CONTROLLED NANOSTRUCTURES FROM RIPENING BASED PATTERN FORMATION IN UNSTABLE THIN LIQUID FILMS

NARAYANAM S K CHAITANYA

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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NARAYANAM S K CHAITANYA

Department of Chemical Engineering

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Certificate

This is to certify that the thesis titled **"CONTROLLED NANOSTRUCTURES FROM RIPENING BASED PATTERN FORMATION IN UNSTABLE THIN LIQUID FILMS"** being submitted by **Mr. Narayanam S K Chaitanya** in the Department of Chemical Engineering, Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, is a record of bona-fide research work carried out by him under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree. The results contained in this thesis have not been submitted for the award of any other degree, diploma, associateship or similar title of any university or institution.

Dr. Rajesh Khanna
Professor
Department of Chemical Engineering
Indian Institute of Technology Delhi

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Abstract

The self-arranging, far-from equilibrium, unstable thin film systems have wide range of technological applications, and the most significant among them is generating controlled nanostructures and patterns. My doctoral research focuses on investigating the possibility of creating precisely defined nanostructures from spontaneous self-organization of unstable thin liquid films. A free-energy functional that facilitates a double tangent construction characterizes thin films on coated substrates under the influence of gravity. These films spontaneously phase separate into a thinner equilibrium phase and a thicker equilibrium phase when subjected to random fluctuations. This phenomenon has been termed as 'true morphological phase separation' (true MPS), owing to the formation of two true equilibrium phases, unlike general dewetting or normal MPS in thin films not influenced by gravity. Two distinct pathways of true MPS have been observed for these thin film systems, namely the 'defect pathway' and the 'direct pathway'. Both pathways show an initial power law decay with exponent 1/4 in time followed by a plateau in the number density of domains/defects for $2-D$ simulations. Thereafter, the defect pathway shows another universal power law decay with exponent 1/3 and ends with a logarithmic decay. The direct pathway skips second power law decay and goes directly to logarithmic decay.

The free-energy functional for these thin film systems is asymmetric and most of the unstable film thicknesses are closer to the thinner equilibrium phase. The morphological evolution of an unstable film closer to the thinner equilibrium phase, results in the appearance an equilibrium flat-film and circular droplets. The flat-film corresponds to the thinner equilibrium phase, while the droplets are all at various

thicknesses are aptly called defects. These defects are not at equilibrium and hence coarsening proceeds at a rapid phase (growth exponent 1/4) until the droplets reach the thickness corresponding to the thicker equilibrium phase. Thus, there is a time delay in the appearance of the thinner equilibrium phase and the thicker equilibrium phase. This pathway has been termed as the 'defect pathway' and results in the formation of 'flat-film and cylindrical droplets' pattern. Most of the films undergoing true MPS follow the defect pathway and the extent of defect-coarsening stage depends on the initial thickness of the film. The defect-coarsening is similar to the ostwald ripening of domains and hence true MPS is a ripening based pattern formation process.

Films with thickness almost halfway to both the equilibrium phases undergo true MPS through the 'direct pathway'. Here, both the equilibrium phases appear simultaneously in the system, thus negating the existence of defect-coarsening stage as there is no time delay. A bicontinuous pattern formation is observed for thin films undergoing true MPS through direct pathway. For films that are closer to thicker equilibrium phase, the thicker phase appears first in a reverse defect pathway and they are characterized by a 'circular-holes and cylindrical ridges' pattern formation. The mid-point of both the equilibrium thickness lies closer to the spinodal boundary due to asymmetricity and hence almost all the films undergo true MPS either through defect pathway or the direct pathway. The longer the time delay between the appearance of the first and second equilibrium phases in true MPS, the higher is the probability that the structures overcome the disorder on the substrate. Thus, for any given system, a thicker equilibrium film has higher chances of getting arrested by random disorder on the substrate than the thinner films.

For chemically heterogeneous substrates, the direction of diffusion is from less wettable regions to more wettable regions. But, the structures (liquid droplets) appearing on the wettable patches spill out of the patch area and never replicate the shape of the patch, when it is sharp-edged. Also, equilibrium structures appearing in the more wettable outer region never spill over into less wettable patches. Hence, the system is divided into three sub-regions to create complex structures. The more

wettable (least chemical potential) inner region is separated from the outer region by a boundary that is the least wettable (highest chemical potential) of all three regions. The gradient of diffusion is towards the inner region and hence any droplet in the region coarsens until it completely fills the area of the region (taking the shape of the patch in the process). The boundary acts as a potential barrier that restricts the spill-over of the structure in the inner region. The ripening of domains in the outer region continues until asymptotic time scales, but the structure in the inner region remains unperturbed. Also, for systems with multiple wettable regions and boundaries, patterns which are unrelated to the equilibrium structures can spontaneously emerge and stabilize in the outer region by geometrical frustration. This technique uses neither 'freezing' nor 'quenching' and still enables the creation of either single or multiple nanostructures from a single template with precisely defined shapes and sizes. This methodology presents a new paradigm of understanding pattern formation in nature and lays out simple protocols which are experimentally realizable and applicable in hugely diverse fields such as fluid flow and cell biology, engineering and science of information theory, biomimetics, nano-fabrication and tailored materials.

सार

आत्म-व्यवस्था, संतुलन से दूर, अस्थिर पतली फिल्म प्रणालियों की व्यापक रेंज है तकनीकी अनुप्रयोगों और उनमें से सबसे महत्वपूर्ण नियंत्रित नैनोस्ट्रक्चर और पैटर्न उत्पन्न कर रहा है। मेरा डॉक्टरेट अनुसंधान जांच पर केंद्रित है अस्थिर पतली तरल फिल्मों के स्वतःस्फूर्त स्वैच्छिककरण से सटीक रूप से परिभाषित नैनोस्ट्रक्चर बनाने की संभावना। एक मुक्त ऊर्जा कार्यात्मक है कि एक सुविधा है डबल स्पर्शरेखा निर्माण के तहत लेपित सब्सट्रेट पर पतली फिल्मों की विशेषता है गुरुत्वाकर्षण का प्रभाव। ये फिल्में अनायास चरण में एक पतले संतुलन और एक मोटे संतुलन के चरण में अलग हो जाती हैं जब यादृच्छिक उतार-चढ़ाव के अधीन होती हैं।

इस घटना को 'वास्तविक रूपात्मक चरण पृथक्करण' कहा जाता है, दो सच्चे संतुलन चरणों के गठन के कारण, सामान्य डीवेटिंग के विपरीत या पतली फिल्मों में सामान्य एमपीएस गुरुत्वाकर्षण से प्रभावित नहीं होते हैं। दो अलग-अलग रास्ते इन पतली फिल्म प्रणालियों के लिए सच्चे देखे गए हैं, जिनका नाम 'दोष मार्ग' और 'प्रत्यक्ष मार्ग' है। दोनों रास्ते एक प्रारंभिक शक्ति कानून के क्षय को दर्शाते हैं डोमेन / दोषों की संख्या घनत्व में एक पठार के बाद समय में 1/4 घटक 2 के लिए - डी सिमुलेशन। इसके बाद, दोष मार्ग एक और सार्वभौमिक शक्ति दिखाता है विधि 1/3 घातांक के साथ क्षय और एक लघुगणक क्षय के साथ समाप्त होता है। सीधा रास्ता दूसरा पॉवर लॉ क्षय करता है और सीधे लॉगरिदमिक क्षय को जाता है। इन पतली फिल्म प्रणालियों के लिए मुक्त ऊर्जा कार्यात्मक असममित और सबसे अधिक है अस्थिर फिल्म की मोटाई पतले संतुलन के चरण के करीब होती है। एक अस्थिर फिल्म के रूपात्मक विकास, जो पतले संतुलन के करीब है, परिणाम एक समतल सपाट फिल्म और परिपत्र बूंदों में दिखाई देते हैं। फ्लैट फिल्म पतले संतुलन के चरण से मेल खाती है, जबकि बूंदों सभी विभिन्न हैं मोटाई को उपयुक्त रूप से दोष कहा जाता है। ये दोष संतुलन में नहीं हैं और इसलिए बूंदों तक पहुंचने तक एक तीव्र चरण (विकास घातांक 1/4) पर मोटे हो जाते हैं गाढ़ा संतुलन चरण के अनुरूप मोटाई। इस प्रकार, एक समय है पतले संतुलन चरण और मोटा संतुलन की उपस्थिति में देरी चरण। इस मार्ग को 'दोष मार्ग' के रूप में जाना जाता है और इसमें परिणाम आते हैं 'फ्लैट-फिल्म और बेलनाकार बूंदों' के पैटर्न का गठन। ज्यादातर फिल्में चल रही हैं

सच एमपीएस दोष मार्ग का अनुसरण करता है और दोष-मोटे चरण की सीमा निर्भर करती है फिल्म की शुरुआती मोटाई पर। दोष-मोटे होना ओस्टवाल्ड के समान है डोमेन के पकने और इसलिए सच एमपीएस एक पकने वाली पैटर्न पैटर्न प्रक्रिया है।
दोनों समानताओं वाले मोटाई वाले फिल्म्स सच से गुजरते हैं
'सीधा मार्ग' के माध्यम से एमपीएस यहां, दोनों संतुलन चरण एक साथ प्रणाली में दिखाई देते हैं, इस प्रकार दोष-मोटे चरण के अस्तित्व को नकारते हैं समय की देरी नहीं है। पतली फिल्मों के लिए एक विचित्र पैटर्न का गठन देखा जाता है सीधे रास्ते के माध्यम से सच एमपीएस गुजर रहा है। ऐसी फिल्मों के लिए जो अधिक घनी होती हैं संतुलन चरण, मोटा चरण पहले एक रिवर्स दोष मार्ग में प्रकट होता है और वे एक गोलाकार छेद और बेलनाकार लकीरें 'पैटर्न गठन की विशेषता है।

दोनों संतुलन की मोटाई के मध्य-बिंदु असममितता के कारण स्पीनोडल सीमा के करीब है और इसलिए लगभग सभी फिल्में सही से गुजरती हैं दोष मार्ग या प्रत्यक्ष मार्ग के माध्यम से। बीच में जितना लंबा समय होगा सच एमपीएस में पहले और दूसरे संतुलन चरणों की उपस्थिति, उच्चतर है संभावना है कि संरचनाएं सब्सट्रेट पर विकार को दूर करती हैं। इस प्रकार, के लिए किसी भी प्रणाली, एक मोटी संतुलन वाली फिल्म द्वारा गिरफ्तार होने की संभावना अधिक होती है पतले फिल्मों की तुलना में सब्सट्रेट पर यादृच्छिक विकार। रासायनिक रूप से विषम सब्सट्रेट के लिए, प्रसार की दिशा कम से है अधिक गीला क्षेत्रों के लिए गीला क्षेत्र। लेकिन, संरचनाओं (तरल बूंदों) को हटाने योग्य पैच पर दिखाई देते हैं जो पैच क्षेत्र से बाहर निकलते हैं और कभी भी प्रतिकृति नहीं करते हैं पैच का आकार, जब यह तेज धार वाला हो। इसके अलावा, संतुलन संरचनाओं दिखाई दे रहे हैं अधिक गीला बाहरी क्षेत्र में कम गीला पैच में फैल कभी नहीं। अत, जटिल संरचनाओं को बनाने के लिए सिस्टम को तीन उप-क्षेत्रों में विभाजित किया गया है। अधिक गीला (कम से कम रासायनिक क्षमता) भीतरी क्षेत्र द्वारा बाहरी क्षेत्र से अलग किया जाता है एक सीमा जो तीनों क्षेत्रों की सबसे कम क्षमता वाली (उच्चतम रासायनिक क्षमता) है। प्रसार की प्रवणता आंतरिक क्षेत्र की ओर होती है और इसलिए किसी भी बूंद में जब तक यह क्षेत्र के क्षेत्र को पूरी तरह से भर नहीं लेता है, तब तक क्षेत्र मोटे हो जाते हैं इस प्रक्रिया में पैच)। सीमा एक संभावित अवरोधक के रूप में कार्य करती है जो इसे प्रतिबंधित करती है आंतरिक क्षेत्र में संरचना का फैलाव।

बाहरी में डोमेन के पकनेक्षेत्र तब तक जारी रहता है जब तक कि स्पर्शोन्मुख समय न हो, लेकिन आंतरिक क्षेत्र में संरचना बेपरवाह बना हुआ है। इसके अलावा, कई गीला क्षेत्रों और सीमाओं के साथ सिस्टम के लिए, संतुलन के लिए असंबंधित पैटर्न जो पैटर्न आसानी से हो सकते हैं ज्यामितीय कुंठा द्वारा बाहरी क्षेत्र में उभरना और स्थिर होना। यह तकनीक न तो 'फ्रीजिंग' और न ही 'शमन' का उपयोग करता है और अभी भी एकल के निर्माण में सक्षम बनाता है या ठीक से परिभाषित आकृतियों के साथ एक एकल टेम्पलेट से कई नैनोस्ट्रक्चर आकार। यह पद्धति प्रकृति में पैटर्न के गठन को समझने का एक नया प्रतिमान प्रस्तुत करती है और सरल प्रोटोकॉल को प्रस्तुत करती है जो प्रयोगात्मक रूप से साध्य हैं और द्रव प्रवाह और कोशिका जीव विज्ञान, इंजीनियरिंग और जैसे बेहद विविध क्षेत्रों में लागू सूचना सिद्धांत, बायोमेटिक्स, नैनो-निर्माण और अनुरूप सामग्री का विज्ञान।

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