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Pattern formation by capillary instabilities in thin films

Morariu, Mihai Dorin

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Chapter 8

Conclusions

The subjects investigated in this thesis center on the pattern formation in thin polymer films. A multitude of surface morphologies can be generated by the amplification of capillary waves in external fields or by the spontaneous destabilization of the liquid surface due to surface tension gradients. We were interested in both applied and fundamental aspects of structure formation on micrometer and nanometer length scales.

The spontaneous break-up of polymer films of thicknesses less than 10 nm is commonly attributed to the destabilizing effect of van der Waals forces. These forces can be considered in terms of the confinement of the electromagnetic fluctuation spectrum. The consideration of the confinement of thermal fluctuations (phonons) leads to an acoustic analogy of the van der Waals pressure. We showed that forces stemming from thermally excited acoustic fluctuations (thermal noise) in thin films, give rise to a disjoining pressure that is comparable to van der Waals forces. Under certain conditions, the acoustic effect is the dominating destabilizing force.

To demonstrate the presence of the thermo-acoustic destabilizing pressure we investigated the characteristic patterns in thin liquified polymer films. Because the spectrum of spontaneously amplified waves is very sensitive to

the detailed force balance acting at the surface of the film, we were able to quantify the magnitude of the destabilizing force by measuring the instability wavelength. We performed three sets of experiments that used polymer films bounded between a substrate and air, in a manner that unambiguously pointed out the presence of the acoustic pressure.

In the first class of experiments, we found a variation of the film destabilization with temperature, in contradiction to predictions based exclusively on a van der Waals theory. In the second approach, we chose a system in which p_{ac} and p_{vdW} pressures had opposing signs. The experiments showed the distinct signature of a capillary instability even though the van der Waals forces were stabilizing the polymer films. The third experiment involved the variation of the acoustic boundary conditions. By suitable choosing the substrates and films we demonstrated that the acoustic pressure could be switched on and off as a function of the acoustic boundary conditions. As a consequence we were able to destabilize films that should otherwise be stable.

For hundreds of nanometers thick films, van der Waals forces are too weak to influence the film stability. In the absence of any other external force, polymer films can become spontaneously unstable and break-up by other mechanisms. We demonstrated that a polymer film containing a macromolecular surfactant shows a surface instability when heated above its glass transition temperature. Our model system was a binary blend of polystyrene and poly(vinyl methyl ether). PVME has a much lower surface tension than PS and forms an enrichment layer at the surface. Composition fluctuations at the surface led to a variation of the surface tension. The response to the lateral gradient in the surface tension was the flow of material towards regions with highest surface tension (Marangoni flow). Analyzing the instability wavelength versus the film thickness and composition, we demonstrated the interplay between the surface tension gradients and the hydrodynamic response of the thin film.

A further way to induce and control the structure formation process is to use externally applied electric fields. The destabilization is caused by the much stronger electrostatic force. Opposed by the surface tension, the instability shows a characteristic wavelength. Using a polymer bilayer, the polymer–polymer and polymer–air interfaces are destabilized at different times. We used the sequential destabilization of a polymer bilayer to induce a hierarchical structure formation in a process. By using a topographically structured electrode, we imposed a lateral force modulation, thereby focusing the insta-

bilities towards regions of high electric fields. The field modulation resulted in the formation of hierarchical patterns with primary and secondary independent lateral dimensions. The secondary instability led to structure widths significantly smaller (by about a factor of 10) than the primary polymer–air instability. Washing away the upper polymer layer, the remaining structures were in the range of ~ 100 nm, much smaller than the pattern size of the master electrode. The advantage over the simple EHD technique is that two materials can be patterned in a single–step procedure instead of several steps used in other lithographic techniques. Our approach could be in principle extended to lateral hierarchical structures consisting of a larger number of different materials and more than two independent lateral length scales.

Harnessing the demixing process of a polymer blend opens new routes to produce nanostructured materials. We developed a method to manufacture nanoporous hard films with improved optical properties. The technique we applied was based on the demixing of a binary polymer blend during spin-coating. One of the polymers was replaced by an inorganic phase produced by a sol–gel approach. After film deposition, the organic phase was removed by washing the sample in a good solvent for the polymer. The resulting nanoporous film had broad–band antireflective properties and improved mechanical strength. We were also able to coat plastic substrates with these hard AR coatings. A homogeneous SiO_x film was used to increase the adhesion of the nanoporous film to the plastic substrate. By fluorinating the surface of our coatings, an improved cleanability was obtained. Surfaces coated with these films exhibited an outstanding optical transmission ($T > 99\%$ averaged from 400 to 680 nm). In particular, for the reference wavelength ($\lambda = 600$ nm), a transmission $> 99.8\%$ was achieved.

The investigated subjects still pose fundamental problems or experimental challenges. Our predictions regarding the thermo–acoustic instability were based on a theory that considers the densities of states of longitudinal modes perpendicular to the film surfaces. The imbalance in radiation pressures exerted onto the film boundaries leads to a destabilizing pressure. While this theory should accurately predict the correct order of magnitude of the acoustic effect, a more accurate model should include transverse modes, non–perpendicular modes and the elastic coupling of the film with the surrounding media.

Other possible experimental approaches include the investigations of in-

stabilities of a free standing polymer film. The disintegration of a liquid polystyrene film may be prevented by capping it with two cross-linked polystyrene layers. Because of the conceptual simplicity of the experimental system, any deviation from a model based on the predictions of a van der Waals driven instability would be a clear indication for other destabilizing effects. Due to the different scaling behavior of acoustic and retarded van der Waals pressures with distance, by increasing the thickness of the film, the retarded van der Waals pressure decreases more rapidly with the film thickness than the acoustic pressure. For films thicker than 100 nm, the acoustic pressure dominates over the much weaker van der Waals pressure leading to a reentrant instability. Analyzing this instability would be a further demonstration of the presence of the thermo-acoustic pressure. The high viscosity of polymer melts leads, however to very long times that are needed for the instability to develop. One solution to this problem would be the use of very low molecular liquids such as PDMS together with a careful chosen substrate-film-environment combination.

Regarding the surface tension induced instability, it would be instructive to build a theoretical model that attempts to explain our experimental results. Using the Navier-Stokes equation to describe the hydrodynamics of the unstable liquid film coupled with a diffusion-type of equation, it should be possible to develop a theoretical model that describes composition-gradient driven instabilities. Numerically solving the system of the two coupled differential equations, should yield the most amplified wavelength.

In conclusion, we have analyzed several mechanisms that destabilize thin polymer films. These new ideas bring us a step closer in understanding the multitude of effects that affect the stability of polymer coatings. We have developed new methods to obtain porous materials with enhanced optical properties and patterned surfaces with 100 nm sized structures. However, all the bits and pieces that we know today have yet to come together to complete the great puzzle of film instabilities. Once we understand the main picture, the science of thin polymer films will start revealing its true beauty.