

**DEWETTING IN THIN LIQUID FILMS OF THICKNESS
DEPENDENT VISCOSITY**

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DEWETTING IN THIN LIQUID FILMS OF THICKNESS DEPENDENT VISCOSITY

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Certificate

This is to certify that the thesis titled “**DEWETTING IN THIN LIQUID FILMS OF THICKNESS DEPENDENT VISCOSITY**” being submitted by **Mr. Tirumala Rao Kotni** 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, associateship or similar title of any university or institution.

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Abstract

Spontaneous dewetting of supported thin liquid films of thickness dependent viscosity was studied based on numerical simulations of the thin film equation in 2-D as well as 3-D. Numerical simulations reveal the emergence of sub spinodal lengthscales without need of heterogeneous substrate/nucleated dewetting. It has been recently observed in the experiments that the liquid viscosity can either increase or decrease with film thickness due to entanglement, molecular weight, molecular mobility and monomer monomer interactions. The liquid viscosity decreases with decrease in film thickness has been seen in polystyrene (PS) films and in contrast, the liquid viscosity increases with decrease in film thickness in polyethylene glycol (PEG) films. Instabilities in such thin liquid films was studied based on numerical simulations of thin film equation in 2-d as well as 3-d with two excess intermolecular forces.

In the first scenario, liquid viscosity decreases with decrease in film thickness and force filed to be Lifshitz Van der Waals attraction and Born repulsion have been considered. Numerical simulation of such unstable thin liquid films on a homogeneous substrate reveal the emergence of sub spinodal lengthscales through formation of satellite holes during dewetting. These satellite holes appears between already growing primary holes without invoking the need of heterogeneous substrate or nucleation if mobility of the liquid film increases non monotonically with film thickness. It was also found that sub spinodal lengthscales was possible for certain range of mean film thicknesses lies between the maximum mobility and the mobility at the radius of gyration. Kinetics of dewetting highlights the existence of distinct regions which are responsible for spinodal and sub spinodal dewetting. These regions are established

based on the exponents obtained between the maximum growth rate versus mean film thickness and linear time of rupture versus mean film thickness. Kinetics of dewetting is characterized by the maximum growth rate, time of rupture in pre-rupture phase and growth of radius of the hole and their exponents in post rupture phase. Exponent in sub spinodal regions exhibits different rather than outside of it. Sequential exponent of $2/3 \rightarrow 1/4 \rightarrow 1/2$ during the hole growth phase indicate the formation of satellite holes rather than rises upto form a intervening droplet ($2/3 \rightarrow 1/4 \rightarrow 4/5$).

On the other hand the liquid viscosity increases with decrease in film thickness and this system subjected to Lifshitz Van der Waals force only. In this case substrate is coated by coating of a uniform thickness (which is in nanometer thickness). Influence of antagonistic forces on thin films lead to formation of two phases namely, thinner flat film phase and thicker high curvature phase. The formation and growth of these phases were investigated based on the dynamic tracking of number of droplets or defects and the total free energy during the spinodal phase separation. Morphological phase separation was described by the three stages *viz.* early, intermediate and late stages of phase separations. Emergence of sub spinodal length scales in the intermediate stage via subspinodal phase separation through formation of satellite droplet/thicker high curvature droplet. These satellite droplets are forming between growing primary droplets during phase separation if the mobility of the liquid in thinner portions are very low. Decay of number density drops in the intermediate stage as well as late stages exhibit different exponents. These exponents are responsible for different coarsening events and mobility of the film. But early stage does not effect and exhibits an exponent of $-1/4$. Exponents of $-1/7$, $-1/4$, $-1/5$, $-1/3$, $-2/5$ in the intermediate stage and $-2/5$, $-1/3$ in the late stage of phase separation were found. Spinodal phase separation also highlights the bimodal and multi modal distribution of maximum height in the defects.

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