¹S. Y. Chou and L. Zhuang, J. Vac. Sci. Technol. B **17**, 3197 (1999).

²S. Y. Chou, L. Zhuang, and L. J. Guo, Appl. Phys. Lett. **75**, 1004 (1999).

³E. Schaffer, T. Thurn-Albrecht, T. P. Russell, and U. Steiner, Nature (London) **403**, 874 (2000).

⁴G. Binnig, M. Despont, U. Drechsler, W. Haberle, M. Lutwyche, P. Vettiger, H. J. Mamin, B. W. Chui, and T. W. Kenny, Appl. Phys. Lett. **74**, 1329 (1999).

⁵L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984), p. 33.

⁶S. Herminghaus, Phys. Rev. Lett. **83**, 2359 (1999).

⁷M. Trau, S. Sankaran, D. A. Saville, and I. A. Aksay, Nature (London) **374**, 473 (1995).

⁸D. A. Saville, Annu. Rev. Fluid Mech. **29**, 27 (1997).

⁹E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Dover, New York, 1999).

¹⁰W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, UK, 1989).

¹¹J. Liang and Z. Suo, *Uniform island arrays by height-constrained Stranski–Krastanov growth* (unpublished); Preprint: Publication 112, <http://www.princeton.edu/~suo/>.