INVESTIGATION OF SURFACE DEFORMATION DUE TO SURFACE TENSION DRIVEN FLOWS

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Introduction

In many thin film applications such as organic and printed electronics, biosensors and optical coatings there is a growing demand for functional layers with highly homogeneous surface topology. The thickness of these layers is in the range of 10 nm to 10 µm with an accepted mean deviation of $1-2\%$ of the final coating thickness. The surface tension of the applied polymer-solvent solutions is a function of solvent content and temperature (see Figure 1, right). Since these both parameters (temperature and concentration) alter as drying proceeds, inhomogeneous evaporation rates cause gradients in surface tension.

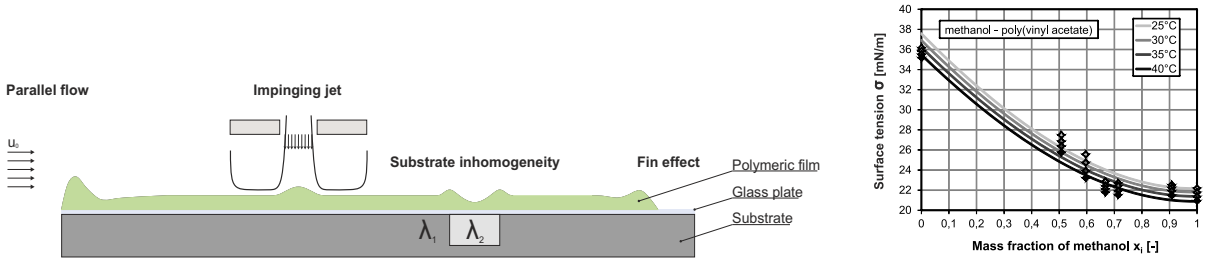

Figure 1: Possible reasons for surface deformation due to Marangoni-instability (l.), surface tension of a binary methanol-poly(vinyl acetate) solution as function of solvent content and temperature (r.).

Depending on form and evolution of the occurring gradients, shear stresses at the surface occur. The stress at the surface is transferred in surface flow and due to viscosity a flow in the bulk fluid arises. Inhomogeneous drying rates may appear as a result of local differences in the flow conditions of the surrounding drying gas or by varying material properties (see Figure 1, left). Another reason for surface tension driven flows can be found by forcing the interface into a state off equilibrium by deformation of the surface [1].

As the objective of this work is to numerically describe surface tension driven flows during the drying of polymer films, an understanding for the occurring phenomena is essential. For this reason two test rigs have been developed to in-situ observe the resulting surface deformation and the respective flow field.

Experimental

Surface reconstruction: Figure 2 shows a schematic cartoon of the developed test rig and the evaluation process. The fluid is cast on a thin glass substrate with a random dot pattern on the downside. To capture sequences of images a CCD camera is positioned perpendicular to the drying film. To be able to reconstruct the surface topology from the displacement field of the dot pattern, information about the optical properties of the system (i.e. refraction index of the polymer solution and the glass substrate) and due to the shrinkage of the film a reference height from an unaffected area are needed. More detailed information on procedure and the evaluation routine can be found in a

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previous publication [2]. To induce local varying energy transfer boundary conditions and hence lateral temperature gradients throughout the glass substrate, the glass substrate is placed on a plate with laterally varying material properties.

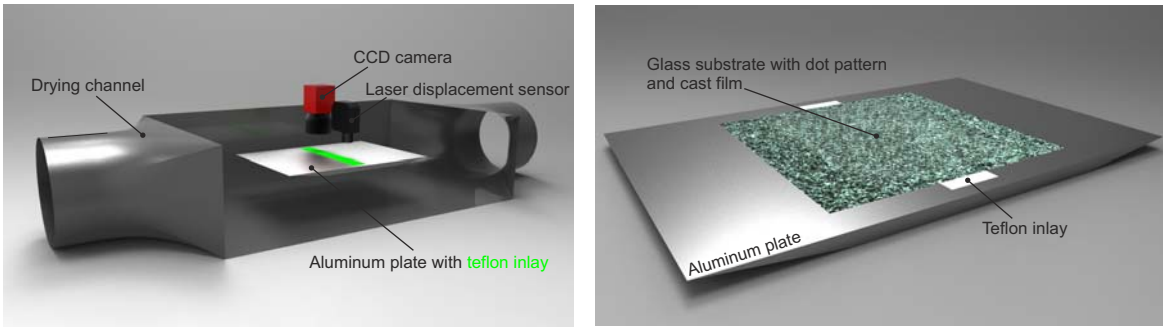

Figure 2: Schematic of the experimental setup. Drying channel with aluminum plate and Teflon inlay, equipped with a CCD camera and a laser displacement sensor (left). Detailed view of the situation during experiment: Glass plate with random dot pattern on the downside with polymer film cast on it (right).

The measurement technique to observe surface deformations of thin transparent films is based on the analysis of the refracted images of a random dot pattern. As a result of the surface deformation the beam path of the incident light shifts and so does the observed location of the dot pattern [2, 3]. A scheme visualizing of the principle is shown in Figure 3.

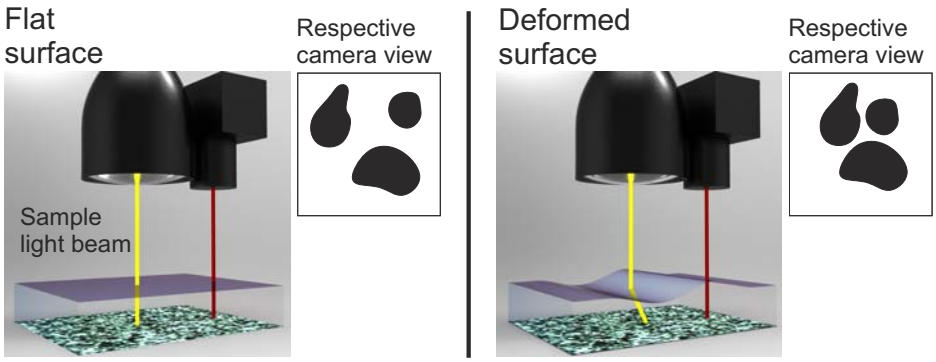

Figure 3: Schematic of the measuring principle: The refraction of light differs depending on the present surface topology. This virtual shift of a random dot pattern can be captured using a CCD camera. Combined with the information of the actual film height, the displacement field can be translated into the actual surface topology.

As an example for the various experiments that have been performed, the results obtained by observing the drying of a binary methanol-poly(vinyl acetate) solution with 67 wt. % methanol (detailed information on the drying process can be found in [4]) are presented. To induce locally different drying rates the glass plate is placed on an aluminum substrate with a small cavity. The experiment has been performed in a temperature-controlled flow channel with constant conditions at the inlet ($u_0 = 0.5\frac{m}{s}$ and $T = 30°C$).

During the evaporation of the solvent, the system consumes latent heat from its surrounding. This results in a temperature profile throughout the substrate. Depending on the material properties of the substrate, different heat fluxes will occur. Since the surface tension of the polymer solution decreases with rising temperature and increases with decreasing solvent concentration (see Figure 1, right) it is hard to tell which effect will dominate, as regions with higher temperature do show higher drying rates and therefore higher polymer content. By the evaluation of the described experiment (see Figure 4), it becomes clear that for the chosen setup the increase of surface tension due to the higher polymer content shapes the surface. The positive gradient in surface tension from the air supported to the aluminum supported region results in a convective flow in radial direction away from the hole. As the drying proceeds, the structure freezes and remains in the dried film.

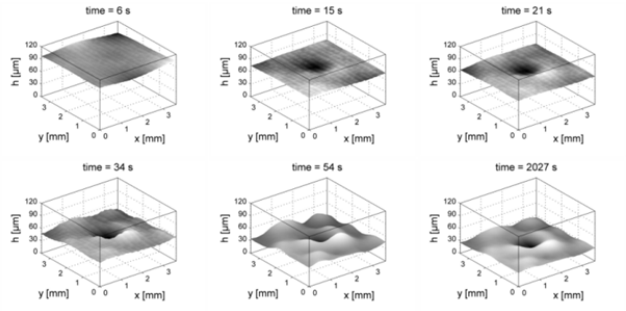

Figure 4: Reconstructed surface topology at several time steps during inhomogeneous drying of a methanol-poly(vinyl acetate) solution with 67 wt. % methanol: $\boldsymbol{u_\infty = 0.5\ m/s, T_\infty = 30°C}$ *and* $\boldsymbol{s_0 \cong 150\ \mu m}$*. The inhomogeneous drying conditions are applied using a round hole in the substrate.*

Flow field visualization: As implied by the results presented above, a surface tension driven flow occurs due to inhomogeneous drying of the polymer solution (methanol-poly(vinyl acetate)). In the following a method is described that offers the possibility to analyze the developing flow field using fluorescence particle tracking. Again the material system methanol-poly(vinyl acetate) is used with 67 wt. % methanol. In order to visualize the flow field 1.5 µl green fluorescent polystyrene microspheres (d = 0.52 µm) were added to 75 µl polymer solution. To observe the particle movement an inverted fluorescence microscope equipped with an oil immersion lens and an automatic z-scan has been connected to a CCD camera.

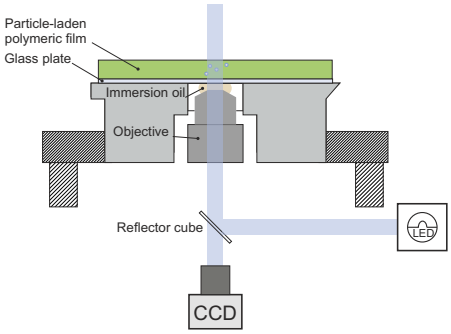

Figure 5: Test rig for flow field visualization using fluorescent particle tracking. The system consists of an inverted fluorescence microscope equipped with an immersion lens, a CCD camera to capture images and a LED light source.

The fact that the particles are observed from the downside makes it difficult to realize inhomogeneous substrate properties. Therefore inhomogeneous drying rates are applied by different gas phase boundary conditions. In a first step the drying film has been partially covered (see Figure 6). Due to the saturation of the gas phase under the cover, the mass transfer is slowed down compared to the uncovered area at ambient conditions. This results, as shown above, in a lateral gradient in surface tension. Hence a mass transport from the covered to the uncovered area has to be expected.

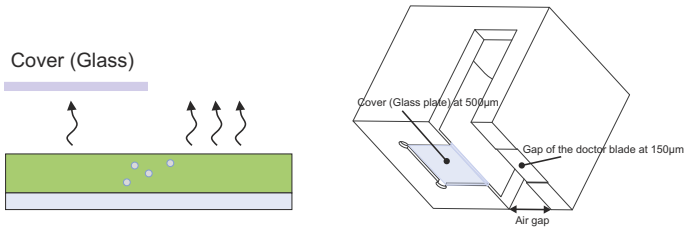

Figure 6: Boundary conditions of setup 1, (left) and scheme of the respective doctor blade system, (right).

By analyzing the resulting velocity distribution located at the center of the covered area, one comes to the conclusion that the surface tension as a driving force causes an accelerated Couette-flow (see Figure 7, left).

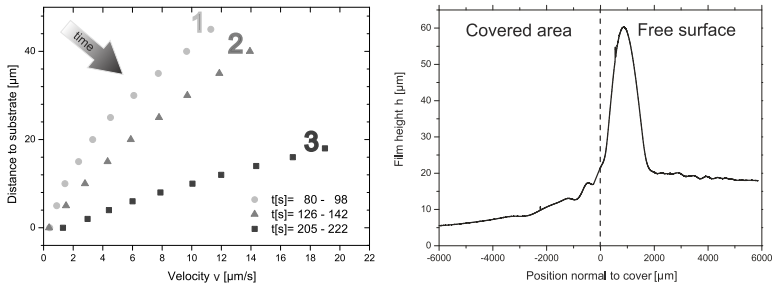

Figure 7: Velocity profiles (at the center of the covered area) over film height at different drying times. At the beginning of drying time (left) velocity profiles No. 1 - 3 and cross profile of the dried film normal to the cover. Methanol-poly(vinyl acetate) solution with 67 wt. % methanol: $\boldsymbol{T_\infty = 20°C}$ *and* $\boldsymbol{s_0 \approx 150}$ $\boldsymbol{\mu m}$*. The inhomogeneous drying conditions are applied by partially covering the film.*

To get proof for the mass transfer and to determine the surface topology, the dried films have been characterized using profiler measurements. Figure 7 (right) shows the profiles normal to the edge of the cover. The final profiles show the frozen wave due to the surface tension gradient in the direction normal to the cover.

Numerical

In the sections above two measurement techniques have been presented to analyze the surface deformation of transparent fluids and the involved surface tension driven flows. The governed information will be used to complete the numerical setup which is under development. This numerical model, based on the VOF model implemented in the commercial solver FLUENT®, shall be able to predict surface tension driven flows within drying polymer films under consideration of mass transfer. For a first step solely thermocapillary convection in methanol has been investigated. Figure 8 (left) shows the boundary and initial conditions that have been applied to a film of methanol with a height of $s_0 \approx 300$ μm. To induce thermocapillary motion, a lateral temperature gradient (linear) of $\Delta T = 10$ K has been applied. On the right the resulting flow field is visualized by the velocity magnitude.

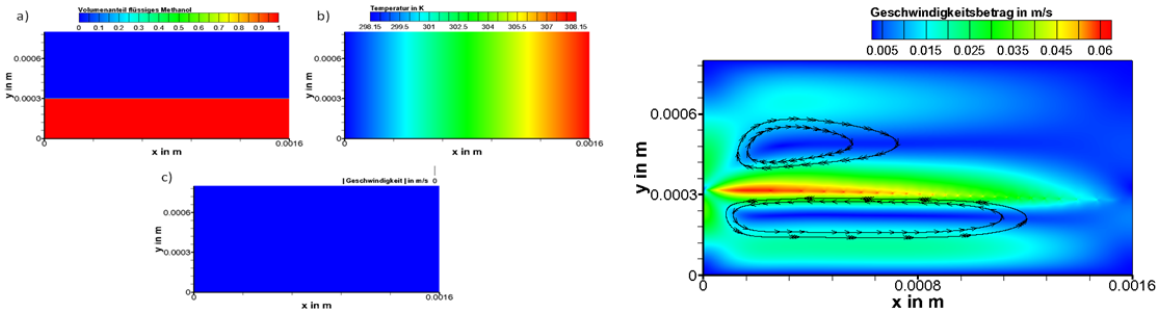

Figure 8: ***Left****: Boundary and initial conditions set to induce thermocapillary flow. Up-left: Volume fraction of methanol. Up-right: Initial temperature distribution. Down: Initial velocity distribution.* ***Right****: Resulting flow field visualized by the velocity magnitude.*

Acknowledgements

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