

**Proposal within the SPP 2171:****Relation between swelling ability / swelling kinetics and dynamic wetting of adaptive polyelectrolyte surfaces****Regine v. Klitzing (TU Darmstadt): Applicant****Olaf Soltwedel (TU Darmstadt, from 1.1.2019 on): Jointly responsible**

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**Project Description**

The project addresses the relation between swelling ability / kinetics and dynamic wetting of adaptive polyelectrolyte surfaces in presence of water. In the present project adaptation refers to swelling of the polymer coating caused by the (partial) uptake of water. In order to separate evaporation from wetting effects, well-defined experimental conditions have to be ensured. For evaporation studies with water experiments in an open cell will be carried out. Experiments which should exclude evaporation are carried out in a closed cell in saturated vapor. This is inherently connected to a pre-swelling of the polymer coating. Therefore, also glycerol will be used as wetting liquid. The polyelectrolyte layers can swell in glycerol, but it is almost not volatile at room temperature. Glycerol gives the opportunity to place a droplet onto a polyelectrolyte surface without evaporation and without pre-swelling of the polyelectrolyte layer. The most obvious question related to our preliminary work is, why certain polyelectrolyte layers have the same swelling ratio in saturated vapor and against liquid water (under the droplet) and others show a different swelling degree under both conditions. Is that related to the odd-even effect, to charge effects or the swelling ability? Therefore different polyelectrolyte coatings, i.e. PEM and PNIPAM microgel layers of different charge density and sign of charge, different swelling ability and different hydrophilic/ hydrophobic balance will be prepared. In case of PNIPAM microgels the swelling ability is controlled via temperature. Therefore their dynamic wetting will be studied below and above the VPTT. The relaxation time determined by deposition of a sessile drop onto the substrate and will be studied. The relaxation time will be related to the advancing/receding angle which occur during sucking and pumping a droplet or at a moving droplet. Therefore additional scenario will be used to realize advancing and receding contact angles (G. Auernhammer). The relaxation time of the contact angle and the difference in advancing and receding contact angle will be correlated to the change in molecular structure at the polymer surface (B. Braunschweig, M. Sega). The dissipation energy of the change in molecular structure will be determined from the dynamic wetting data. Electrokinetic effects will be studied by changing the surface charge (amount of charge during synthesis, pH) and by changing the salt concentration of the wetting aqueous solution (C. Holm). In order to increase the complexity a water-ethanol mixture will be studied as wetting liquid. The co-nonsolvency effect in case of PNIPAM will lead to different swollen states which probably will lead to a change in wetting behavior. Towards applications, our polymer coatings will be wetted by lipid vesicles (M. Tanaka) and they will be used as model systems for a better understanding of dynamic wetting processes in the fibrous network. (M. Biesalski).

# 1 State of the art and preliminary work

([A1]-[A10] refers to the own project relevant publications).

Since in the proposed project polyelectrolyte multilayers and layers of adsorbed microgel particles will be studied as adaptive polymer coatings a short introduction is given, before the wetting is addressed.

## Polyelectrolyte multilayers (PEM)

In the proposed project polyelectrolyte multilayers (PEM) are prepared with the layer-by-layer (LbL) method invented by Decher and coworkers in the early 1990's [1]. Thereby polyanions and polycations are alternated adsorbed from aqueous solutions. So far, we have mainly focused on the relation of ion specific effects and charge effects on the structure, mobility and water content of such PEM [3, 2]. In order to get detailed information about the solvent distribution within the polymer coating we use neutron reflectometry [A1]. Recently, we improved the fitting procedure by using at least three contrasts, and a model based on the volume fraction profiles of all chemical components is employed. It allows self consistent fitting with a minimum number of fitting parameters [A2]. Many studies show an odd-even effect with respect to swelling. It means different swelling properties for PEM with odd numbers of deposited layer and with even numbers [A3]. Recently, we started to disentangle the storage and the loss modulus of the PEM by dynamic force spectroscopy (AFM) in order to get a deeper insight into the mechanics of PEM [5].

## Layers of PNIPAM microgels

Besides macrogels [6], in the last 20 years microgels got more and more impact [7, 8, 9, 10, 11]. The advantage of microgels are the faster response kinetics to external stimuli due to their smaller distances [12]. Microgel particles are mostly synthesized by emulsion or precipitation polymerisation. For instance in Poly(N-isopropyl-acrylamide) (PNIPAM) microgels NIPAM is often cross-linked by N,N'-methylene-bis-acrylamide (BIS) [8]. The microgels have a lower critical solution temperature (LCST) of about 32°C, where the polymer-polymer interactions start over-compensating the hydration of the polymer. Due to the mentioned less sharp transition in case of microgels the LCST is often called volume phase transition temperature (VPTT). The copolymerisation with charged units like acrylic acid (AAc) ( $\rightarrow$ P(NIPAM-co-AAc)) leads to an increase in VPTT, since the charge counteract a polymer collapse [7, 8].

For the preparation of stimuli-sensitive coatings microgels are deposited at a surface. Lyon and coworkers fixed microgel particles on Poly(ethylene terephthalate) (PET) surface by spin coating and covalent tethering afterwards [13]. A 2D monolayer of PNIPAM microgel particles with a regular distance was obtained by Kawaguchi and coworkers [14]. Serpe et al. prepared multilayers of negatively charged microgel particles and polycations via spin coating them alternately [15]. After adsorption the microgels show a compression in volume by about one order of magnitude [A4]. Nevertheless, adsorbed microgels show still a reversible swelling/shrinking in dependence of temperature or pH. We can control the amount of cross-linker and of comonomer (e.g. acrylic acid (AAc), allyl acetic acid (AAA), allyl amine (AA) and allyl glycine (AG)). The initiator is either

negatively charged (potassium persulfate, KPS) or positively charged (2,2'-Azobis(2-methylpropionamidine)dihydrochloride). This offers a large variety for tuning the sign of charge and the amount of charge as well as the hydrophilicity/hydrophobicity ratio and the mechanical properties [A5]. These microgels can be spin coated, and we are able to control the hydrogel particle number density [A4]. The elastic modulus was measured across the adsorbed microgel with a high spatial resolution by AFM indentation [A5].

### Effect of solvent composition: the cononsolvency effect

Besides the well-studied temperature effect, there are other stimuli that can influence the swelling degree of PNIPAM microgels. One phenomenon is the cononsolvency effect, which occurs in ternary mixtures of PNIPAM with water and organic solvents like short-chained alcohols (methanol, ethanol, or (iso-) propanol) [16, 17, 18, 19]. Both water and alcohol are good solvents for PNIPAM, but adding a small amount of alcohol to an aqueous solution of PNIPAM microgels leads to collapse of the microgel [A6],[A7],[A8]. Further addition of alcohol causes a reswelling. The VPTT of microgels decreases with the addition of small alcohol fractions [17, 18, 21, 22], [A7],[A8].

### Wetting of polymer surfaces

Wetting of polymer coating is of specific interest for the adhesion of cells or proteins and the technical control of wetting. In this context a lot of effort has been made to design structured surfaces [23, 24]. In contrast to this the studies on fundamental research of wetting of polyelectrolyte surfaces is rather low. Only a few studies on the water wettability of polyelectrolyte-coated surfaces exist [25, 26, 27, 28, 29]. Tay et al. found an effect of osmotic pressure on the contact line in wetting studies of charged and uncharged polymeric coatings [30].

As mentioned above polyelectrolyte coatings are often adaptive, i.e. they swell in liquid. That makes the wetting process rather complex, since different time scales but also different length scales come into play. The adaptive surface needs a certain time until the swelling process is finished. The swelling doesn't stop at the three phase contact line, and the liquid sucks laterally into the region in contact with the gas phase. Hansen and Miotto called that the peripheral thickness [31]. This deforms the surface and the contact line is not well-defined anymore.

Fig. 1 shows the water contact angle on PEM with different polycations poly(ethylene imine) (PEI), poly(allylamine hydrochloride) (PAH) and poly(diallyldimethyl ammonium hydrochloride) (PDADMAC) as an outermost layer ([A9]).

On the left the data points are shown which are measured in an open cell, where evaporation takes place. The contact angle decreases linearly according to

$$\theta(t) = \theta_0 - a * t \quad (1)$$

with values of the initial contact angle  $\theta_0$ ; the time derivative  $a = d\theta/dt$ . An approximately linear decrease of the contact angle with time is characteristic for droplet evaporation at a constant contact diameter of the droplets, which is often found for wetting systems, i.e., systems with equilibrium contact angles less than  $90^\circ$ . The evaporation rate  $a$  depends on the coating. This seems to depend on the chemical structure of the PEM surface, strongly. A significant enhancement of the droplet evaporation rate is found for a coating with PDADMAC as the exposed layer, which is attributed to the existence of a surface energy related driving force to the swelling of this polyelectrolyte coating.

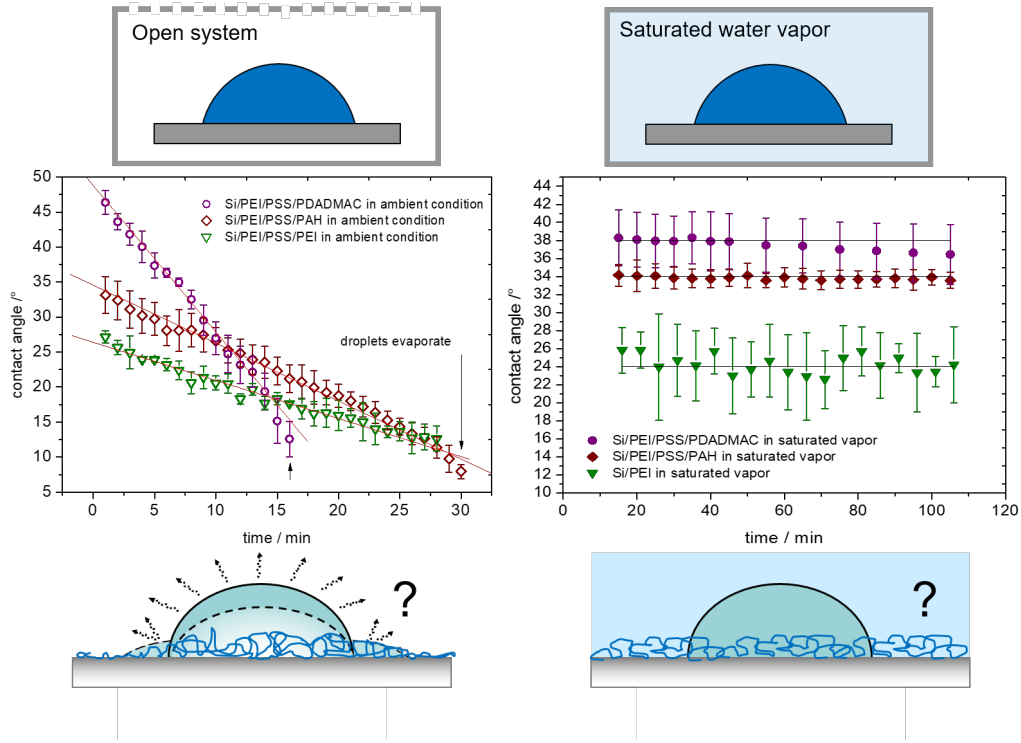


Figure 1: *Water contact angle vs. time for polyelectrolyte-coated silicon substrates with a polycation in the outermost layer. The dipping sequence was Si/PEI/PSS/PDADMAC (circles), Si/PEI/PSS/PAH (diamonds) and Si/PEI (triangles). Left: In an open cell at ca. 40 % relative humidity, where evaporation takes place. Right: in water-saturated atmosphere with horizontal lines showing the mean values  $\theta_e$  for each system. Data from [A9].*

On the right of fig. 1 the contact angle was recorded in water-saturated atmosphere. The contact angle is constant over time, which shows that no evaporation took place and that the swelling ratio of the PEM in saturated vapor and in liquid (under the droplet) seems to be the same.

Fig. 2 shows on left hand side the water contact angle vs. time on PSS terminated PEM in water-saturated atmosphere [A9].

In contrast to the polycation terminated PEM the contact angle is not constant but decreases exponentially with time irrespective of the saturation time in water vapor. The data are fitted with

$$\theta(t) = \theta_e + (\theta_i - \theta_e) \exp -t/\tau \quad (2)$$

where  $t$  is the time elapsed after the deposition of the droplet;  $\theta_i$  and  $\theta_e$  represent the contact angle directly after deposition ( $t=0$ ) and the final (equilibrium) value, respectively; and  $\tau$  is a relaxation time.

Obviously, the PSS terminated PEM swells further in water even after saturation in water. So far, this phenomenon is not clarified. This phenomenon indicates an odd-even effect for wetting processes which was observed also observed in another study for PSS/PAH multilayers [A10].

Probably, the reason for the longer relaxation processes is not the negative charge of PSS terminated PEM, since positively charged microgel layers show also a decrease in contact angle, but much faster as for the PSS terminated PEM.

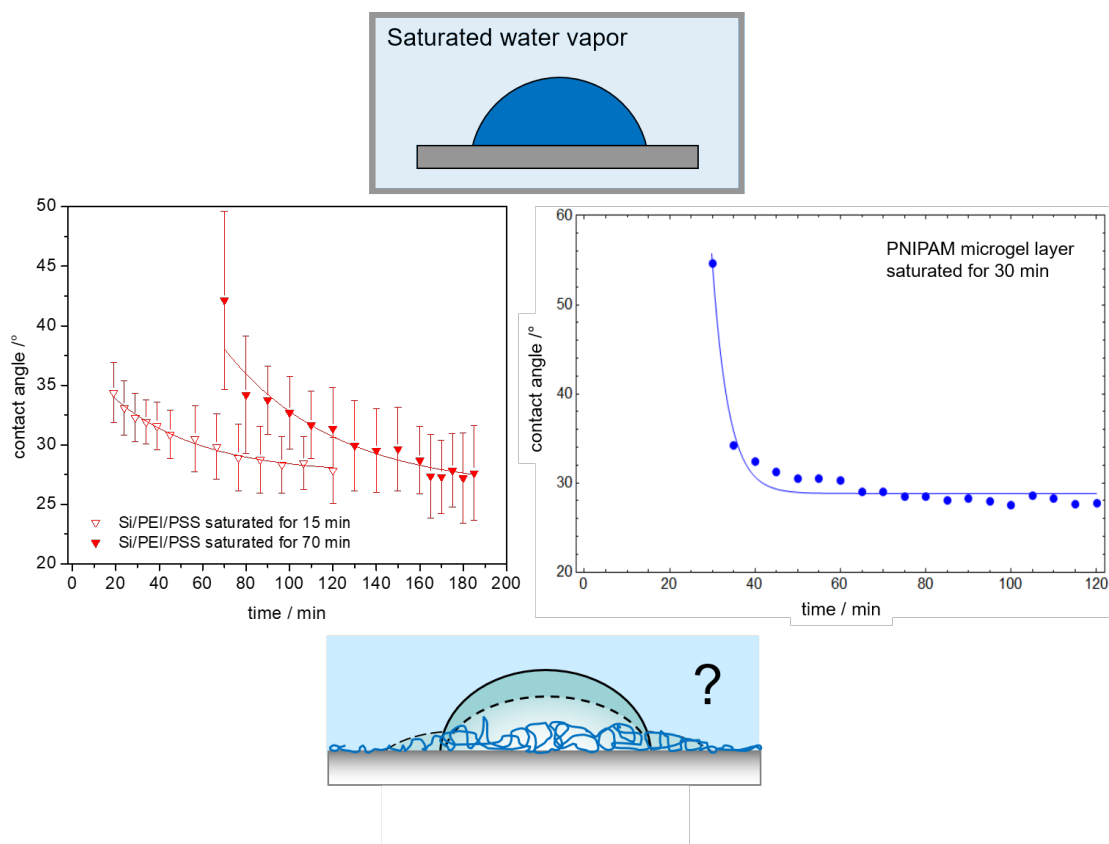


Figure 2: Water contact angle vs. time in water-saturated atmosphere. The lines show fits of the data by equation 2. Left: On silicon wafers coated with PEI/PSS at two different pre-saturation periods: open triangles 15 min saturation time, filled triangles 70 min saturation time. Right: On a layer of positively charged PNIPAM microgels. Data from [A9] and from the Bachelor thesis of Franziska Jakob.

## Open Questions

- Explanation for the quantitative difference in contact angles and evaporation rate for polycation terminated PEM?
- Explanation for the different type of adaptation for PEM terminated with polycations and with PSS and microgel layer.
- How can the relaxation time from eq. 2 be related to the hysteresis occurring between advancing and receding contact angle in a pumped droplet or at a moving droplet. Recently, a model in this direction was presented by Butt and coworkers [32].

## 1.1 Project-related publications

### 1.1.1 Articles published by outlets with scientific quality assurance

[A1] R. Köhler, C. Chevigny, R. von Klitzing, (2012): "Neutron Reflectometry at Polyelectrolyte Multilayers", Ch. 11, pp. 219 – 268, in *Multilayer Thin Films E2* Wiley VCH, eds: G. Decher, J. Schlenoff.

**[A2]** O. Löhmann, S. Micciulla, O. Soltwedel, E. Schneck, R. von Klitzing (2018): “Swelling behavior of composite systems: Mutual effects between polyelectrolyte brushes and multilayers” *Macromolecules* **51** 2996 – 3005.

**[A3]** M. Zerball, A. Laschewsky, R. von Klitzing (2015): “Swelling of Polyelectrolyte Multilayers: The Relation Between, Surface and Bulk Characteristics” *J. Phys. Chem. B* **119** (35), 11879 - 11886.

**[A4]** A. Burmistrova, R.v.Klitzing (2010): “Control of number density and swelling / shrinking behavior of P(NIPAM–AAc) particles at solid surfaces”, *J. Mat. Chem.* **20** 3502 – 3507.

**[A5]** A. Burmistrova, M. Richter, M. Eisele, C. Uzun, R. von Klitzing (2011): “Effect of co-monomer content on the swelling/shrinking and mechanical behaviour of individual adsorbed PNIPAM microgel particles” *Polymers* **3** 1575 – 1590.

**[A6]** M. Richter, M. Hunnenmörder, R. von Klitzing (2014): “The impact of the con-non-solvency effect on PNIPAM based microgels at interfaces” *Coll. Polymer Sci.* **292** 2439–2452.

**[A7]** S. Backes, P. Krause, W. Nasilowska, M. U. Witt, D. Mukherji, K. Kremer, R. von Klitzing (2017): “PNIPAM microgels under alcoholic intoxication: When a LCST polymer shows swelling with increasing temperature”, *ACS Macro* **6** 1042.

**[A8]** S. Backes, P. Krause, W. Tabaka, M. U. Witt, R. von Klitzing (2017): “Combined Cononsolvency and Temperature Effects on Adsorbed PNIPAM Microgels”, *Langmuir* **33** 14269 – 14277.

**[A9]** K. Hänni–Ciunel, G. H. Findenegg, R. v. Klitzing (2007): “Water Contact Angle on Polyelectrolyte-Coated Surfaces: Effects of Film Swelling and Droplet Evaporation”, *Soft Materials* **5** 61 – 73.

**[A10]** J.E. Wong, F. Rehfeldt, P. Haenni, M. Tanaka, R. v. Klitzing (2004): “Swelling Behavior of Polyelectrolyte Multilayers in Saturated Water Vapor”, *Macromolecules*, **37**, 7285 – 7289.

### **1.1.2 Other Publications**

None

### **1.1.3 Patents**

None

## 2 Objectives and working programme

### 2.1 Anticipated total duration of the project

We ask for 3 years funding by DFG from 1.10.2019 on.

### 2.2 Objectives

The global aim of the project is the understanding of the relation between the adaptation of polymer surfaces and their dynamic wetting properties. In the present project adaptation refers to swelling of the polymer coating caused by the (partial) uptake of the wetting liquid which is water or an aqueous solution in most of the experiments.

In order to separate evaporation from wetting effects, well-defined experimental conditions have to be ensured. For evaporation studies with water experiments in an open cell will be carried out. Experiments which should exclude evaporation are carried out in a closed cell in saturated vapor. This is inherently connected to a pre-swelling of the polymer coating. Therefore, also glycerol will be used as wetting liquid. The polyelectrolyte layers can swell in glycerol, but it is almost not volatile at room temperature. Glycerol gives the opportunity to place a droplet onto a polyelectrolyte surface without evaporation and without pre-swelling of the polyelectrolyte layer.

The most obvious question related to our preliminary work is, why certain polyelectrolyte layers have the same swelling ratio in saturated vapor and against liquid water (under the droplet) and others show a different swelling degree. Is that related to the odd-even effect, to charge effects or the swelling ability? Therefore different polyelectrolyte coatings, i.e. PEM and PNIPAM microgel layers of different charge density and sign of charge, different swelling ability and different hydrophilic/hydrophobic balance will be prepared. In case of PNIPAM microgels the swelling ability is controlled via temperature. Therefore their dynamic wetting will be studied below and above the VPTT.

The relaxation time determined by deposition of a sessile drop onto the substrate will be studied. The relaxation time will be related to the advancing/receding angle which occur during sucking and pumping a droplet or at a moving droplet. Therefore additional scenario will be used to realize advancing and receding contact angles (coop.: Günter Auernhammer). If the droplet moves faster than the relaxation time of the polymer coating, the difference between receding and advancing contact angle should be quite small. The relaxation time of the contact angle and the difference in advancing and receding contact angle will be correlated to the change in molecular structure at the polymer surface (coop.: **Björn Braunschweig, Marcello Sega**). The dissipation energy of the change in molecular structure will be determined from the dynamic wetting data.

Electrokinetic effects will be studied by changing the surface charge (amount of charge during synthesis, pH) and by changing the salt concentration of the wetting aqueous solution (coop.: **Christian Holm**).

In order to increase the complexity a water-ethanol mixture will be studied as wetting liquid. The co-nonsolvency effect in case of PNIPAM will lead to different swollen states which probably will lead to a change in wetting behavior.

The results on the relation between swelling ability and dynamic wetting properties will be compared to theoretical predictions of **Uwe Thiele, Thomas Speck and Barbara Wagner**.

Towards applications, our polymer coatings will be wetted by lipid vesicles (coop.: **Motomu Tanaka**) and they will be used as model systems for a better understanding of dynamic wetting processes in the fibrous network. (coop.: Markus Biesalski).

The following questions are addressed (summary):

- Global question: How do the swelling kinetics and the swelling ability affect the change in contact angle?
- Electrokinetic effects: Effect of density of charged surface groups, Effect of pH and of salt concentration electrolyte solutions as wetting liquids?
- Effect of volume phase transition caused by temperature changes?
- Co-nonsolvency effects including partition coefficient of water and ethanol in the microgel layer and the surrounding liquid?
- Change in molecular structure of the surface during the wetting process?
- Separation of evaporation effects from wetting effects?

In the second funding period, switchable surfaces will be studied and the effect of surfactant will be included.

## **2.3 Work programme incl. proposed research methods**

### **2.3.1 Research Methods**

Following methods are relevant for the project:

#### a) Characterisation of the microgels (aqueous microgel dispersion):

- Dynamic light scattering (DLS): determination of hydrodynamic radius, length scale ( $< 1 \mu m$ )
- Zetasizer: Zeta-Potential of microgels

#### b) Preparation of polymer coatings:

- Spin-coater (preparation of PEM)
- Dip robot (preparation of microgel layers)

#### c) Characterisation of polymer coatings:

- Ellipsometry: determination of thickness and refractive index. The swelling kinetics will be measured by changing the relative humidity.
- Scanning force microscopy (AFM): Determination of surface topology / roughness
- Indentation method (AFM): Determination of coating thicknesses up to  $10 \mu m$
- Neutron reflectometry: Determination of thickness, density and roughness of polymer coatings. Only selected samples will be studied. Deuterated solvents will be used. In binary solvent mixtures at least one of the solvents is deuterated. We will apply for neutron reflectometry at large facilities, mainly at MLZ (Munich) and at the ILL (Grenoble).



For all methods we have cells which allow measurements under controlled relative humidities (1% – 98% r.h.) and against different solvents. The swelling properties of the polymer coatings will be studied by comparing the measurands under dry (1% r.h.) and humid conditions as well as against solvent.

d) Surface tension and wetting:

- Tensiometry: Surface tension of liquid surfaces: Wilhelmy plate and du Nouy ring
- Wetting Sessile drop against ambient conditions or against saturated vapor.

Wetting experiments: Since the focus of the project is on wetting experiments, they are described more in detail. The contact angle is measured by the sessile drop technique. Three scenarios are used:

1) The droplet is deposited onto the horizontal substrate and the contact angle is measured over time. The evaporation rate is measured against ambient conditions and is analysed by eq. 1. The relaxation time  $\tau$  will be analysed by eq. 2.

2) The advancing and receding contact angle is measured by pumping/ sucking liquid into/out of the droplet. For selected samples the receding and advancing contact angle will be compared to results achieved by methods in the lab of **Günter Auernhammer** which allow a higher velocity of the liquid: Drop slider ( $> 100 \mu\text{m/s}$  to several  $\text{mm/s}$ ) and rotating drum ( $> 1 \text{ mm/s}$ ).

3) The substrate is tilted at different angles in order to achieve different velocities of the droplet. Unless stated otherwise in the working programme, all three scenarios will be carried out for getting information about the dynamic contact angle.

In order to separate changes of contact angle caused by evaporation and caused by adaptation of the wetting due to molecular changes of the polymer surface the evaporation will be avoided in some measurements. To avoid evaporation in case of volatile liquids (water or/and ethanol) wetting experiments will be carried out in a closed cell which contains a reservoir of the respective wetting liquid. The polymer coatings will be pre-swollen in the vapor. The home-built cell exists for horizontal samples but has to be constructed for tilted samples. The contact angle will be determined by a commercial software included within the apparatus (Oca 15 Plus, upgraded with a tilting table, Dataphysics).

The group of **Björn Braunschweig** proposes the development of a cell which allows co-localized studies of Sum Frequency Generation (SFG) spectroscopy and contact angle measurements. In collaboration with them we will study the change in molecular structure (via O-H stretching band) of the polymer coatings during the wetting process. Therefore the coatings will be prepared on optically transparent wafers (e.g. Quartz,  $\text{Al}_2\text{O}_3$ ).

## **Work programme**

### **Workpackages (WP)**

#### WP 1: Dynamic wetting of polyelectrolyte multilayers (PEM) by aqueous solutions

A) Different layer numbers of polycations and polyanions are deposited onto a Silicon wafer from an aqueous solution by a dip robot. The outermost layer is either a polycation (PEI, PAH or PDADMAC) or a polyanion (PSS or hyaluronic acid (HA)). PEMs of different numbers of polyelectrolyte layers are prepared. The swelling behavior is studied with ellipsometry, AFM and neutron reflectometry as mentioned above. The dynamic contact angle is measured and analysed according to the three scenarios listed above: 1) relaxation of contact angle, 2) advancing receding contact angle, 3) moving droplet). The

wetting of water and glycerol is measured both in an open and in a closed cell. The experimentally determined contact angles will be compared with contact angles predicted by the atomistic model of **Marcello Sega**. This would allow a deeper understanding of the effect the outermost layer of a PEM on its wetting properties.

B) Samples from part A with different relaxation times will be selected for further investigations. The dynamic contact angle of aqueous solutions containing different amounts of NaCl ( $10^{-3}$  – 1 mol/l) will be measured and analysed against saturated vapor. The experimental results on different salt concentrations will be compared with theoretical predictions of the group of **Christian Holm**. They model a multilayer surface with a lattice Boltzmann electrokinetic model.

In addition PEM will be prepared with different amount of NaCl (0.1 – 1 mol/l) in the respective polyelectrolyte solutions during dipping. The dynamic water contact angle will be measured against ambient conditions and against saturated vapor. For selected samples SFG spectroscopy and wetting experiments on PEM will be combined in the cooperation with the group of **Björn Braunschweig**.

#### WP 2: Dynamic wetting of microgel layers by aqueous solutions

A) PNIPAM based microgels will be synthesized by precipitation polymerisation in our lab by Marcus Witt, a PhD student funded by TU Darmstadt. The focus will be on PNIPAM microgels co-synthesized with acrylic acid (AAc), allyl acetic acid (AAA) and allylamine (AA), respectively. The initiator has the same charge as the respective co-monomer: potassium persulfate (KPS, negatively charged) and allylamin (AA), 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH, positively charged). The microgels will be characterised by DLS and zeta potential measurements at different temperatures (20 – 60°C) in water. Layers of microgel particles will be prepared via spin coating at low rotation velocities (300 – 500 rpm) to get densely packed layers. The microgels will be adsorbed onto negatively charged Silicon substrates (at intermediate pH). For a better immobilisation the substrate should be oppositely charged to the microgel. Positively charged P(NIPAM-co-AA) microgels can be directly adsorbed onto the the Silicon wafers. In case of negatively charged P(NIPAM-co-AAc) or P(NIPAM-co-AAA) microgels a polycation layer (PAH) is adsorbed before spin-coating of the microgels. Beside monolayers also multilayers of oppositely charged microgels and of microgels and oppositely charged will be prepared. The swelling behaviour will be studied at different pH (pH 3 - 9) and temperatures (20 – 60°C).

B) The dynamic wetting behavior of water (3 scenario) on the microgel layers will be studied at different temperatures (20 – 60°C) in a closed cell. Evaporation experiments in an open cell are carried out at room temperature only. Also comparing experiments with glycerol in an open and in a closed cell are carried out at room temperature only. Reference systems are PEM from WP1 which should be not temperature sensitive [33].

C) In a next step the dynamic contact angle of water droplets at different pH (pH 3 - 9) will be studied. The experimental results on different pH will be compared with the outcome of the lattice Boltzmann electrokinetic model of the group of **Christian Holm**.

For selected samples SFG spectroscopy and wetting experiments on PEM will be combined in the cooperation with the group of **Björn Braunschweig**.

#### WP 3: Dynamic wetting of microgel layers by water/ ethanol mixtures (Co-nonsolvency effect)

A) First the co-nonsolvency effect of water and ethanol will be studied with DLS and zeta potential measurements at microgels in liquid bulk phase (water/ ethanol mixtures) as presented in section 1. Selected layer systems from WP2 will be used to study the co-nonsolvency effect on the swelling behavior of the microgel layers. Special attention will be drawn to the ethanol/water ratio within the microgel. Therefore neutron reflectivity measurements will be carried out with contrast variation (3 contrasts) by using deuterated and non-deuterated solvents. To analyze the reflectivity curves in a self-consistent manner with a minimal number of independent parameters, a model based on the volume fraction profiles of all chemical components is employed [34], **[A2]**. Together with **Björn Braunschweig** we will test if SFG spectroscopy can be also used to determine the ethanol/water ratio in the microgel layer.

B) The dynamic wetting properties of microgel layers by mixtures of different ethanol/water ratios will be studied. These measurements will be carried out in a closed cell only to avoid changes in liquid composition due to different evaporation rates of water and ethanol. The vapor phase will be stabilized by placing a water/ethanol reservoir of same composition of the droplet into the cell. Again all 3 scenario will be used and analysed. In addition, for studying the consequences of the co-non-solvency the interaction between a water droplet and an ethanol droplet deposited onto a PNIPAM microgel layer will be studied together with **Günter Auernhammer**. The challenge is do the measurements under well-defined conditions, since there will be a gradient in composition of the vapor phase. To stabilize the gradient one idea is to place an ethanol reservoir close to the ethanol droplet and a water reservoir close to the water droplet.

As a reference system for all measurements a bare Silicon wafer will be used.

The experimental data of the contact angle vs. time will be offered to several theoreticians (**Barbara Wagner, Uwe Thiele, Thomas Speck**) to compare them with their results of theoretical simulations and model predictions.

#### **Working plan:**

WP 1A: 6 months

WP 1B: 6 months

WP 2A: 6 months

WP 2B: 3 months

WP 2C: 3 months

WP 3A: 6 months

WP 3B: 6 months

In a kind of feed-back control the microgel particles will be adapted for different purposes. During the whole project period the microgel particles will be adjusted for the cooperation partners if needed. We will ask for beamtime at large facilities. It depends on the outcome of the evaluation process when the beam time will be.

## **2.4 Data handling**

There is enough server space for our group at TU Darmstadt. We will save the data on the server, which contains also space for back-ups.

## 2.5 Other information

None

## 2.6 Explanations on the proposed investigations

None of the listed investigations will be carried out.

## 2.7 Information on scientific and financial involvement of international co-operation partners

None

## 3 Bibliography

- [1] G. Decher *Science* **277** (1997) 1232.
- [2] S. Dadoo, R. Steitz, A. Laschewsky, R. von Klitzing *PCCP*(2011),**13**, 10318.
- [3] D. Volodkin, R. von Klitzing *Curr. Op. Coll. Interf. Sci.* 2014 **19** 25–31.
- [4] R. Koehler, R. Steitz, R. von Klitzing, *Adv. Coll. Interf. Sci* (2014) **207** 325-331.
- [5] J. Hellwig, S. Micciulla, J. Strebe, R. von Klitzing, *Langmuir* 2016, 32, 10505-10512.
- [6] T. Tanaka, D. Fimore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah. *Phys. Rev. Lett.*, 45:1636, 1980.
- [7] Y. Deng and R. Pelton. *Macromolecules*, 28:4617, 1995.
- [8] K. Kratz and W. Eimer. *Ber. Bunsenges. Phys. Chem.*, 102:848, 1998.
- [9] K. Kratz, T. Hellweg, and W. Eimer. *Ber. Bunsenges. Phys. Chem.*, 102:1603, 1998.
- [10] H. Senff and W. Richtering. *J. Chem. Phys.*, 111:1705, 1999.
- [11] R. Pelton. *Adv. Coll. Int. Sci.*, 85:1, 2000.
- [12] T. Tanaka. *Phys. A*, 140:261, 1986.
- [13] N. Singh, A. W. Bridges, A. J. Garcia, and L. A. Lyon *Biomacromolecules*, 8:3271, 2007.
- [14] D. Suzuki, J. G. McGrath, H. Kawaguchi, and L. A. Lyon. *Phys. Chem. C*, 111:567, 2007.
- [15] M.J. Serpe, C.D. Jones, and L.A. Lyon. *Langmuir*, 19:8759, 2003.
- [16] S Hirotsu. *J. Chem. Phys.*, 88:427–431, 1988.
- [17] F M Winnik, H Ringsdorf, and J Venzmer. *Macromolecules*, 23:2415–2416, 1990.
- [18] H G Schild, M Muthukumar, and D A Tirrell. *Macromolecules*, 24:948–952, 1991.
- [19] H M Crowther and B Vincent. *Colloid Polym. Sci.*, 276:45–51, 1998.

- [20] M Richter, M Hunnenmörder, and R von Klitzing. *Colloid Polym. Sci.*, 292:2439–2452, 2014.
- [21] H Kojima, F Tanaka, C Scherzinger, and W Richtering. *J. Polym. Sci. B: Polym. Phys.*, 51:1100–1111, 2013.
- [22] I Bischofberger, D C E Calzolari, and V Trappe. *Soft Matter*, 10:8288–8295, 2014.
- [23] X. Huang, N.S. Zacharia<sup>1</sup>, *J. Appl. Polym. Sci.* 2015, 42767.
- [24] S. Guo et al. *ACS Appl. Mater. Interfaces*, 2016, 8 (44), pp 3055230563
- [25] Yoo, D., Shiratori, S.S., and Rubner, M.F. (1998) *Macromolecules*, 31: 4309
- [26] Shiratori, S.S., Rubner, M.F. (2000) *Macromolecules*, 33: 4213.
- [27] Kolasinska, M. and Warszynski, P. (2005) *Bioelectrochem.*, 66: 65
- [28] Kolasinska, M. and Warszynski, P. (2005) *Appl. Surf. Sci.*, 252: 759.
- [29] Kolasinska, M., Krastev, R., and Warszynski, P.J. (2006) *Colloid Interface Sci.*, 305: 46.
- [30] A. Tay, F. Lequeux, D. Bendejacq and C. Monteux, *Soft Matter*, 2011, 7, 4715
- [31] Hansen, R. S.; Miotto, M. Relaxation phenomena and contact angle hysteresis. *J. Am. Chem. Soc.* 1957, 79, 1765-1765.
- [32] H.-J. Butt, R. Berger, W. Steffen, S. Vollmer, S. A. L. Weber, *Langmuir* 2018 **34** 112992 – 11304.
- [33] R. Steitz, V. Leiner, K. Tauer, V. Khrenov, R. v. Klitzing *Applied Physics A* 2002 **74**, S519 – S521.
- [34] D. Boyaciyan, L. Braun, O. Lhmann, L. Silvi, E. Schneck, R. von Klitzing *J. Chem. Phys.*, 2018, **149**, 163322.

## 4 Requested modules/funds

### 4.1 Basic module

#### 4.1.1 Funding for staff

##### **0.75 TVL E13 (West) (PhD student):**

The PhD student will work on the work packages 1 – 3. He/she should be a physico-chemist or a physicist.

**1 Research Student (Studentische Hilfskraft) 40h/month:** The research student will support the PhD student with gel characterisation like zeta potential measurements. Depending on the skills and the motivation the student might also carry out DLS measurements. He/she will prepare PEM (dip coating) and layers of microgels (Spin coating) and will characterize them with ellipsometry.

#### 4.1.2 Direct Project Costs

##### 4.1.2.1 Equipment up to Euro 10.000, Software and Consumables

###### Equipment up to EUR 10.000.

Material for cells (Quartz cell, temperature control etc.) EUR 4.000

###### Consumables per year

Wafers (slides: Silicon, Quartz, Al <sub>2</sub> O <sub>3</sub> )	EUR 3.000
Silicon wafers (neutron reflectometry)	EUR 1.500
AFM Cantilevers	EUR 2.000
Chemicals for microgel synthesis	EUR 1.000
Solvents (incl. deuterated solvents)	EUR 3.000
Cells for zeta potential measurements	EUR 1.000

**Sum** **EUR 11.500 p.a.**

##### 4.1.2.2 Travel expenses

Within the SPP:

1st and 2nd year: SPP workshop (4 days, 2 persons)	EUR 2400
1st year: Advanced School (5 days, 1 person)	EUR 700
2nd year: PhD-candidate workshop (4 days, 1 person)	EUR 600
3rd year: International conference organised by the SPP (5 days, 2 persons)	EUR 1400
Exchange of students between different groups of the priority program and TU Darmstadt	EUR 2.000

Other conferences:

ECIS 2020 in Athens (Greece), 1 person	EUR 1.500
ECIS 2021 in Crete (Greece), 1 person	EUR 1.500
Conference of the German Physical Society (DPG) (1 person, every year)	EUR 2.400

**Sum** **EUR 12.500**

##### 4.1.2.3 Visiting Researchers

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**

Colour-print figures or cover page

EUR 2.250

#### **4.1.3 Instrumentation**

None

#### **4.2 Module Temporary Position for Principle Investigator**

None

#### **4.3 Module Replacement Funding**

None

#### **4.4 Module Temporary Clinician Substitute**

None

#### **4.5 Module Mercator Fellows**

None

#### **4.6 Module Workshop Funding**

None

#### **4.7 Module Public Relations Funding**

None

### **5 Project requirements**

#### **5.1 Employment status information**

Applicant: v. Klitzing, Regine, Prof. Dr., university professor (W3) permanent position at TU Darmstadt in the department of Physics.

Jointly responsible: Soltwedel, Olaf, Dr., permanent researcher in our group from 1.1.2019 on.

#### **5.2 First-time proposal data**

None

### 5.3 Composition of the project group (Basic funding by TU Darmstadt)

- Regine v. Klitzing: project leader, applicant.
- Olaf Soltwedel: jointly responsible for the supervision of the PhD student, mainly responsible for neutron reflectometry. He was for 5 years local contact at NREX, neutron reflectometer at the FRMII in Garching, and he is an expert in neutron reflectometry.
- Marcus Witt (PhD student): introduces the PhD student into synthesis and characterisation (DLS, zeta-potential measurements) of microgels.
- Michael Ludwig (PhD student): introduces the PhD student into AFM measurements.
- Alexandra Karbacher: Chemical technician, responsible for the chemical and physicochemical labs, routine measurements, permanent position.
- Access to the mechanical and electronic workshop of the Physics department.
- Henny Walter: carries out the administrative part of the project, permanent position.

### 5.4 Cooperation with other researchers

#### 5.4.1 Researchers with whom I have agreed to cooperate on this project (within SPP 2171)

##### Information on scientific cooperation within SPP 2171

*In general:* We offer different types of polymer coating our group is specialized on to all SPP partners: PEM, layers of adsorbed PNIPAM based or PEG based microgels, polymer brushes (PNIPAM, PDMAEMA, PMETAC), even if not all of these coatings are examined in our proposed project. Furthermore, we offer support for neutron reflectometry measurements in order to study the swelling ability of the polymer coatings.

##### Planned collaboration

**Günter Auernhammer / A. Fery / P. Uhlmann** (IPF Dresden):

We will compare our results of the co-nonsolvency effect on the dynamic wetting of PNIPAM microgel layers with the results on PNIPAM brushes obtained by G. Auernhammer. With that, we are able to validate the effect of molecular architecture and thickness of the PNIPAM layer. Further, the wetting of water and a neighbored ethanol droplet will be studied in cooperation with G. Auernhammer.

For selected samples the receding and advancing contact angle will be compared to results from methods in the lab of G. Auernhammer, which allow a higher velocity of the liquid: Drop slider ( $> 100 \mu\text{m}$  - mm/s) and rotating drum ( $> 1 \text{ mm/s}$ ).

**Markus Biesalski / Tobias Meckel** (TU Darmstadt):

Our swellable polymer microgel (PNIPAM-co-AAc) layers serve as model systems for the surface of the fibrillated fibers in papers which carry carboxyl groups at their surface. The amount of charges of the PNIPAM-co-AAc microgels can be adjusted by number density during synthesis and via pH. An understanding of the wetting properties of the model system contributes to a better understanding of dynamic wetting processes in the



fibrous network.

**Björn Braunschweig** (U Münster):

The group of **Björn Braunschweig** proposes the development of a cell which allows co-localized studies of Sum Frequency Generation (SFG) spectroscopy and contact angle measurements. In collaboration with them the change in molecular structure (via O-H stretching band) of the polymer coatings during the wetting process will be studied. Further, they will run some tests to check if the ethanol/water ratio within the PNIPAM microgel layers can be determined by SFG spectroscopy.

**Christian Holm** (U Stuttgart):

They are interested in electrokinetic effects on wetting properties. We will provide them our experimental data on contact angles of droplets of varying electrolyte concentration and pH on surfaces made up polyelectrolyte multilayers and microgels with different charges. The multilayer surface will be modeled with a lattice Boltzmann electrokinetic model and the surfaces will be designed according our experimental setup. We can compare experimentally obtained wetting angles and drop shapes with the simulations.

**Marcello Sega** (FZ Jülich):

The atomistic model of Marcello Sega will allow quantitative predictions, which might explain the difference in contact angle of PEM with different polyelectrolytes in the outermost layer.

**Motomu Tanaka / Marcus Müller**(U Heidelberg / U Göttingen):

We will study together the wetting of microgel substrates by lipid vesicles in combination with coarse grained simulation. For this purpose we will synthesize PNIPAM-based microgels with tailored charge (variable amount of AAc, AAA, AA) and hydrophilic/hydrophobic balance (variable amount of AAA). Substrates of different microgel number density on the solid wafers will be provided to Motomu Tanaka.

Further agreements are made with three other theoreticians (**Thomas Speck** (U Mainz), **Uwe Thiele** (U Münster), **Barbara Wagner** (TU Berlin)). We will provide the experimental data like contact angle vs. time or swelling data, and they will test their models and simulations.

**Current/former collaborations with SPP cooperation partners**

**Markus Biesalski / Tobias Meckel:**

We are working together in the frame of a recently started “DFG- Paketantrag” PAK 962 on “Chemische und geometrische Struktur funktionalisierter Papiere” (“Chemical and geometrical structure of functionalised papers”) (2018 – 2021).

**Christian Holm / Marcello Sega:**

We compared results of experimental and theoretical studies of ionic effects on the structure of PEM and polymer brushes:

S. Micciulla, P. A. Sanchez, J. Smiatek, B. Qiao, M. Sega, A. Laschewsky, C. Holm, R. von Klitzing (2014): “Layer-by-layer formation of oligoelectrolyte multilayers : a combined experimental and computational study” *Soft Materials* **12** S14 – S21.

S. Micciulla, J. Michalowsky, M. A. Schroer, C. Holm, R. von Klitzing, J. Smiatek (2016): "Concentration Dependent Effects of Urea Binding to Poly(N-isopropylacrylamide) Brushes: A Combined Experimental and Numerical Study" *Phys. Chem. Chem. Phys.* **18** 5324–5335.

**Günter Auernhammer:**

We collaborate on PNIPAM microgels at the oil/water interface.

S. Huang, K. Gawlitza, R. von Klitzing, L. Gilson, J. Nowak, S. Odenbach, W. Steffen, G. Auernhammer (2016): "Microgels at the water/oil interface: In-situ observation of structural ageing and two-dimensional magnetic bead microrheology" *Langmuir* **32** 712-722.

S. Huang, K. Gawlitza, R. von Klitzing, W. Steffen, G. Auernhammer (2017): "Structure and Rheology of Microgel Monolayers at the Water/Oil Interface" *Macromolecules* **50**, 3680 - 3689.

**Motomu Tanaka:**

Within the second funding period of a DFG financed French-German network (2003 - 2006) we worked together on the structure of thin polymer layers.

J.E. Wong, F. Rehfeldt, P. Haenni, M. Tanaka, R. v. Klitzing (2004): "Swelling Behavior of Polyelectrolyte Multilayers in Saturated Water Vapor", *Macromolecules*, **37**, 7285 – 7289.

F. Rehfeldt, R. Steitz, S. P. Armes, R. v. Klitzing, A. P. Gast, M. Tanaka (2006): "Reversible Activation of Diblock Copolymer Monolayers at the Interface by pH Modulation (1): Lateral Chain Density and Conformation", *J. Phys. Chem. B* **110** 9171 – 9176.

F. Rehfeldt, R. Steitz, S. P. Armes, R. v. Klitzing, A. P. Gast, M. Tanaka (2006): "Reversible Activation of Diblock Copolymer Monolayers at the Interface by pH Modulation (2): Membrane Interactions at the Solid/Liquid Interface", *J. Phys. Chem. B* **110** 9177 – 9182.

**5.4.2 Scientific cooperations within the past three years**

G. Auernhammer, IPF Dresden, T. Hellweg (U Bielefeld), O. Holderer, H. Frielinghaus, D. Richter (FZ Jülich), C. Holm (U Stuttgart), J. Smiatek (U Münster), K. Kremer (MPI-P, Mainz), A. Laschewsky (U Potsdam), P. Müller-Buschbaum (TU Mnchen / MLZ), K. Saalwächter (Universitt Halle), S. Santer (U Potsdam), F. Schacher (U Jena), A. Schönhals (BAM), E. Schneck (MPI KG, Potsdam), S. Seiffert and T. Speck (U Mainz), N. Willenbacher (KIT), J. Genzer (NCSU Raleigh, USA), R. Lamb (U Melbourne/Canadian Light-source), P. Mulvaney (U Melbourne, Australia), D. Volodkin (Nottingham Trenc, UK).

**5.5 Scientific equipment available in the group**

- MFP 3D AFM for scanning force microscopy and force spectroscopy (Asylum)
- Cypher AFM for fast scanning force microscopy and force spectroscopy (Asylum)

- AFM for scanning force microscopy in liquid under temperature control (NanoWizard II, JPK, Berlin)
- Dynamic light scattering (DLS)/diffusing wave spectroscopy (DWS) (LS instruments)
- Quartz Crystal Microbalance (QCM-D, Q-Sense, distributor: LOT, Germany)
- Fluorescence microscope with imaging system (Zeiss)
- Zeta particle sizer (Malvern, Germany)
- Ellipsometer (Optrel Kleinmachnow)
- Thin Film Pressure Balances (TFPB), homebuilt
- Dark field microscope (Olympus)
- Pendant Drop / Sessile Drop Technique (Oca 15 Plus with upgrade for tilting table, Dataphysics)
- Wilhelmy Plate / du Nouy Ring (K11, Krüss)
- Langmuir Trog (R & K, Berlin)
- Techniques for preparation of films: Spin-coater and dip robot

#### **5.5.1 Project-relevant cooperation with commercial enterprises**

None

#### **5.5.2 Project-relevant participation in commercial enterprises**

None

## **6 Declarations**

I have not requested funding for this project from any other sources. In the event that I submit such a request, I will inform the Deutsche Forschungsgemeinschaft immediately. I informed the "Vertrauensdozent" of the TU Darmstadt, Prof. Johannes Jannicka about the proposal.

## **List of appendages**

- Regine v. Klitzing: CV and recent publications