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Rupture of ultrathin solution films on planar solid substrates induced by solute crystallization

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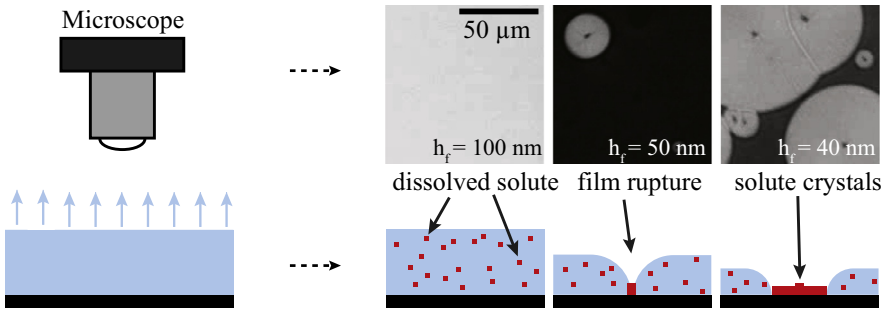
GRAPHICAL ABSTRACT



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ABSTRACT

On-line optical imaging of continuously thinning planar films in a spin cast configuration reveals the rupture behavior of ultra-thin films of binary mixtures of a volatile solvent and a nonvolatile solute. The pure solvents completely wet the silica substrates whereas the solution films rupture at certain film thicknesses, $h_{rupture}$, which depend on, c_0, the initial weighing in solute concentrations. With small c_0, $h_{rupture}$ increases proportional to c_0. With high c_0, all films rupture at $h_{rupture} \approx 50$ nm, independent of c_0. The findings can be explained by the solute enrichment during the evaporative thinning. Solute crystallization at the liquid/substrate interface upon reaching solute supersaturation leads to locally different wetting properties. This induces locally the rupture of the film as soon as it is sufficiently thin. A proper data rescaling based on this scenario yields a universal rupture behavior of various different solvent/ solute mixtures.

1. Introduction

A liquid deposited on a solid surface may wet the surface completely or only partially. As a result it may form a planar closed film or rupture and form a film with holes, or even rearrange into individual droplets. The wetting and rupture behavior of thin films on planar solid substrates is a permanent research topic [1–5] not the least because it is of eminent practical relevance [6–11].

For liquid films thinner than millimeters gravitational forces can be neglected. Their wetting behavior is determined by the interactions between the substrate and the film [12–15]. With smooth substrate surfaces the interactions depend on the composition and state of the film (e.g. its temperature). It depends also on the film thickness and of the bulk properties of the substrate (e.g. with VdW interactions the disjoining pressure and its sign).

Typical wetting studies address the relation between all these parameters and the wetting and film rupture behavior. There have

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been experimental studies on the rupture of liquid films [16–20], as well as thin polymer or thin metal films [21–26]. The film rupture has also been investigated theoretically [27–30]. In most cases investigated up to now the composition of the liquid film was kept fixed.

However, in most naturally occurring and industrially applied cases, in particular with volatile liquid components, the composition of the liquid changes with time and film thickness [31]. Aside from the film thickness this constitutional change can have a very strong impact on the interactions determining the wetting and rupture behavior. The change in film composition, for instance, may switch its behavior from inherently wetting to non-wetting and thus lead to film rupture.

For experimental investigations addressing the impact of the (changing) film composition on the rupture behavior the composition has to be (continuously) controlled and known while the wetting and rupture behavior is monitored. In the following we will present studies on the wetting/rupture behavior of continuously thinning liquid planar films consisting of binary solvent/solute mixtures deposited on smooth planar substrates. The wetting/rupture properties are investigated by continuously imaging a small area of the liquid film with reflection optical microscopy, while the film is continuously thinning due to the evaporation of the volatile liquid component. At the same time the nonvolatile solute gets continuously enriched in the thinning film. Practically the experiments are performed in a spin cast configuration, where the thinning of the film and the evolution of its composition is well known [32,33]. The investigations show that the film composition affects the wetting and rupture behavior. The local crystallization of the solute at the interface leads the formation of holes at these locations if the film is thin enough so that film rupture is energetically favorable.

2. Methods and material

2.1. Experimental setup

The wetting/rupture of the thinning liquid films is investigated in a "spin cast configuration" by time resolved reflection microscopy [34–38] as depicted in Fig. 1. The microscope setup was implemented with a Axio Scope.A1 Vario from Zeiss. The images were recorded with a fast CMOS camera (EoSense® CL MC1362, Mikrotron GmbH). A blue diode laser (6 W, 445 nm, LDM-445-6000, LASERTACK) was used for illumination. The laser light was de-speckled by a combination of a liquid light guide and a rotational diffuser. The samples were placed on the sample plate of a spin coater within a home-build environmental chamber to control/adjust the gaseous environment. The spin coater itself was mounted on a X-Y table to adjust the sample position relative to the optical microscope. An optical encoder on the spin coater rotation axis provided a periodic trigger signal for image recording at fixed rotational angles. Thus 60 images per rotation could be recorded phase-locked with the axis rotation. The images were processed and analyzed by a custom-made image analysis software. In post processing the frames were rotated and shifted relative to each other to yield a sequence (movie) of non-rotating images.

2.2. Hydrodynamic-evaporative film thinning

In a spin cast configuration film thinning as well as the evolution of the solvent composition are meanwhile quantitatively well understood for mixtures of non-volatile solutes and volatile solvents [32,33]. All thinning films were prepared and investigated under constant rotation speed. A small amount of liquid

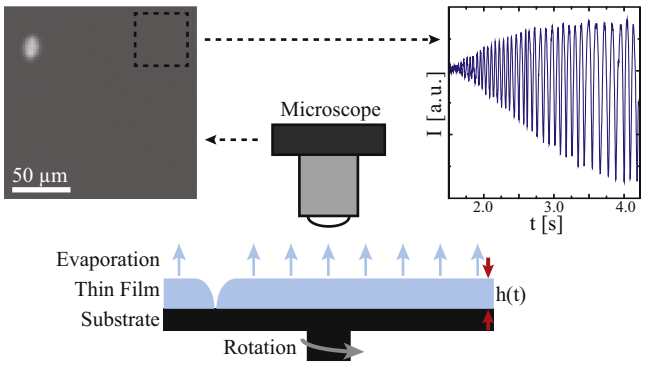

Fig. 1. Experimental setup to investigate the thinning and rupture behavior of thin planar films of volatile liquids on rotating planar solid substrates. With volatile liquids and sufficiently thin films, film thinning is dominated by evaporation. A small area of the evaporating film is continuously monitored with time-resolved optical reflection microscopy. Interference effects of the various parallel planar interfaces of the system cause oscillatory brightness variations. These are used to measure the overall film thinning behavior. In addition optical imaging reveals the evolution of local structures such as holes (film rupture).

($\approx$ 200 µl = "excess volume", see [32,33]) is deposited on the rotating planar substrate. Right after liquid deposition the interplay of hydrodynamics and viscous forces planarizes the liquid into a flat film [39]. With volatile liquids this planar film is continuously thinning due to hydrodynamically driven flow as well as evaporation [40]. Whereas at the beginning, with relatively thick films, the film thinning is dominated by hydrodynamics, at later stages its thinning is dominated by evaporation. The crossover between hydrodynamic and evaporative film thinning occurs at the so-called transition height h_{tr} [32,33]:

$$h_{tr} = (E/2K)^{1/3} \quad (1)$$

(K = "Spin-Off" coefficient, ω = rotational speed, and ν = kinematic viscosity) With typical evaporation rates of $E = 1.5$ µm/s and typical spin cast parameters of $K = \omega^2/(3\nu) = 5 \cdot 10^{-9}$ mm^{-2} s^{-1} ($\omega = 1000$ rpm, $\nu = 0.65$ mm^2/s) h_{tr} is in the range of a few µm. Therefore, as soon as the films are thinner than $\approx$ µm the time evolution of the film thickness is dominated by evaporation.

2.3. Film thickness determination and thickness/time resolution

The system of the thinning film on the solid substrate contains several parallel planar interfaces. Under illumination in the reflection microscopy configuration these interfaces lead to optical interference effects. As a result the reflected intensity varies during the film thinning. These intensity variations are used to determine the liquid film thickness. With the addition of interference enhancement through artificially grown SiO_2 layers on the substrates and image processing (background subtraction, oversampling) the liquid film thickness can be determined with nm resolution [41,42] (the lateral imaging resolution is diffraction-limited and in the range of about 500 nm). With the installed camera (typical frame rate: 1000 s^{-1}, exposure time for each individual frame < 80 µs) individual images can be recorded for film thickness increments of typically nanometers.

2.4. Example of a film thinning measurement

Fig. 2 shows an example of the hydrodynamic-evaporative thinning of a film of pure toluene performed in a spin cast configuration. The imaging of the planar film shows uniform gray areas with oscillating gray levels as the film is thinning. The combination of gray level variation, (known) refractive indices and (known)