Title: Wetting Kinetics of Stimuli-Responsive Polymer Carpets

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Project Description

Abstract

The aim of this proposal is the time-resolved investigation of the reaction of stimuli-responsive layers of polymer carpets (polymer brushes grafted to flexible, ultrathin nanosheets) to changes of the properties of liquids, which are in contact with these layers. Changes of the pH of the liquid, its ion composition, its solvent composition, etc., can induce layer swelling, buckling, other structural changes. This in turn changes the wetting behaviour of the polymer carpets. We will study the carpet responses with optical reflection interference microscopy on time scales between milliseconds and minutes, on lateral scales of micrometers, and on vertical scales of nanometers.

1 State of the art and preliminary work

The wetting/dewetting/rupturing behaviour of thin liquid films on solid subtrates has been investigated mostly for the case of thin polymer films[1]. Due to the rather high viscosity, in these cases the kinetics of the changes of the film topography is rather slow and can be observed rather easily. The kinetics of the wetting/rupture behaviour of really thin closed films (thinner than 1 µm) of “true” (i.e., low viscosity) liquids, such as water, or biologically relevant aqueous mixtures (water plus ions) has barely been investigated for two reasons: 1.) it is not easy to start in this case with a well-defined film (thickness, composition) and, 2.) in particular, to change the conditions rapidly and well-defined enough to study the response to this change. For instance, with thin films (< micron thickness), film rupturing occurs within fractions of seconds. There have been only very few investigations[2], addressing this topic through a combination of spin casting and time resolved optical microscopy.

Spin casting as a tool to form ultrathin films on solid substrates and to investigate their thinning and wetting behaviour.

In recent years we have made significant progress in a better understanding and control of the properties of planar liquid films that are thinning by evaporation in a “hydrodynamic-evaporative spin cast configuration”[3,4]. In this configuration an aliquot of a liquid with volatile components is deposited on a rotating planar substrate. Rotation-induced shear forces form a planar film from the deposited bulk liquid. At later stages evaporative losses dominate and cause a continuous decrease of thickness of the resulting liquid film. The detailed experimental and theoretical analysis reveals that hydrodynamic-evaporative spin casting in essence is the formation of a planar liquid film, which is continuously thinning due to evaporation of its liquid component. Rheology plays only a role at the beginning of the process. Throughout most of the film thinning

process, in particular towards the end of the process, rheology can be neglected (during approximately 70% of the total process time film thinning occurs only by evaporation!).
Hydrodynamic-evaporative spin casting essentially means evaporative drying of a thin film on a substrate. Because the process is known in detail, by variation of the process parameters (initial composition, evaporation rates, rotation speed, etc.), **it is possible to adjust, determine, and control the (time-dependent) composition of this continuously thinning liquid film**. This can be used to **investigate the interaction between this liquid film and the substrate (substrate surface) as a function of the film composition on time scales down to milliseconds**.

Time resolved film thinning microscopy

A significant step to better understand the spin cast process and, in particular to use it for fundamental and applied research was the implementation of “time resolved film thinning microscopy”[5]. This means, the thinning of the film, its topography, composition, etc, as well as the substrate properties are investigated with a home-build, interference-enhanced optical reflection microscopy setup with an imaging time resolution of milliseconds. This is depicted in Fig. 1 for example for the case of dewetting induced by the precipitation of a nonvolatile solute in the course of its enrichment above saturation[5].

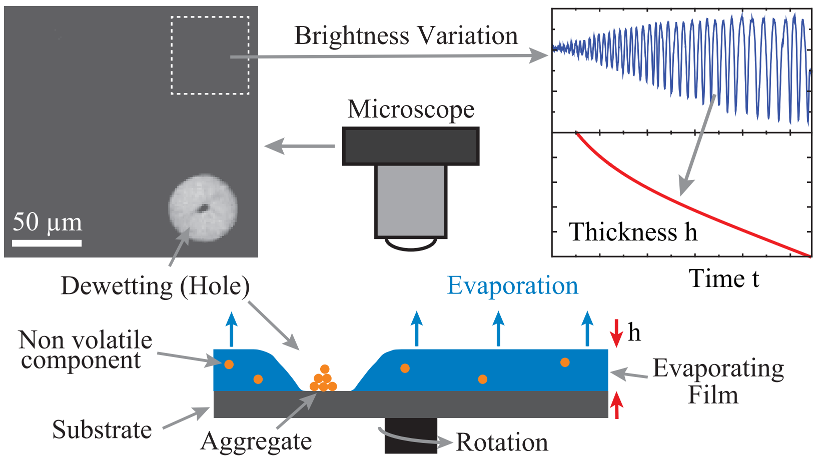

Fig.1: Schematic of the time resolved film thinning optical microscopy. A liquid film consisting of volatile and non-volatile components is imaged from the top. The planar film initially formed due to the sample rotation is continuously thinning. During most of the time this thinning is dominated by evaporation. The film thickness is continuously monitored by interferometry and imaged. Therefore, if the film ruptures, as depicted here for example due to a local precipitation[5], this can be monitored as function of the film properties (thickness, composition).

The instrument allows to analyze the global film thinning behaviour and to study local evolutions of the film topography (e.g. rupture). Thus we could for instance investigate film rupture caused by local nucleation and growth of precipitating film compounds or study the formation of surface undulations by Marangoni flows. In another study we could show how the location of individual nanoparticles as small as 25nm in diameter embedded in ultrathin films can be visualized optically and their surrounding surface distortion (meniscus) can be measured[6].
This proposal is centered around the application of film thinning optical microscopy to investigate the response of the substrate surfaces as well as that of thin(ning) films to changes of film thickness and film composition (e.g. the enrichment or depletion of certain components).

Other recent investigations in the field of wetting.

In recent years our group has investigated various other systems in the context with interfaces and wetting. For instance, a research focus was the evaporation behaviour of sessile drops and the interaction between sessile drops [7,8]. There also have been studies on nucleation[9] or the crystallization of peptides at the liquid/solid/vapour contact line under specific interfacial conditions (Marangoni-controlled precipitation) [10].

1.1 Project-related publications

[1] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, **Wetting and spreading**, Rev. Mod. Phys. **2009,** 81 (2), 739.

[2] D.T. Toolan, A. Dunbar, S. Ebbens, N. Clarke, P.D. Topham, J.R. Howse, et al., **Direct observation of morphological development during the spin-coating of polystyrene–poly (methyl methacrylate) polymer blends**, J. Polym. Sci. Part B: Polym. Phys. **2013** 51(11), 875–881.

[3] S. Karpitschka, C.M. Weber, H. Riegler, **Spin casting of dilute solutions: Vertical composition profile during hydrodynamic-evaporative film thinning,** *Chem. Eng. Sci.* **2015,** *129*, 243.

[4] J. Danglad-Flores, S. Eickelmann, H. Riegler, **Deposition of polymer films by spin casting: A quantitative analysis**, *Chem. Eng. Sci.* **2018,** *179*, 257.

[5] S. Eickelmann and H. Riegler, **Rupture of ultrathin solution films on planar solid substrates induced by solute crystallization,** *J. Coll. Interface Sci.* **2018,** *528*, 63

[6] S. Eickelmann, J. Danglad-Flores, G. Chen, M.S. Miettinen, and H. Riegler, **Meniscus Shape around Nanoparticles Embedded in Thin Liquid FIlms**, *Langmuir* ***2018**, 34, 11364-11373*.

[7] Stefan Karpitschka and Hans Riegler, **Noncoalescence of Sessile Drops from Different but Miscible Liquids: Hydrodynamic Analysis of the Twin Drop Contour as a Self-Stabilizing Traveling Wave**, *Phys. Rev. Lett.* ***2012**, 106, 066103*.

[8] Virginie Soulie, Stefan Karpitschka, Florence Lequien, Philippe Prene, Thomas Zemb, Helmut Moehwald and Hans Riegler, **The evaporation behavior of sessile droplets from aqueous saline solutions**, *Phys. Chem. Chem. Phys., **2015**, 17, 22296-22303.*

[9] Rodrigo Perez-Garcia and Hans Riegler, **Controlled Self-Organized Positioning of Small Aggregates by Patterns of (Sub)nanosized Active Sites**, *Cryst. Growth Des.* **2017***, 17, 1870–1875.*

[10] Bingbing Sun, Qi Li, Hans Riegler, Stephan Eickelmann, Luru Dai, Yang Yang, Rodrigo Perez-Garcia, Yi Jia, Guoxiang Chen, Jinbo Fei, Krister Holmberg, and Junbai Li, **Self-Assembly of Ultralong Aligned Dipeptide Single Crystals,** *ACS Nano* **2017***, 11, 10489-10494.*

1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

None

1.1.2 Other publications

None

Patents

None

2 Objectives and work programme

2.1 Anticipated total duration of the project

3 years, starting 01.10.2019

2.2 Objectives

The aim of this project is the time-resolved investigation of the **reaction** of stimuli-responsive layers of polymer attached to rigid substrate surfaces or polymer carpets (polymer brushes grafted to flexible, ultrathin nanosheets) **to changes of the properties of liquids**, which are in contact with these layers. The liquid property changes may concern its pH, its ion composition, its solvent composition, its viscosity, etc.. These changes can induce layer swelling, ablation, buckling, and other structural changes. This in turn may change the wetting behaviour of the polymer coated substrate surface or of the polymer carpets. We will study the responses of the substrate surfaces (carpets) as well as the liquid (wettability, rupture, etc) with optical reflection interference microscopy on time scales between milliseconds and minutes, on lateral scales of micrometers, and on vertical scales of nanometers.

Fig. 2 shows our principle experimental approach for several configurations from the most simple case (which may serve as reference behaviour) to the rather complicated case of a substrate covered with a polymer carpet. It should be noted that the Figure selectively displays some rather specific cases. For instance, the film consists of a volatile liquid component only (A), or in cases (B), (C) and (D) in addition contains some non-volatile component (e.g. some ion). And it is assumed that the film thins continuously through solvent evaporation. This is the currently established approach, which already has been used successfully[6-8].

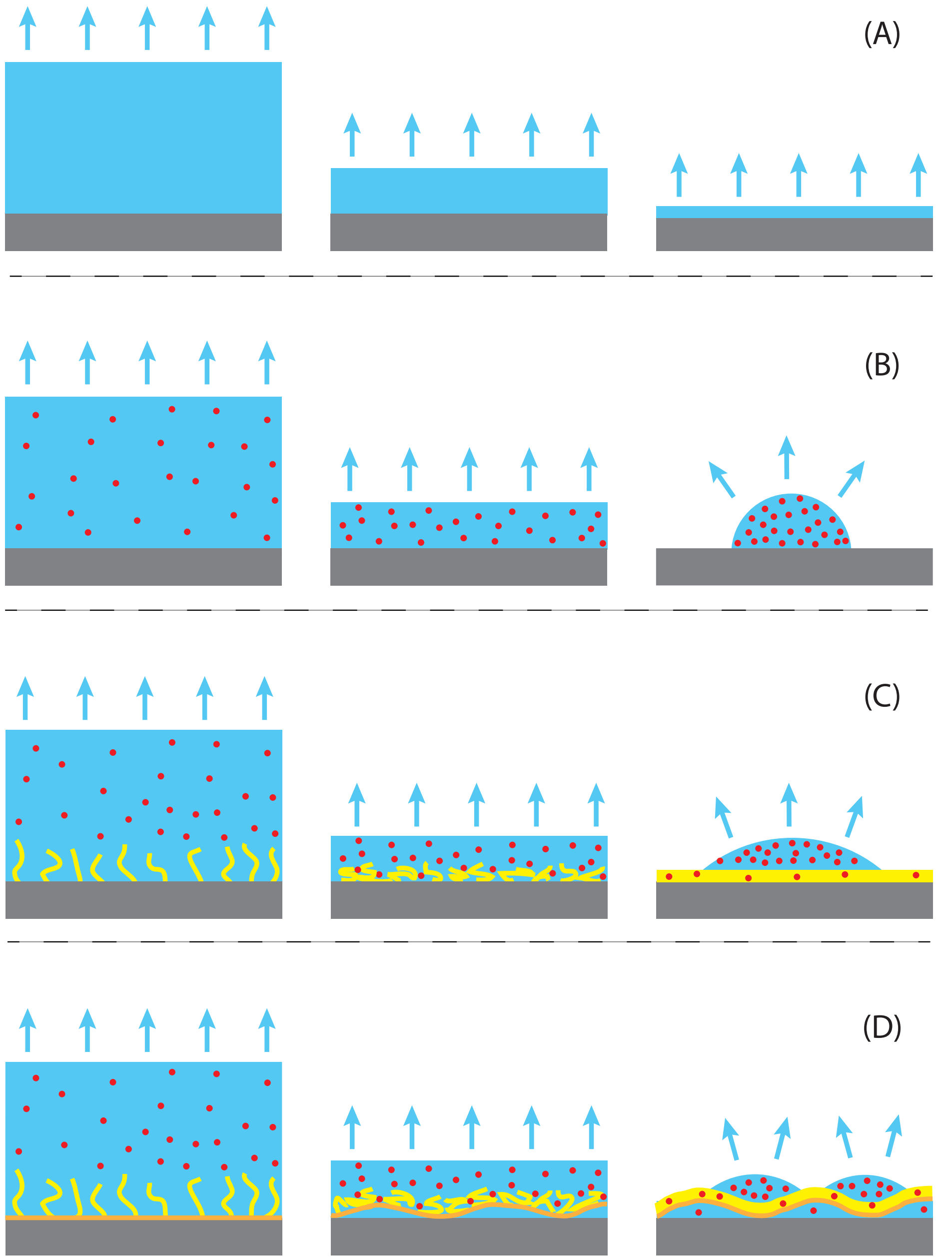

Fig. 2: Examples of the proposed research activities. In case (A) the liquid film, consisting of a pure volatile liquid may wet the substrate completely irrespective of the film thickness. In (B) the liquid contains a non-volatile component, which enriches during evaporation of the volatile component. As as result the liquid properties change. The film may rupture (at a certain thickness and/or film composition) and the liquid may form a sessile. In case (C) polymer molecules are linked to the substrate surface. During solvent evaporation the non-volatile component changes the wetting properties of substrate and/or solution. This leads to the formation of drops. In case (D) the polymer molecules are linked to a thin llayer/film. This layer is attached to the substrate surface. Here the enrichment of the non-volatile component may lead to buckling of the thin layer as well as drop formation.

It should be noted that the proposed spin cast configuration investigations are much more flexible regarding the behaviour of the film thinning and compositional changes than what has been practically used so far.
It can and will be used also probing other conditions, such as:

1.) Adjusting and holding a certain, pre-determined liquid film thickness.

The evaporative film thinning can be stopped at a certain, pre-determined liquid film thickness and film composition if the liquid consists of a volatile and a non-volatile component. In this case the resulting final liquid film thickness can be adjusted by the initial ratio between both components. If the liquid contains other non-volatile components, their concentration at the pre-determined final liquid film thickness can also be adjusted through their weighing in concentration.
A similar approach even works if all liquid components are volatile. In this case the vapor phase has to be saturated with the component, which shall form a film of a certain final thickness. Thus the volatile component will not evaporate and remain as film. Its thickness can be adjusted by the weighing in ratio of the volatile components.
With this approach it will be possible to adjust and keep the composition and the thickness (down to very thin films) of the liquid film in contact with the substrate within seconds (and faster).

2.) Depletion instead of enrichment of certain components.

By selection of the component volatility or its adjustment (through the saturation of the vapour phase) it is possible to even deplete components during thinning. Thus it is for instance possible to increase or to decrease the pH of the thinning film.

2.3 Work programme incl. proposed research methods

A main part of our proposed work will be the investigation of the reaction of stimuli-responsive layers of polymers and polymer carpets (polymer brushes grafted to flexible, ultrathin nanosheets) to changes of the properties of a thinning liquid film, which is in contact with the polymer layer (polymer carpet). The experimental procedure is depicted schematically in Figures 1 and 2.
In a first approach the polymer-coated sustrates or polymer carpets are in contact with a liquid film, whose properties (pH, ion concentration, solvent composition, thickness, etc.) are continuously changing. Analogous experiments with uncoated substrate surfaces have been performed before, as described above.
In a second approach, we will try to adjust a fixed liquid film thickness and film composition as described above and investigate the response.
It is expected that the optical microscopy will reveal the rupture behaviour of the thinning film in response to the (changing) wetting properties of the substrate surface (i.e. the polymer coated substrate or the “polymer-carpeted” substrate).
It is further expected, that the optical microscopy imaging will also reveal changes of the polmer carpet film structure (buckling, liquid dewetting) laterally on a micrometer scale if the changes (swelling, surface undulations) are vertically exceeding interferometric (nanometer) scales. Responses/changes can be studied on time scales down to milliseconds. The partial wetting and

rupture behaviour can be quantified by the dynamics of the hole growth.
In addition to polymer carpets that are laterally homogeneous (unstructured) also carpets with gradients as well as patterned carpets will be studied to induce for instance buckling gradients (directed buckling).
The investigations will be performed in close collaboration with the group of Rainer Jordan (where also a more detailed work program, structured in successive work packages can be found).

2.4 Data handling

Measured data will be documented in logbooks, which will be stored for at least 10 years in a safe way. In addition all digitally documented data (data on computers) is stored on the work group server of our group at the MPI.

2.5 Other information

None

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

None

2.7 Information on scientific and financial involvement of international cooperation partners

None

2.7 Information on scientific cooperation within the SPP2171

Our contribution to the cooperation within the SPP2171 shall be providing for anybody interested our scientific expertise regarding the wetting and evaporative properties of sessile drops and, in particular the behaviour of thin liquid films in a hydrodynamic-evporative spin cast configuration. We will be happy if other groups want to use our thinning film microscopy setup.
In particular we will collaborate closely with the group of Rainer Jordan (TU Dresden) as descibed in detail above. In addition, we will collaborate with the group of Stefan Karpitschka (MPI Göttingen). His group focuses on the three-phase contact line, addressing similar questions as we do. Aside from that we consider a collaboration with the group of Svetlana Santer (Uni Potsdam).

3 Bibliography

None

4 Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

One position ¾ TVL E13 for one PhD student for 3 years. The background knowledge of the applicant should be in physical chemistry or physics. The student will perfom measurements with the thinning film microscopy, its analysis, and related laboratory work (substrate preparation, etc.).

<u>Request for 3 years: 1 position ¾ TVL E13</u>

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to Euro 10,000, Software and Consumables

Consumables, such as chemicals and solvents, as well as AFM tips.

<u>Request for 3 years: Euro 15.000,-</u>

4.1.2.2 Travel Expenses

For participation on all the SPP2171 events/workshops (PI and PhD student):

<u>Request for 3 years: Euro 5.000,-</u>

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

None

4.1.2.4 Expenses for Laboratory Animals

None

4.1.2.5 Other Costs

None

4.1.2.6 Project-related publication expenses

<u>Request for 3 years: Euro 6000.-</u>

4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

None

4.1.3.2 Major Instrumentation exceeding Euro 50,000

None

5 Project requirements

5.1 Employment status information

Hans Riegler, Group Leader, MPIKG, permanent position since 1995.

5.2 First-time proposal data

5.3 Composition of the project group

Hans Riegler, group leader, funded by MPIKG
Jose Danglad-Flores, PhD student, funded by DAAD.

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

National and international collaborations within the IRTG1524 (Various groups in Germany and the US).
Collaboration with CEA and the Institut de Chimie Séparative de Marcoule (Thomas Zemb).
With Ghent University (Andre Skirtach).
With Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics (Junbai Li).

5.5 Scientific equipment

In our group we have availabel a thinning film microscopy and other optical microscopes, AFM, as well as all kinds of lab instrumentation suitable for the proposed field of research, including specific instruments such as vapor environment control unit. In addition we do have access to many more instruments used in other groups/departments of the MPIKG and the neighboring Fraunhofer institute (IAP).

5.6 Project-relevant cooperation with commercial enterprises

None

5.7 Project-relevant participation in commercial enterprises

None

6 Additional information

No direct relation between proposed project and other ongoing projects. If this will change, the DFG will be notified. The administration of the MPIKG is informed about the submission of this proposal.