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Pattern Formation Induced by an Electric Field in Thin Liquid Films

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Abstract

This paper addresses some nonlinear problems arising from thin film pattern formation induced by an electric field. The physical setup is a thin liquid film confined between two electrodes and separated by an air gap from the top mask electrode. The objective is to study the dependence of the interfacial morphology on certain parameters. The mathematical model consists of a lubrication equation including the effects of surface tension describing the thin film thickness and Maxwell's equations describing the electric field strengths. In the long wavelength limit, a single interfacial evolution equation is derived. A weakly nonlinear stability analysis of the planar interface solution to this equation shows that the thickness ratio of the air gap to the liquid plays a critical role in the pattern formation process.

I.Introduction and Model Formulation

In a lithographically induced self-assembly (LISA[1]) process, the application of an electrostatic force is used to create and replicate lateral structures in polymer films on a submicrometer length scale[9]. The physical configuration consists of a layer of a smooth thin polymer film cast on a flat silicon substrate. A pattern-free mask is placed above the film at a distance less than $1\mu m$, leaving a thin air gap. Then the system is heated above the glass transition temperature of the polymer liquid and allowed to cool down to room temperature. Next an external electric field is imposed on the substrate and mask to produce a driving force that competes with the surface tension on the interface of the film and induce sufficiently long wavelength fluctuations. Such an instability is characterized by a hexagonal order pattern[9]. When the two electrodes are at a fixed distance, and the initial film thickness is adjusted from thinner ($93nm$)to thicker($193nm$), the lateral hexagonal packing becomes more orderly, clear, and complete[9]. Gravitational effects are negligible due to the very small thickness of the film. Compared to the electric force, the intermolecular forces, including van der Waals attraction and extremely short range Born repulsion, are much too weak to affect the pattern formation process[13]. The electric field induced pattern generation process has stimulated much work toward understanding the underlying mechanism. Although it is believed that electric fields can be used to control and organize the replication of a master pattern from the mask onto the thin film surface, a theoretical explanation is so far incomplete. The existing research on such pattern formation employs a linear stability analysis to study the evolution of the interface between a polymer film and an air gap, or between two layers of polymer film. The critical wave length λ is examined to predict the onset of the destabilizing process[3, 6, 7, 9, 10]. In the cases involving leaky dielectric films, conductivity and the thickness ratio are found to be critical parameters[5, 11]. In the case of perfect films, the thickness ratio of the air gap to the film is an important control parameter[9, 13]. In order to explain this pattern formation process more fully, a thorough investigation is needed to analyze nonlinear factors. A weakly nonlinear analysis is conducted in this work to discover the dependence of these patterns on the thickness ratio, for a nonconducting thin film with an air gap.

A weakly nonlinear stability analysis basically pivots a perturbation procedure about the critical point of linear stability theory to examine the effects of including nonlinear terms in the relevant model system. Such a nonlinear theory allows one to deduce the relationships between system parameters and stable patterns, which are valuable for experimental design and difficult to determine using numerical simulation alone.

Consider a thin polymetric liquid layer of mean thickness h_0 spin-coated onto a planar silicon substrate located at $z = 0$ and bounded above by an interface satisfying $z = h(x, y, t)$, where (x, y, z) represents a laboratory coordinate system and t is time. A planar silicon mask is mounted at a distance $d > h_0$ from the bottom, leaving a thin air gap. The system is subject to a constant electrostatic potential U. We assume the polymer is of relatively low molecular weight so gravity may be neglected while the flow is slow enough so that a continuum mechanical approach is valid. The dimensionless dielectric constants of the polymetric film and air are ϵ_p and $\epsilon_a = 1$ respectively.

In the long wavelength limit[4, 12], the following thin film lubrication equation describes the spatio-temporal evolution of the film interface $z = h(x, y, t)$:

$$3\mu\frac{\partial h}{\partial t} - \nabla \cdot [h^3 \nabla P] = 0$$

where μ is the constant viscosity of the polymer and P is the pressure distribution on the interface, which consists of the atmospheric pressure p_0, the surface tension, the intermolecular interaction p_i and the electrostatic pressure p_E. In short,

$$P = p_0 - \gamma \nabla^2 h + p_i + p_E.$$

The intermolecular potential is smaller than the electro-static potential by two orders of magnitude, and is therefore ignored in the model. The instability arises from the competition between the surface tension and the electrostatic effects. The surface tension tends to minimize the area of the film-air interface, thus stabilizing the polymer film. In opposition to this, the electric field destabilizes the film by acting on the polarization field and free charge at the interface. In the next section we will consider the derivation of the electrostatic pressure.

II.Derivation of the Electrostatic Pressure and Model Nondimensionlization

Following the formulation of Saville[8], under static conditions, electric and magnetic phenomena are independent since their fields are uncoupled. Maxwell's equations can be simplified by neglecting magnetic fields due to the fact that the magnetic phenomena time scale is much shorter than that of electrical phenomena. Hence these take the reduced form $\nabla \cdot \vec{E}_i = 0, i = p, a$ because the net charge in the liquid layer and in the air layer may be assumed to be zero, where $\vec{E_i}$ represent the electric field strength in each layer. There exists the potential Ψ_i such that $\vec{E}_i = -\nabla\Psi_i$ under the condition $\nabla \times \vec{E}_i = 0$. We thus obtain a Laplace equation for the potential Ψ_i: $\nabla^2\Psi_i = 0$. In the long wave limit, $E_i = -\dfrac{\partial \Psi_i}{\partial z}$, and the Laplacians simplify to the following:

$$\frac{\partial^2 \Psi_p}{\partial z^2} = 0, \quad \frac{\partial^2 \Psi_a}{\partial z^2} = 0. \tag{1}$$

The boundary conditions at the two solid plates are:

$$\Psi_p = U \quad \text{at} \quad z = 0, \quad \text{and} \quad \Psi_a = 0 \quad \text{at} \quad z = d. \tag{2}$$

The balance of Ψ_i and the zero surface charge on the interface require that

$$\Psi_a = \Psi_p, \quad \text{and} \parallel \epsilon E \parallel = \epsilon_p E_p - \epsilon_a E_a = 0 \quad \text{at} \quad z = h(x, y, t), \tag{3}$$

where $\parallel \cdot \parallel$ denotes the jump of the dielectric displacement ϵE across the interface.

Solving equation (1) with the boundary conditions (2) and (3) yields:

$$E_p = \frac{U}{\epsilon_p d - (\epsilon_p - 1)h} \quad \text{and} \quad E_a = \frac{U\epsilon_p}{\epsilon_p d - (\epsilon_p - 1)h}. \tag{4}$$

The electrostatic and hydrodynamical phenomena are coupled through the Maxwell stress tensor. The applied electric field produces a pressure p_E on the surface of the thin film, which is equal to the jump of the isotropic components of the Maxwell electrical stress tensor[2, 8]:

$$p_E = \frac{1}{2} \parallel \epsilon E^2 \parallel = \frac{\epsilon_0}{2}(\epsilon_p E_p^2 - \epsilon_a E_a^2) = -\frac{\epsilon_0 \epsilon_p (\epsilon_p - 1)U^2}{2[\epsilon_p d - (\epsilon_p - 1)h]^2}, \tag{5}$$

where ϵ_0 is the vacuum dielectric permittivity.

Incorporating the function of (5) into the thin film equation, and nondimensionalizing the resulting equation by introducing the scale factor $\frac{\mu h_0^2}{\epsilon_0 U^2}$ for time, and h_0 for both length and layer thickness, we obtain the dimensionless equation governing the interface evolution

$$\frac{\partial H}{\partial t} + \alpha \nabla \cdot [H^3 \nabla (\nabla^2 H)] + \beta \nabla \cdot [H^3 (\epsilon_p \xi + \epsilon_p - (\epsilon_p - 1)H)^{-3} \nabla H] = 0 \tag{6}$$

for the nondimensional thickness $H = h/h_0$, where

$$\alpha = \frac{\gamma d}{3\epsilon_0 U^2 (\xi + 1)}, \quad \beta = \frac{\epsilon_p (\epsilon_p - 1)^2}{3},$$

and $\xi = \frac{d - h_0}{h_0} = \frac{d}{h_0} - 1$ stands for the thickness ratio of the air gap to that of the thin film. Note that the larger the value of ξ, the greater the air gap, which suggests a weaker electrostatic driving force, and thus the instability is expected to be weaker as well.

III. Stability Analysis

In order to find the critical wavenumber when instabilities occur, and to discover certain parameter ranges for pattern formation, we perform a weakly nonlinear stability analysis on the one dimensional model:

$$\frac{\partial H}{\partial t} + \alpha \frac{\partial}{\partial x}[H^3 \cdot \frac{\partial^3 H}{\partial x^3}] + \beta \frac{\partial}{\partial x}[H^3 \cdot (\epsilon_p \xi + \epsilon_p - (\epsilon_p - 1)H)^{-3} \cdot \frac{\partial H}{\partial x}] = 0. \tag{7}$$

Consider a solution of (7) through third order truncation of the form[12]:

$$\begin{aligned} H(x,t) \sim\ & 1 + A\cos(kx) + A^2[H_{20} + H_{22}\cos(2kx)] \\ & + A^3[H_{31}\cos(kx) + H_{33}\cos(3kx)], \end{aligned} \tag{8}$$

with the amplitude function $A(t)$ satisfying the Landau equation:

$$\frac{dA}{dt} \sim \sigma A - a_1 A^3, \tag{9}$$

where k is the wavenumber; σ, the growth rate; and a_1, the so called Landau constant. The Landau equation governs the amplitude growth of the perturbation. The patterning process can only develop when both $\sigma > 0$ and $a_1 > 0$ (super-critical instability), or when both $\sigma < 0$ and $a_1 < 0$ (sub-critical instability, or meta-stability)[12].

Substituting the solution of (8,9) into equation (7), we obtain the dispersion relationship between σ and k to the first order of perturbation:

$$\sigma = \beta(\epsilon_p \xi + 1)^{-3} k^2 - \alpha k^4, \tag{10}$$

from which the critical wavenumber when instability takes place is deduced to be:

$$k_c = \sqrt{\frac{\beta}{\alpha(\epsilon_p \xi + 1)^3}} = \sqrt{\frac{\epsilon_0 \epsilon_p (\epsilon_p - 1)^2 U^2 (\xi + 1)}{d(\epsilon_p \xi + 1)^3 \gamma}}. \tag{11}$$

This value compares favorably to the results in [9, 10] for one layer of film and to that for the double layer situation obtained through a completely different approach (refer to Lin[3]).

Equation (11) suggests that the instability depends only on the thickness ratio ξ once the dielectric material is chosen therefore determining ϵ_p, the electrodes are kept at a fixed distance, and the electric potential U is prescribed.

Given the representative values[10, 13]

$$\epsilon_0 = 8.854 \times 10^{-12} C^2/Nm^2, U = 70V, \epsilon_p = 2.5, \gamma = 3.8mN/m, d = 100nm,$$

the relationship of k_c versus ξ is depicted in Fig.1. We observe from Fig.1 that k_c decreases as ξ increases which means that the number of active wave modes is reduced, and implies that the instability becomes weaker. This agrees with the fact that the electrostatic force is weaker when the air gap is larger relative to the thinner layer of the polymer film, so that the driving force of instability is weakened.

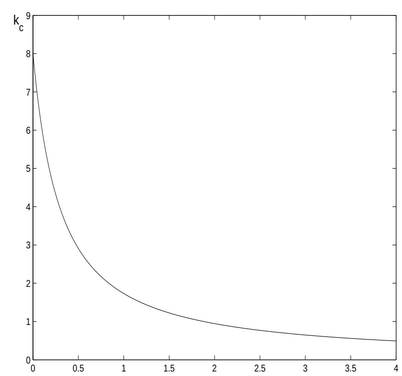

Figure 1: Plot of the critical wavenumber k_c versus thickness ratio ξ.

The dispersion relationship reveals the onset of instability, but does not explain the pattern formation process which is the result of competition between nonlinear factors. In order to explain the underlying nonlinear mechanism, we obtain the value of the Landau constant from the third order perturbation:

$$\begin{aligned} a_1 &= 2\sigma H_{31} + \frac{3}{4} k^4 \alpha - \frac{3(\epsilon_p \xi + \epsilon_p)(\epsilon_p \xi + 2\epsilon_p - 1)\beta k^2}{4(\epsilon_p \xi + 1)^5} \\ &+ (\frac{21}{2} k^4 \alpha - \frac{3k^2 \beta(\epsilon_p \xi + \epsilon_p)}{2(\epsilon_p \xi + 1)^4}) \frac{3\beta(\epsilon_p \xi + \epsilon_p) - 3k^2 \alpha(\epsilon_p \xi + 1)^4}{14k^2 \alpha(\epsilon_p \xi + 1)^4 - 2\beta(\epsilon_p \xi + 1)}. \end{aligned} \tag{12}$$

The constant a_1 can be expressed as a function of ξ when we consider the limiting case $k \to k_c$, or equivalently $\sigma \to 0$. We plot a_1 in Fig.2.

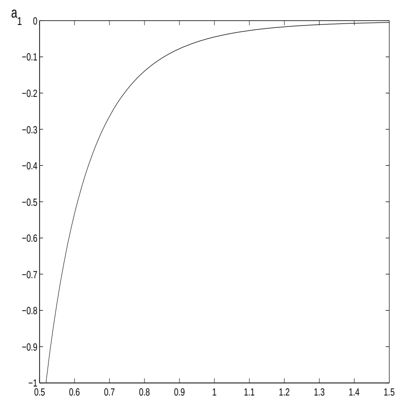

Figure 2: Plot of the Landau constant a_1 versus ξ. As a matter of fact, a_1 is negative for all values of ξ.

We observe that the Landau constant is always negative and hence meta-stability is expected to be the reason for the pattern formation. The magnitude of the Landau constant measures the strength of the nonlinear effects. We notice that as the value of ξ increases, namely as the air gap gets larger, the magnitude of a_1 decreases. Therefore, the effect of nonlinearity decreases, and the instability becomes weaker. In order to have pattern formation take place, the nonlinear effects need to be large enough and therefore the air gap needs to be relatively small. But if the air gap is too small, we see the nonlinearity gets extremely large, and no pattern can be expected to occur because the pattern has ruptured. To select a reasonable range of ξ values, we plot both k_c and a_1 on the same graph as shown in Fig.3. From that figure, the patterning is observed in the range $0.6 \leq \xi \leq 1$. At any given initial thickness of the film, we notice that the growth rate grows negative at larger wavenumber, which corresponds to smaller wavelength. This implies that the patterns are the short length scale shapes, which agrees with the experimental observations for circular holes and columns[1, 9].

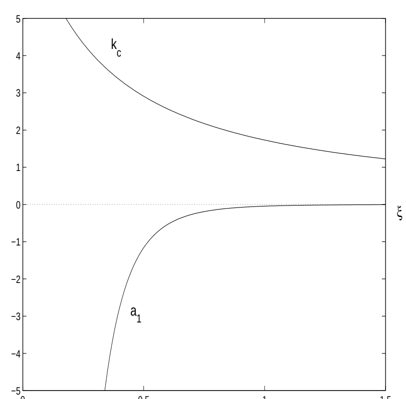

Figure 3: Graphs of k_c and a_1 versus ξ. A reasonable range of ξ is chosen for the pattern formations.

IV.Conclusion and Discussions

The current result has explained the nonlinear effects contributing to pattern formation in a thin liquid film. Under the influence of an electrostatic field, it is discovered that the thickness ratio of the air gap to the thin film is crucial in driving the nonlinear patterning process. The case of a patternless mask has been considered. In order to better understand the nonlinear effects, a two dimensional study is necessary, which will be reported in future work. Although pattern duplication from the patterned mask onto the film is the ultimate purpose in applying electrostatic forces in thin film systems, so far the mathematical formulation is too complicated to investigate. Only very limited results have been found in the relevant experiments and simulations[9, 13].

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References

[1] Chou S. Y. and Zhuang L., Lithographically Induced Self-Assembly of Periodic Polymer Micropillar arrays, *J. Vac. Sci. Technol. B*, **17**(6),(1999), 3197-3202.

[2] L.D.Landau and E.M. Lifshitz, Electrodynamics of Continuous Media, *Pergamon Press*, 1960

[3] Lin Z., etc, Electric Field Induced instabilities at Liquid/Liquid Interfaces, *Journal of Chemical Physics*, **114**(5), (2001), 2377-2381.

[4] Oron A., Davis S.H., Bankoff S.G., Long-scale evolution of thin liquid films, *Reviews of Modern Physics*, **69**(3), (1997), 931-980.

[5] Pease L.F.III, Russel W.B., Linear stability analysis of thin leaky dielectric films subjected to electric fields, *Journal of Non-Newtonian Fluid Mechanics*, **102**, (2002), 233-250.

[6] Pease III L.F. and Russel W.B., Electrostatically induced submicron patterning of thin perfect and leaky dielectric films: A generalized linear stability analysis, *Journal of Chemical Physics*, **118** (8), (2003), 3790-3803.

[7] Pease L.F.III and Russel W.B., Limitations on Length Scales for Electrostatically Induced Submicrometer Pillars and Holes, *Langmuir*, **20**, (2004), 795-804.

[8] Saville D.A., Electrohydrodynamics: The Taylor-Melcher Leaky Dielectric Model *Annu. Rev. Fluid Mech.*, **29**, (1997), 27-64.

[9] Schäffer E., Thurn-Albrecht T., Russell T.P., and Stelner U., Electrically induced structure formation and pattern transfer, *Nature*, **403**, (2000), 874-877.

[10] Schäffer E., Thurn-Albrecht T., Russell T.P. and Stelner U., Electrohydrodynamic Instabilities in Polymer Films, *Europhysics Letters*, **53**(4), (2001), 518-524.

[11] Shanker V. and Sharma A., Instability of the interface between thin fluid films subjected to electric fields, *Journal of Colloid and Interface Science*, **274**, (2004), 294-308.

[12] Tian E.M. and Wollkind D.J., Nonlinear Stability Analyses of Pattern Formation in Thin Liquid Films, *Interfaces and Free Boundaries*, **5**, (2003), 1-25.

[13] Verma R., Sharma A., Kargupta K., and Bhaumik J., Electric Field Induced Instability and Pattern Formation in Thin Liquid Films, *Langmuir*, **21**(8),(2005), 3710-3721.