SPINODAL PHASE SEPARATION IN UNSTABLE THIN LIQUID FILMS

by

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Certificate

This is to certify that the thesis titled **"SPINODAL PHASE SEPARATION IN UNSTABLE THIN LIQUID FILMS"** being submitted by Manish Vashishtha 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 to any other university or institute for the award of any degree or diploma.

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Abstract

Spinodal Phase separation (**SPS**) in technologically and scientifically important system of thin liquid films supported on homogeneous and heterogeneous solid substrates was studied based on numerical simulations of the thin film equation in $2-d$ as well as $3-d$. The numerical simulations reveals that an unstable thin liquid films under the influence of antagonistic forces leads to formation of two phases namely, a thinner (true) flat-film phase and a thicker (pseudo) circular-defect phase. The formation and growth of these phases is explained based on evolution of film morphology and dynamic tracking of five simple markers *viz.,* number of defects, total free energy and its components, maximum and minimum film thicknesses, fractional flat area and fractional completion of SPS. Fourier and Minkowski functional analysis was also performed to characterize the film morphology. Vastly different morphological pathways ranging from circular-defect based to circular-hole based were seen in $3-d$ SPS. A universal curve between the number density of defects and rescaled time describes the kinetics of the early stage in $2-d$ and $3-d$ films. The Lifshitz-Slyozov exponent of $-1/3$ describes the kinetics of the late stage in 2-d even in the absence of coexisting equilibrium phases. The study presents a detailed framework of SPS and arrives at three morphological stages of SPS using a simplified marker based approach.

It is also shown that quenched chemical disorder has a pronounced effect on the early and intermediate stages of SPS in thin liquid films. However, the late stage kinetics is universal and follows the Lifshitz-Slyozov (LS) growth law. These findings are in sharp contrast to the effects of quenched disorder seen in usual phase-separation processes, viz. the early stages remain undisturbed and domain growth is slowed

down in the asymptotic regime. The early-stage kinetics shows different qualitative behavior, depending on the relative sizes of disorder patches and the spinodal length-scale. Thus, the inverse problem of estimating disorder by thin-film experiments was also addressed.

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