

Project Description – Project Proposals

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Investigation of dynamic wetting, swelling, and capillary-driven fluid transport in paper

Summary

The interaction of aqueous fluids with paper fibers plays a central role in the production, analysis, modification, functionalization and application of paper products. However, a quantitative understanding of the physicochemical processes that determine the initial wetting, subsequent fiber swelling, and capillary transport of water on, within, and between the fibers of a paper sheet is still poor. In particular, the high speed of the processes, which run on different length-scales, are still of great challenge for scientists, in particular, if it comes down to the analysis of capturing these interactions. To make the situation even worse, as of today it is still not trivial, to independently determine the abovementioned three processes, wetting, fiber swelling and capillary transport, in paper.

The proposed project addresses this particular point and intends to better understand these processes by combining new paper imbibition studies using a "spinning device" and defined double-layer papers with temporally and spatially high-resolution light microscopy methods.

With regard to the microscopy methods, confocal and super-resolution fluorescence microscopy as well as high-speed and fluorescence videography will be used. Specific attention will first be paid to the detection of the wetting of the paper fibers by pure water. With the help of a microfluidic rotational device, the capillary filling of the macropores in paper will first be decoupled from wetting by counteracting the capillary force with a corresponding centrifugal force. This setting allows to investigate the influence of paper-intrinsic (fiber type, porosity, etc.) and extrinsic parameters (fiber pre-modification, pH of the aqueous solution) on the wetting of the fibers immediately at the forefront of imbibition, in order to better understand the role that initial wetting plays on capillary flow in paper sheets. In a similar fashion, the swelling behavior of the fibers and the influence on imbibition will be investigated. Finally, the project aims for a better understanding how wetting, swelling and capillary transport can affect mechanical properties of paper sheets. The latter will be studied by investigation of macroscopically measurable deformations of the paper webs during imbibition. If successful, the project will provide a large base of novel fundamental insights of wetting of paper fibers, and how such a process will determine subsequent processes such as fiber swelling and capillary imbibition.

Project Description

1 State of the art and preliminary work

Paper, a man-made material made from renewable raw materials, has been used intensively for almost two thousand years. It is a flat, highly porous, flexible and foldable but hardly elastic material consisting of largely randomly arranged and interconnected fibrous basic building blocks with a very wide range of sizes and shapes. Previous research work has primarily focused on the processing and usage properties of paper in its standard applications as packaging material, writing and printing substrate or as a hygiene product. To date, the technology of production and processing of paper can be considered as to be highly advanced and developed for its market usage. Due to the necessity of satisfying more and more of our needs from renewable resources, paper as a biogenic, easily recyclable and, with respect to its production, technologically optimized material is moving into focus, especially for high-tech applications such as paper-based construction materials and medical diagnostics. However, the complexity of the material is an enormous challenge and requires analysis across scales in order to capture its chemistry, structure, geometry, and dynamic behavior. As a result, questions of correlations between constitution, structure, manufacturing process and property profile of paper are largely unanswered from a fundamental point of view. The interaction of a porous paper with a fluid, in particular, with aqueous based fluids, is of utmost importance for many technological applications such as in printing as well as paper-based microfluidics. With a focus on the imbibition of water by paper, i.e. the process of absorption without dissolving the cellulosic material, in our proposed studies, we aim to investigate a very basic property of paper that is widely used but far less understood at its core than assumed.

1.1 Structural hierarchies contributing to the imbibition of water by paper

Paper fibers consist of Cellulose polymers, the most abundant macromolecule on earth, and they are insoluble in water, but can take-up large amounts of aqueous fluid by swelling. Plants are able to exploit these properties for e.g. stability or water transport needs by tuning the final properties of their cell walls via secondary additions in the form of hemicellulose, lignin, pectin or suberin. If cellulose, in turn, is used for manmade materials, like paper, textiles, building materials, adhesives or as additives in consumables such processed foods or medical products, a similar, secondary tuning is usually required to yield the desired properties.

As materials based on natural cellulose fibers, like e.g. paper, are essentially made of chemically processed but morphologically still intact plant cell walls (Fig.1), they inherit many of their complex properties.

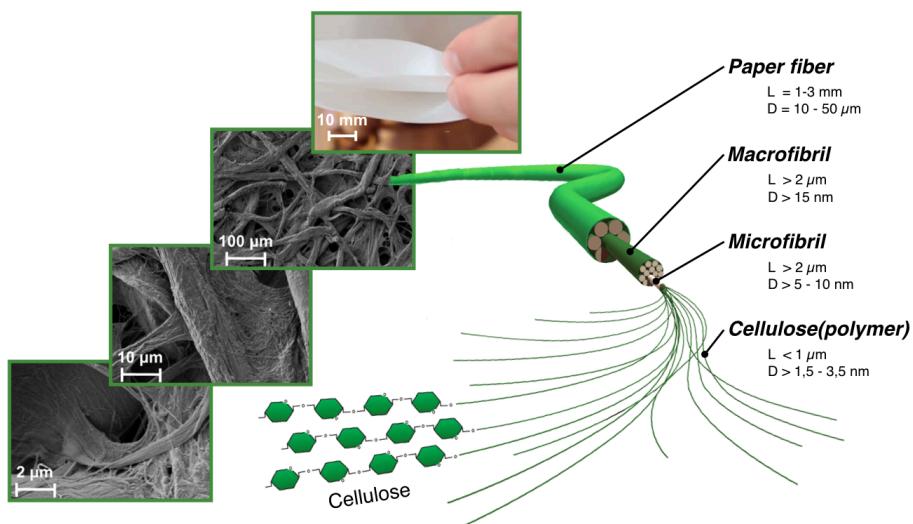


Figure 1 – Paper is a flat, highly porous, flexible and foldable but hardly elastic material. It consists of largely randomly arranged and interconnected fibers which are made of cellulose polymers. The latter arrange into semi-crystalline, hierarchical ordered structure that span multiple length scales visible, e.g. by various microscopy methods (inserts: SEM images of a filter paper).

In particular the contact (i.e. wetting), uptake and transport of water is a highly complex process that takes place on many time and length scales. To understand the process of paper fiber wetting, swelling, and capillary driven fluid transport in the porous matrix of paper, i.e. imbibition, there are two distinct structural hierarchies which contribute to and hence need to be considered to gain a better understanding of this complex process: Firstly, the fiber wall with its complex architecture and, secondly, the three-dimensional arrangement of fibers within the paper sheet. Hence, the imbibition of water into paper is a sequence of events that takes places in both of these hierarchies, creating a process of very high spatial and temporal dynamics. Our current understanding of these dynamics is by far not complete.

1.2. Fiber walls – construction, wetting and swelling

The contribution of fiber walls to the process of imbibition into paper is governed by their chemical composition as well as their nano- and microscale architecture. First and foremost, cellulose, a polysaccharide made of a linear chain of several hundred to many thousands of $\beta(1\rightarrow 4)$ linked D-glucose units, is a hydrophilic polymer. These linear chains align into long parallel bundles, which firmly hold together by hydrogen bonds between hydroxyl groups and oxygen atoms on either side of adjacent chains, causing them to pack closely into cellulose microfibrils. [1] Thanks to this highly ordered arrangement, cellulose is able to form several different crystalline structures, where natural cellulose is cellulose I, and regenerated cellulose (e.g. rayon) is cellulose II. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. With various chemical treatments it is possible to produce the structures cellulose III and cellulose IV. [2]

In a paper fiber made, e.g. of cotton linters, the cuticle (e.g. for fibers from cotton linters) and primary cell walls (e.g. for wood fibers) are lost in the pulping process, leaving mainly the secondary wall. The latter is composed of many separate 0.1 to 0.4 micron thick layers of parallel oriented microfibrils which change their prime orientation from layer to layer. Occasionally crystalline regions may also contain defects, e.g. folds or kinks, which vary in type and number in different fibers. [3] More importantly with respect to its swelling properties, besides ordered crystalline regions cellulose also consists amorphous regions. While a two-phase model with regions of high and low orders has already been proposed in 1950s [4], detailed information, e.g. that crystalline regions are interrupted by non-crystalline amorphous regions around every 60 nm are only available more recently. [5]

The swelling of fibers is determined by a number of properties. Fiber type, i.e. its detailed architecture, as well as changes induced during pulping are large contributors to a differential swelling behaviour. [1] On the molecular scale, swelling is a result of water entering in between individual cellulose chains thereby replacing the above-mentioned hydrogen bonds. Especially carboxylic groups, present to different amounts along the cellulosic backbones can dissociate in water, and by this can greatly promote further fiber swelling [6,7]

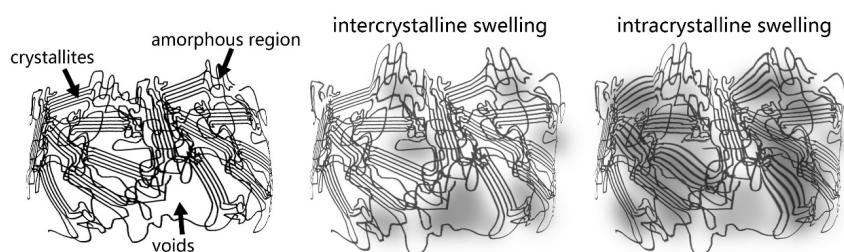


Figure 2 – Schematic illustration of intercrystalline and intracrystalline swelling [8].

From a morphological point of view, swelling can be divided into intercrystalline and intracrystalline swelling (Fig. 2). Water is thought to first interact with amorphous, less compact regions (intercrystalline swelling). Intracrystalline swelling, in turn, is slower and follows the former, but causes a far more drastic change to the lattice structure of the cellulose crystal and is accompanied by a large volume increase of the fiber. The latter also comes with significant changes in local mechanics of the fibers. Hence, water not only fills voids but rather forces fiber components apart. [8] Swelling however, only extends to a certain degree and reaches a maximum governed by thermodynamic equilibrium.

1.3 Paper sheets – fluid transport in porous media

In contrast to wetting and swelling of fiber walls, the uptake and transport of water within the three-dimensional arrangement of fibers, i.e. in a *paper sheet*, is a process that is based on an entirely different physical principle and takes place on far different time and length scales. Parameters that govern such interactions are among further fiber length, stiffness and orientation, which again determine the paper sheet density and porosity. However, dynamic studies of liquid transport in paper have so far largely been limited to macroscopic studies in which the liquid is recorded "from the macroscopic outside" during its migration through the paper by means of photography or video recordings, whereby the running front can only be recognized as a discrete line (Fig. 3). A very large number of studies of this kind are available. Prominent examples are works by Paul Yager, George Whitesides, and Robert Pelton, respectively, who addressed paper-based fluid timers for sensing applications. [9, 10, 11] A more comprehensive overview can be found in a recent review. [E8]

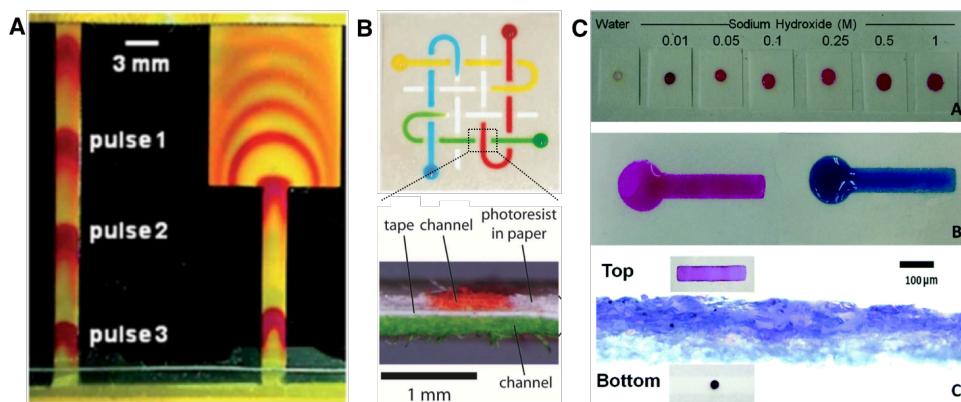


Figure 3 – Macroscopic investigations on liquid transport in paper. Works by, Yager (B [9]), Whitesides (A [10]), and Pelton (C [11]).

From a macroscopic point of view, the transport of liquids in paper can be described as capillary imbibition of liquid in porous media which in turn is described by Darcy's law. However, only in a few cases have such investigations been carried out with a resolution sufficient to reveal the fiber-based structure of paper. [12] In contrast to dynamic processes in paper, still images have been recorded at the highest spatial resolution, so that detailed image data exists on the structure of paper as well as individual cellulose fibers and their surfaces. A variety of methods were used, such as electron [13], scanning probe [14, 15] and, of course, optical microscopy. [13, 16-22, E3, E4]

As mentioned above, while there is an enormous number of publications devoted to the microscopic study of the structure, investigation of dynamic processes, such as fluid uptake, have almost exclusively been carried on a macroscopic scale. For the investigation of dynamic processes, however, a purely macroscopic view is not sufficient to understand the absorption and distribution of liquids in paper. As we have shown, given the complexity of fluidics in paper, it is particularly important to investigate dynamic processes with higher spatial resolution. [E3] In addition, a quantitative analysis of the processes on the microscale is required in order to incorporate these data into models and simulations and thus derive empirical or even physico-chemical laws on the behavior of liquids in paper. In our view, the understanding of these processes will decisively contribute to the ability to develop and produce papers with predictable and properties tailored to specific needs. Recent work on the theoretical level on the infiltration of liquids into paper impressively underlines the need for such experimental investigations. [23, 24]

1.4 The whole picture of Imbibition into paper – fluid transport into swellable porous media

The combined consideration of all processes, namely wetting, swelling and capillary-driven fluid transport is so far missing, but necessary to achieve a complete description of imbibition into the, swellable porous medium paper. In particular wetting and swelling, i.e. the nanocapillary processes described above, have so far largely been ignored in descriptions of paper imbibition. The challenge to record fast processes at high spatial resolution may have been one reason

behind this omission. Recently, Ha and coworkers [25] were able to extend the theories of Darcy and poroelasticity, which applies for materials, where imbibition causes a deformation of the porous structure due to an increase of the pore pressure with the water content, i.e. the amount of liquid inside the pore, which in turn causes the porous matrix to swell. [26] While this theory holds for many porous media, such as soil, sandstone, or hydrogel, it does not apply for materials, whose pore walls consist of a swellable and expandable material like e.g. paper fibers. Here, as the fluid front progresses, porous matrix at the spreading front expands due to swelling of the surrounding walls, not by increased pore pressure (Fig 4). In fact, the pore pressure decreases because of the overall volume expansion. Hence, as the framework of poroelastic theory does not apply, the hygroscopic expansion of cellulosic porous materials needs reconsideration.

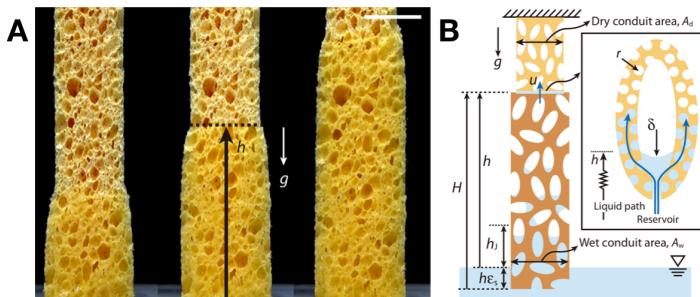


Figure 4 – Hygroscopic expansion of a cellulosic porous material, here a cellulose sponge, as a result of imbibition (A). Schematic of the sequence, in which imbibition takes place in a cellulose sponge: Micropores within the wall material are filled with liquid, upon which the wall expands. This leads to an increase of macropores, which can cause them not to fill due to insufficient capillary forces.
Figure adapted from [25].

1.5 Preliminary work

Paper microfluidics: In our own preliminary work we have carried out investigations on the capillary-driven flow of aqueous solutions in prepared channels of model lab-engineered papers. These showed that the flow in the paper channels macroscopically follows a Lucas-Washburn kinetics (static viscous flow). [E6] Furthermore, it could be shown in first studies that a reproducible flow in the channels is guaranteed especially when paper fleeces are produced exclusively from one fiber type and without further additives, and it could be shown for the first time that the capillary flow can be easily modulated within certain limits by adjusting the fleece density and porosity (Fig. 5A+B). [E5]

These findings were obtained with papers made from cotton linters as pulp. How the capillary flow will vary in dependence of fiber type and fiber pretreatment (fiber beating/grinding, fiber length fractionation, chemical oxidation etc.) is not well understood and will be a part of this project.

In addition, we have built a centrifugal microfluidic platform (Fig. 5C). The system consists of a motor that drives an axis whose rotation is picked up by a hall sensor. That way, a certain rotation can exactly be maintained, and the angular position can be used as a trigger for the illumination and the camera. With this setup we currently achieve images with a motion blur of around $10\text{ }\mu\text{m}$, so that macropores are just recognizable in images recorded at 4000 rpm. In an exemplary run, in which the rotational speed has been lowered from 2400 rpm to 1200 rpm at around $t = 30\text{s}$ demonstrates, that progression of imbibition can be stopped and continued at will (Fig. 5D and E). For the experiments proposed in this project, however, resolution has to be increased considerably. This will be achieved by using a camera with a much shorter exposure and far improved optics.

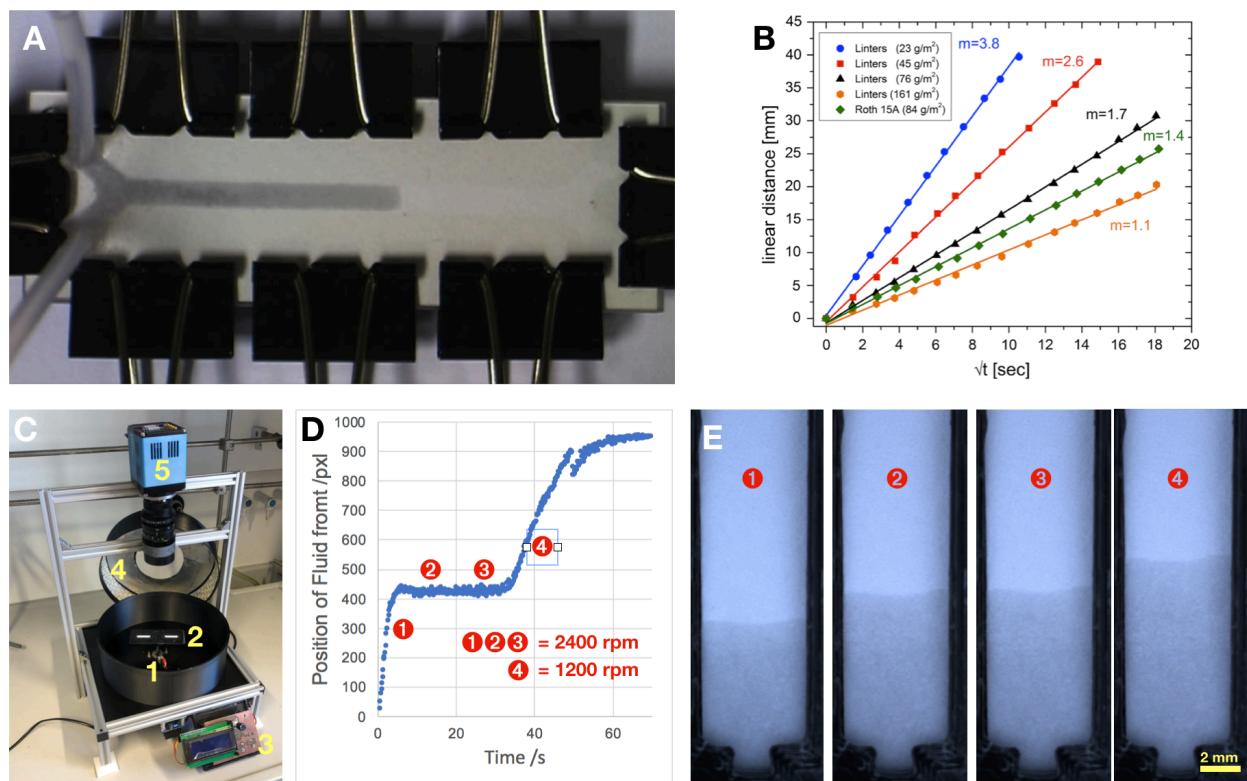


Figure 5 – Videographic analyses of the imbibition in paper. Video recording of water transport through a paper based microfluidic channel, whose barriers were prepared by immobilizing a hydrophobic polymer by means via photolithography (A). Lucas-Washburn-like behavior is observed for all papers, however with a strong dependence on the paper's grammature (B). To image microfluidics in presence of centrifugal forces, a spinning device (centrifugal microfluidic platform) as build consisting of a motor and a hall sensor (1) that rotates the mounted paper (2). Rotation is controlled by electronics (3) that also trigger illumination (4) and the camera(5) (C). A plot of fluid front positions against time where rotation has been lowered from 2400 rpm to 1200 rpm at $t = 30\text{s}$ demonstrates, that progression of imbibition can be stopped and continued at will (D). Corresponding images to the run shown in D (E). (Figure A and B is adopted from reference [E5]).

Microscopy of the dynamics of imbibition by paper: To image the dynamics of imbibition at much higher resolution we have applied the fluorescence microscopic toolkit to investigations of dynamic processes in paper. We used both widefield as well confocal microscopy, with which we were able to show the quantitative possibilities that open up with the application of state-of-the-art microscopy and subsequent image analyses. [E3] The work shows that fluorescence microscopy techniques allow a quantitative analysis of chemical functionalization as well as liquid movements on the microscale (Fig. 6). We were able to demonstrate recordings with high temporal (widefield) and spatial (confocal) resolution, both providing also very high sensitivity, i.e. radiometric resolution. By selectively marking the individual components of a microfluidic paper channel (paper, hydrophobic polymer and fluid), all components can be examined separately, simultaneously and in four dimensions (x, y, z, t) in the context of a fluid transport. We thus show that all qualities of fluorescence microscopy (spatial resolution = distribution of the polymer on the fibers, temporal resolution = fluid transport, spectral resolution = separation of the components and radiometric resolution = determination of the local quantities of polymer and fluid) can be combined and used for analyses of imbibition by paper.

In particular we showed that imbibition into paper starts with an initial wetting of fibers on their surface and that water transport (mainly) takes place on the fibers' surface or within their wall (Bump et al. 2015). Only at a later stage, water swells the fibers and fills the space between them (i.e. the macropores in paper). Consequently, imbibition into paper is a spatiotemporal process governed by all three processes, namely wetting, swelling and capillary transport.

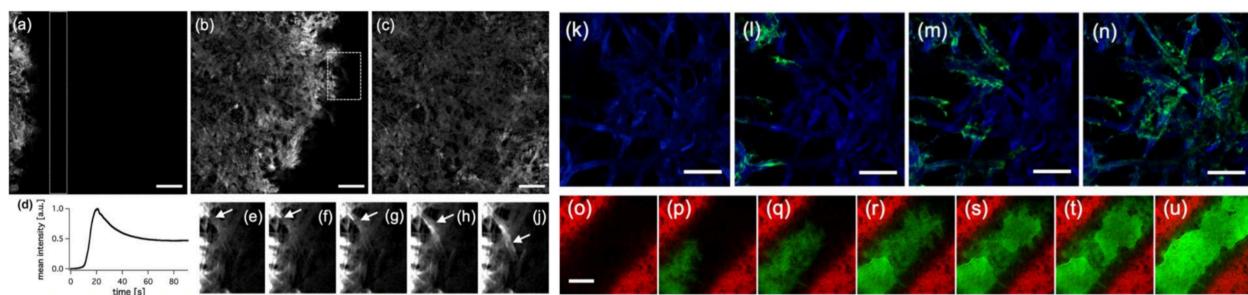


Figure 6 – Fluorescence microscopic analyses of the imbibition in paper. Wide field microscopy of the imbibition of FITC dextran (grey) in paper (black), frame rate = 30 Hz (a-i). Confocal microscopy of the imbibition of FITC dextran (green) in paper (blue)(k-n). Wide field microscopy of the capillary transport of FITC-dextran, frame rate = 1 Hz (green) in a paper-based microfluidic channel, limited by locally immobilized hydrophobic polymer, frame rate = 30 Hz (red). Image adapted from [E3].

1.1 Project-related publications

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

- [E1] C. Dubois, N. Herzog, C. Rüttiger, A. Geißler, E. Grange, U. Kunz, H.-J. Kleebe, **M. Biesalski, T. Meckel**, T. Gutmann, M. Gallei, and A. Andrieu-Brunsen – Fluid Flow Programming in Paper-Derived Silica–Polymer Hybrids, *Langmuir*, **2017**, 33 (1), 332–339
- [E2] C. Rüttiger, S. Mehlhase, S. Vowinkel, G. Cherkashinin, N. Liuc, C. Dietz, R. W. Stark, **M. Biesalski**, M. Gallei – Redox-mediated flux control in functional paper, *Polymer*, **2016**, 98, Pages 429–436
- [E3] S. Bump, A. Böhm, L. Babel, S. Wendenburg, F. Carstens, S. Schabel, **M. Biesalski**, and **T. Meckel** – Spatial, spectral, radiometric, and temporal analysis of polymer-modified paper substrates using fluorescence microscopy. *Cellulose*, **2015**, 22 (1), 73–88
- [E4] M. Janko, M. Jocher, A. Böhm, L. Babel, S. Bump, **M. Biesalski**, **T. Meckel**, and R.W. Stark – Cross-linking cellulosic fibers with photoreactive polymers: Visualization with confocal raman and fluorescence microscopy. *Biomacromolecules*, **2015**, 16 (7), 2179–2187
- [E5] A. Böhm, F. Carstens, C. Trieb, S. Schabel, **M. Biesalski** – Engineering microfluidic papers: effect of fiber source and paper sheet properties on capillary-driven fluid flow. *Microfluidics and Nanofluidics*, **2014**, 16 (5), 789–799
- [E6] A. Böhm, M. Gattermayer, C. Trieb, S. Schabel, D. Fiedler, F. Miletzky, **M. Biesalski**, Photo-attaching functional polymers to cellulose fibers for the design of chemically modified paper, *Cellulose* **2013**, 20, 467–483.
- [E7] S. Wendenburg, M.L. Nachbar, **M. Biesalski**, Tailoring the retention of charged model compounds in paper-based microfluidic devices, *Macromol Chem Phys* **2017**, 218(2), Art. No.1600408.
- [E8] A. Böhm, **M. Biesalski**, Paper-based microfluidic devices: A complex low-cost material in high-tech applications, *MRS Bulletin* **2017**, 42(5), 356–364.

1.1.2 Other publications

none

1.1.3 Patents

1.1.3.1 Pending

DE102013112048A1/WO2015063275A1: Verfahren zur Herstellung von nassfesten Papierprodukten und nassfestes Papierprodukt (Biesalski et al.)

1.1.3.2 Issued

none

2 Objectives and work programme

2.1 Anticipated total duration of the project

3 years (current project description) + 3 years (extension)

2.2 Objectives

The objective of this proposal is to investigate water imbibition into paper with approaches that allow for a selective view on the processes of wetting/swelling and capillary transport, respectively.

A major challenge with understanding water imbibition in paper concerns the fact that multiple overlapping physical phenomena, namely fiber wetting, fiber swelling and capillary imbibition, are acting simultaneously but on different time and length scales. Hence, finding a way to look at a single phenomenon (e.g. wetting) while repressing others (swelling and/or capillary transport) may open possible new insights into such complex dynamic interactions. With this project, we therefore aim to further our understanding of imbibition in paper with the approach of repressing individual processes that contribute and act simultaneously during imbibition. To that end, we will, on one hand, counter capillary transport with centrifugal forces to overemphasize the contribution of wetting and swelling and, on the other hand, counter swelling with special confinement in order to overemphasize the contribution of the capillary transport.

By repressing individual contributions, we will be able to

- (i) estimate at which time and length scale these individual processes dominate the imbibition dynamics, and
- (ii) to learn to what extent paper-intrinsic (fiber type, length, porosity, etc.), as well as extrinsic parameters (chemical and mechanical modification of fibers prior to sheet formation) can be used to understand, control and even modulate imbibition.

As fibers in paper are firmly coupled to one another at all crossing points, their spatial expansion during imbibition will inevitably lead to deformations of the network. Using several imaging techniques (high speed videography, rapid scanning confocal microscopy), we will therefore also investigate these dynamic changes, in order to learn, how deformations of fibers and the macropores in between them impact imbibition into paper.

2.3 Work programme incl. proposed research methods

WP1 Preparation and characterization of model paper substrates

The goal of the first work package is to provide lab-made paper sheets with defined geometry and controlled surface chemistry of the used paper fibers. In addition, model double layered paper sheets consisting of two individually prepared sheets with different porosities, chemical and mechanical fiber pre-modifications will be constructed in this first work package.

WP1.1 Model sheets from Eucalyptus and Cotton Linters fibers

As main fiber source, bleached Eucalyptus-Kraft (Euca) and Cotton Linters (CL) will be used, respectively. Euca fibers are short (app. 1 mm) and very compact fibers, and due to the Kraft-pulping and consecutive bleaching process prior to its use, they consist of very low amounts of hemicelluloses as well as lignin. Note, pulping and bleaching will be carried out by the supplier (Essity Mannheim, Louisenthal and others) of the fibers. CL fibers are longer more flexible fibers (1-3 mm in length) and they consist of more than 99% alpha-Cellulose. CL will be obtained from Louisenthal and Merck. Fiber length and diameter will be characterized prior to sheet formation using a automated Microscopy FiberLab device at the Institute for Papermaking (Prof. Schabel) at TU Darmstadt. In addition, fibers will be refined at defined power output between 50 and 200 kW/h. The latter shortens and fibrillates the fibers, which results in a higher swelling capacity of individual fibers. Lab sheets will then be produced by the Rapid-Koethen Technique according to DIN 54358 and ISO 5269/2, and parameters that will be varied by modulating the degree of refining as well as the overall fiber density in the paper sheet are the porosity, and the grammage, respectively. In this first set of studies we aim for typical paper grammages between 40 and 150 g/m², and porosities between 0.4 and 0.9, respectively. No process and/or functional chemical additives (flocculation agents, dry/wet strength agents) will be used in first place in order to keep the complexity of the paper constitution as low as possible. After preparation, all paper sheets will be stored at least for 24 hours in a norm climate room for equilibration, prior to further use. Because different paper can take-up different amounts of water at equilibrium, and because the latter may cause the interfacial layer of the fibers to swell to a certain degree, it is important to measure and to know the exact level of adsorbed water. The latter will therefore be determined prior to further imbibition and wetting studies (WP2 and WP3, respectively) by common means (paper dry-balance) in our laboratory.

WP1.2 Fiber surface chemistry

Despite the geometry of the porous matrix, wetting, swelling and imbibition of the fibrous mat are to a large extent being governed by the surface chemistry of the individual fibers. Fibers received from a typical pulping process carry negative charges along the lingo-cellulosic constituents, which are to a large extend caused by the presence of carboxylic acids. The latter are typically generated from the hydroxyl-groups by oxidation processes, and due to the nature of the chemical groups, the amount of charges on the fiber surface strongly depends on the pH and it can be determined by zeta-potential measurements. As is shown in Figure 7, the zeta potential of an

Euca fiber is always negative. At very low pH 2-4, the potential shows a decrease until a plateau is reached. This behavior can be attributed to the dissociation of the carboxylic acid groups typically displaying a pK value around 3-4. At pH values above 10, the potential again starts to decrease. This behavior can be attributed to dissociation of the OH-groups.

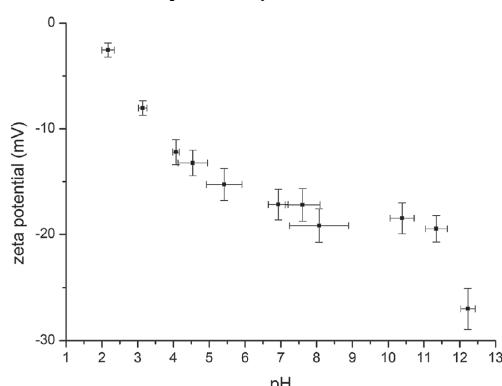
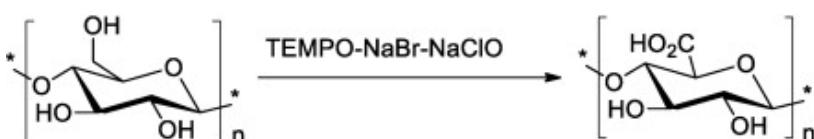


Figure 7 – Zeta potential of eucalyptus sulfate pulp as a function of pH. The error bars represent the standard deviation for three samples. (Figure taken from reference [E9])

Despite the pH, the zeta potential is a function of the number of carboxylic acid groups being present at the surface of the fiber. As pointed out above the latter depends on the type of chemical pulping as well as on storage conditions of the fibers prior to the use for papermaking. Besides this process-immanent number of carboxylic acid groups, the latter can also be introduced to the fiber surface in a more controlled fashion. A well-known technique to transfer OH-groups on the surface of the fiber into carboxylic acids has been introduced by the “TEMPO-oxidation” process [27], schematically outlined in Figure 8. TEMPO-oxidation will be used in WP1.2 to increase and modulate the amount of carboxylic acid groups on the fibers. Such modified fibers will be characterized with respect to surface charge and fiber swelling at norm climate equilibrium conditions, as well as in the presence of defined relative humidity. Finally the chemically modified fibers will be used for sheet preparation according to WP1.1.

Figure 8

Schematic description of the TEMPO-oxidation of cellulose



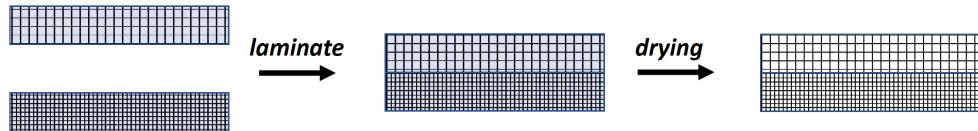
WP1.3 Double layered paper sheets

An interesting situation occurs, if two fibers are in contact that both possess different surface chemistries and/or morphologies, and if the fibers are being wetted by an aqueous solution. In such a case differences in the surface chemistry of the fibers may lead to changes of the wetting process. In order to understand such phenomena in more detail, the aim of WP1.3 is to design and provide model paper substrates, consisting of two individually prepared and laminated sheets (Fig. 9). Model systems that will be in focus here consist of (i) non-modified and TEMPO-oxidized fibers and (ii) low and high porous base sheets, respectively.

To achieve such model double layered sheets, a simple to establish system will be chosen. Paper sheets prepared in WP1.1 and WP1.2, respectively, will be first fully wetted with water and gently pressed together by moderate mechanical forces. Subsequently drying in a Rapid-Koethen Dryer, laminates the individual sheets together. Note, forces holding both sheets in the final dry stage together are mainly H-bonds being formed during drying between adjacent fibers of the individual sheets. This type of lamination works with a large number of different, individual sheets and it ensures that the fibers of the individual sheets are not disintegrated during double layer formation. After preparation, the model substrates are stored in norm climate conditions prior to further use in subsequent work packages. Figure 9 depicts a simplified scheme of the preparation of the double layered paper sheets.

Figure 9

Schematic description of double-layered paper sheet formation



WP2 Wetting of model paper substrates

The goal of the second work package is to understand the dynamic wetting of paper fibers in a paper sheet. In particular, this WP aims for a deeper understanding how the fiber type, the refining (fibrillation) of the fiber and the fibrillation of the fibers on the one hand, as well as the surface chemistry of the fibers on the other hand will affect dynamic wetting processes that occurs at the front of any imbibition-zone of a solution that wicks the (macro)porous fiber mat.

WP2.1 Dynamic wetting of fibers – influence of fiber type and fiber fibrillation

During imbibition, the propagation of water within the paper network is caused by wetting and capillary transport. To separate both processes, we will image the process in presence of strong centrifugal forces against the direction of imbibition until the force of the capillary driven transport is cancelled out. Under this condition, only wetting can be investigated. Due to the low amount of fluid wetting the fiber surfaces, swelling is expected to play a minor role under these conditions. Within WP2.1 a new self-made spinning device (centrifugal microfluidic platform) will be assembled and used for all studies in WP2.1. While such a device was recently developed in our group and successfully demonstrated the applicability of centrifugal forces to investigations on imbibition (preliminary work, Fig. 5C), an upgraded version is required to achieve a resolution sufficient to image fluid transport on and between single paper fibers. Hence, a far brighter light source (Chip-on-Board (COP) LED Array), a better motor, frame and housing are required, to minimize vibrations. Most importantly, however, far lower exposure times are required. We therefore plan to record fluid flow using a *pco.1200 hs* highspeed camera, which provides a minimal exposure of 50 ns, which is required to keep motion blur (i.e. the azimuthal displacement during rotation) below 2 µm.

Data acquisition are as follows: First, a drop of water (MilliQ quality) is placed at the inlet of the chuck that holds the paper strip. Once the strip is wetted by the fluid, rotation of the device will be adjusted until capillary flow stops. Wetting of the fibers will be investigated just above the front of the liquid as a function of: (i) fiber type at similar porosity, and (ii) different porosity (by variation of pre-refining the fibers) with a single fiber type constituting the paper sheets. Note, all experiments will be carried-out at a defined norm temperature of 23°C and relative humidity of 50%, respectively.

With respect to the latter, we also plan to collaborate with groups that address such dynamic wetting processes by both, experimental and theoretical means, respectively. In particular, a collaboration with Professor Uwe Thiele (Univ. of Münster, Dept. of Institute of Theoretical Physics), will add expertise on generic mesoscopic models applied to wetting of porous substrates. The latter will help to further understand and forecast drop-imbibition in paper sheets. More focused on the wetting of single fibers, we will collaborate with the group of Gambaryan-Roisman, TU Darmstadt, in order to investigate and understand three-phase contact lines on model-fibers, as well as to see, whether theoretical models developed there can be applied to the dynamic wetting of the surface of paper fibers generically studied in our project. In addition to collaboration with groups that focus on theoretically describing wetting processes on adaptive surfaces, next to our own experimental studies, we will collaborate with the groups of Prof. Butt and Dr. Berger (MPI for Polymer Research, Physics of Interfaces, Mainz). The latter are investigating wetting processes by high speed imaging of rolling droplets on highly tilted surfaces. To complement the above described analyses on wetting, reliable measurements of contact angles on paper would be highly desirable. However, the speed at which a drop is absorbed by paper generally defeats such measurements in classical contact angle measurements. We will hence provide model substrates made of paper to Prof. Butt and Dr. Berger (MPI for Polymer Research, Physics of Interfaces, Mainz), to determine advancing and receding contact angles of droplets rolling on highly tilted substrates with high speed imaging. With the high speeds, we hope to sufficiently decrease the time for absorption and to average out heterogeneities of the paper's surface to yield contact angles of water on paper.

WP2.2 Dynamic wetting of fibers – influence of pH and fiber zeta potential

Next to the influence of the fiber type and fibrillation of the paper sheet on the wetting of an aqueous solution, we will focus on the surface chemistry of the fibers. The latter will be addressed by two means. First, we will study the wetting on readily prepared paper sheets at different pH values of the solution being used, whereas in a second consecutive set of studies TEMPO-oxidized paper sheets will be set into focus. Because paper sheets carry a variable number of charges on the surface of the fibrillated fibers, and because these fibrils resemble in good approximation swellable polyelectrolyte layers, more simple model systems being can be useful to deepen our understanding of wetting processes on the fibers. To this end, collaboration with Professor Regine von Klitzing (TU Darmstadt, Department of Physics) is planned, where we will

focus on wetting on adaptive model polymer substrates, such as charged PNIPAM-based microgels at surfaces. The models used in their study are highly water swellable, as well as they contain defined amounts of charged carboxylic acids (i.e. acrylic monomers being implemented in the PNIPAM microgels). As such, they can be taken as very simple models from a chemistry point of view, for the fibrous interface in paper substrates having varying amounts of carboxylic acid functions.

WP2.3 Wetting of fibers in double layer model sheets

By generating double-layered sheets of paper where each layer contains differently modified fibers, we aim to create substrates, in which the differences with respect to their wetting, swelling and capillary-transport behavior can directly be observed in a single imaging experiment without the need for any label to differentiate them. As any fluorescent staining would essentially amount to yet another chemical modification, this approach obviates the need for additional labels to differentiate differently modified fibers.

Double layered paper sheets will be cut into appropriate size and mounted onto the spinning device. Fluid flow will be monitored as described in WP 2.1. Data acquisition is again as follows, first a drop of water (MilliQ quality) is placed at the inlet of the chuck that holds the paper strip. Once the strip is wetted by the fluid, rotation of the device will be adjusted until capillary flow stops. Wetting of the fibers will be investigated just above the front of the liquid as a function of (i) fiber type at similar porosity; here double layered sheets, where one side consist of CL and the other side consists of Euca is used in order to differentiate different wetting behavior on different fiber types. (ii) different porosity; here double layered sheets will be used, where both sides are made of identical fiber types but varying porosity (different degree of refining). All experiments will be carried-out at a defined norm temperature of 23°C and relative humidity of 50%, respectively. The scheduled experiments will yield a deeper understanding on the wetting of water on different fiber types and morphologies without the need to discriminate between the adjacent layers by specific labeling.

WP3 Swelling of the fibers

The goal of the third work package aims for a better understanding of the influence of the fiber swelling on wetting processes in the paper sheet. Again both, the influence of paper intrinsic (fiber type and degree of fibrillation), as well as paper extrinsic parameters (pH, fiber surface modification) and their impact on dynamic wetting of the fibers will be taken into focus of the studies in WP3.

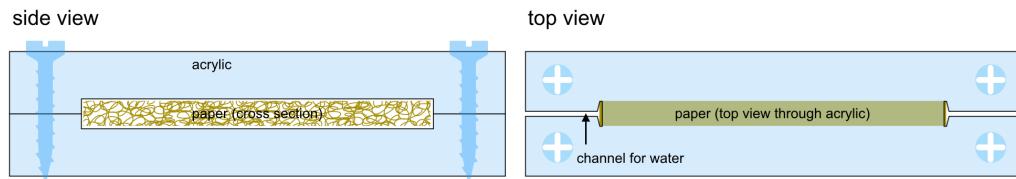
WP3.1 Swelling of fibers in single paper sheets – influence of fiber type and fiber fibrillation

In the absence of externally applied forces (WP2), wetting of paper fibers (with aqueous fluids / solutions) is inevitably coupled to a swelling of the individual fibers, i.e. their fiber walls. In the process, fibers experience an increase mainly in diameter and less in length. Similar to WP2.1 we again aim to create a counterforce to this process – here expansion rather than capillary transport – by spatially confining paper sheets, while investigating water transport within the paper. Under “ideal” conditions, water would then be unable to swell fibers but be limited to a movement within the macropores in between the fibers, i.e. the exact opposite of what is expected to happen under the conditions of strong centrifugal forces (WP2.1). As a spatial confinement around the fibers can never be ideal, the counterforce created e.g. by confining a strip of paper by clamping it within a precisely cut mold (Fig. 10), will never be complete. However, by significantly reducing imbibitional expansion, we expect the water transport to significantly differ from the spatially unconfined case. Note, measurements under unconfined condition will always serve as reference.

To achieve high enough forces for the confinement, grooved acrylic (Fig. 10), will be produced and polished to the accurately enclose a paper strip. Brightfield and fluorescence videography will then be used to follow the transport of fluid at a resolution sufficient to resolve individual paper fibers. In particular, capillary transport will be investigated as a function of: (i) fiber type at similar

porosity, and (ii) different porosity (by variation of pre-refining the fibers) with a single fiber type constituting the paper sheet. Note, the capability of the fibers to take-up water will depend on the degree of refining. All experiments will be carried-out at a defined norm temperature of 23°C and relative humidity of 50%, respectively. In order to understand the effect of confinement, in addition, the degree of swelling of single fibers will be determined from geometric characterization of the fibers in contact with water, using a microscopy fiber lab analysis.

Figure 10
Schematic view
of the grooved
acrylic for
spatially
confining paper



WP3.2 Swelling of fibers in single paper sheets – influence of fiber (surface) chemistry

In work package 3.2 we address the question, how different chemical modification with carboxylic acid functional groups will affect the fiber swelling. Experiments will be carried-out similar to WP 3.1, now with a varying zeta-potential (i.e. amount of charged carboxylics) as the major parameter to be varied. Because carboxylic groups generate strong repulsive electrostatic forces, we expect a major influence on the swelling of the fibers. As such, the capillary transport can be influenced too. Measurements will be carried out at varying pH, in order to learn about the influence of the amount of carboxylic acid groups (on a fiber) on capillary transport under spatially confined conditions.

WP3.3 Swelling of fibers in double layered paper sheets

Once measurements on single paper sheets have established, we turn our focus on double layered sheets. With respect to the latter, we will investigate “Janus-type” sheets, where individual sides of the final sheet differ with respect to paper intrinsic (fiber type and degree of fibrillation), as well as paper extrinsic parameters (pH, fiber surface modification). If, e.g. one side consists of a highly dense fiber network, i.e. very large grammages and low porosities, lower swelling capabilities due to the intrinsic confinement are to be expected. In contrast a high porosity and low grammage will result in a network where individual fibers are intrinsically less confined, and therefore may swell to a larger degree. Again, capillary imbibition is observed by means of videography, in order to learn about the influence of swelling on capillary transport in such paper substrates.

WP4 Deformation of model paper substrates

The goal of the fourth work package is to understand how wetting of fibers, fiber swelling and capillary imbibition of paper sheets impacts a dynamic geometric deformation of the complete fibrous network, and how this by itself impacts capillary flow in paper strips.

WP4.1 Deformation with single sheets

As fibers in paper are firmly coupled to one another at all fiber crossing points, their spatial expansion during imbibition will inevitably lead to deformations of the network. Using several imaging techniques (high speed videography, rapid scanning confocal microscopy, light sheet microscopy), we will investigate these dynamic changes, in order to learn, how deformations of fibers and the macro-pores in between them impact fluid flow in paper.

For videography measurements papers will be produced out of stained and unstained fibers. We will begin with a ration of 1:10 stained vs unstained fibers, with the goal to reliably single out individual fibers within the fiber network during imbibition. In later steps, other ratios may be used in dependence of a favorable image analysis. For rapid scanning confocal or light sheet microscopy, staining of a subset of fibers is not explicitly required but may prove useful for later image processing.

WP4.2 Deformation with double layered sheets – varying porosities & fiber charges

In a second part of the fourth work package, we again turn our attention to double layered sheets. Note, whereas with single sheets (WP 4.1) we expect only isotropic deformations, as long as there are no anisotropic fiber orientations in the sheets, with WP4.2 this may be completely different. Once the two different faces of the sheet consist of either different fiber types, porosities, or surface chemistries of the fibers, one may expect capillary imbibition rate to be anisotropic with respect to the differences in chemistry, and geometrical structure of both sides respectively. Capillary imbibition therefore may force the double layered paper sheet to bend anisotropically towards one side. In order to understand to which extent imbibition rate controls such anisotropic deformation, a series of investigations of such deformation-runs will be carried-out and analyzed by videographic means.

Outlook to subsequent phases of the SPP

Within phase one of the DFG-SPP our main focus centers around setting-up a measurement-platform, where wetting, fiber swelling and capillary imbibition of lab-engineered paper substrates can be investigated in detail with high spatial and temporal resolution. We intent to use very simple fluids, in particular, water of a constant pH and with no additional electrolytes added, for investigating the beforementioned phenomena. Once we have gathered a deeper understanding of the wetting, swelling and capillary imbibition of the paper fibers, it is of course interesting, how additional paper-extrinsic parameters, such as added electrolytes or mixtures of different fluids (e.g. aqueous/organic) wet the fibers, and in turn will affect fiber swelling and capillary imbibition, respectively. These studies are envisioned to be carried-out in possible upcoming phases of the SPP.

In addition, by directly recording the heat release during imbibition via infrared imaging, we aim to correlate this additional parameter in future studies with our recordings on fluid dynamics obtained in the present SPP phase. Therefore, preliminary data will already be collected in phase one of the DFG-SPP in collaboration with Prof. Samuel Schabel (PMV, TU Darmstadt) as well as Dr. Alexandros Terzis (Institute of Aerospace Thermodynamics, Universität Stuttgart). In an exemplary setting. We will test how heat release during imbibition by TEMPO oxidized (high swelling) or spatially confined (low swelling) paper differs.

Table 1: Gantt-Diagram with time-sheet of the respective work packages (WP)

2.4 Data handling

Handling and securing research data is of central concern at TU Darmstadt. Within the project research data management follows DFG Guidelines on the Handling of Research Data. In this sense, the relevant primary data identifying the key for further data analysis and the evaluated data representing relationships between the primary data are being identified. Internally, these data are maintained for at least 10 years.

Data obtained in the project are electronically saved several times and are available to the employees of the working group directly and at any time (read access). This happens because every employee has to maintain an electronic laboratory journal. This lab journal consists of a data repository, with which the relevant documents (test descriptions, spectra, data tables, image material, etc.) are synchronized against the server on the employee's work computer. The document history is automatically tracked according to the philosophy of such repositories. The server is operated at the chair and the data of the server are permanently redundantly mirrored on two hard drives. The correct and timely keeping of the electronic laboratory journal is checked by the head of department. Employees are regularly informed that only duly archived data can be used as the basis for publications and as evidence of the results achieved and as an important basis for further research.

In addition, as part of a research data management initiative of the TU Darmstadt, a university-wide, centrally managed storage solution is currently being implemented. If this is already available at the start of the project, it will be used by the project. In general, evaluated data will be published in the form of articles, dissertations and theses, using the possibility to provide sufficient data in the annexes or "Supporting Information". Wherever possible, these publications are to be made accessible via open access (gold or green), whereby the TUPrints repository of TU Darmstadt can be used. With regard to possible inventions, both project partners will consult closely and, if necessary, apply for a patent through the Technische Universität Darmstadt.

2.5 Other information

not applicable

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

not applicable

2.7 Information on scientific and financial involvement of international cooperation partners

Jean-Francis Bloch, Grenoble University of Technology, will be involved through micro-CT measurements on paper sheets for characterization of the geometric structure of the papers being prepared for wetting studies. Professor Bloch is a well-known and internationally recognized expert in paper physics with focus on understanding the physical structure-property relation of porous paper substrates.

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4 Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

Supervised by Markus Biesalski, and co-supervised by Tobias Meckel

Ph.D. student (1x TVL-13, 75%, 3 years) He/she will be responsible for carrying out the studies as part of the graduation phase (Ph.D.). As such the candidate has a strong background in chemistry and in ideal case already some background in paper chemistry and imaging. Despite carrying out the experiments, he/she is responsible also for writing reports, scientific manuscripts, as well as supervising students (HiWis), who technically support the studies in the laboratory.	145.125,- €
1 Student helper (studentische Hilfskraft) (410 €/month for 24 months) for 18 months to prepare and characterize paper sheets. The PhD student will focus the development of paper substrate preparations as well as on the development of the proposed imaging procedures. Therefore, a student helper will support the PhD student by carrying repetitive tasks. Therefore, a student helper with experience in paper chemistry and technology is required.	9.840,- €

4.1.2 Direct Project Costs

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

Consumables

Chemicals for fiber surface modification, and organic synthesis	8.000 €
Specialities (mainly fluorescent dyes)	6.000 €
Pulp, additives for paper making and wax printing / embossing	5.000 €
Paper Analytics (Consumables for Zeta Potential Measurements, etc.)	5.000 €
Microscopy (Consumables for Microscopy measurements, etc.)	6.000 €
Sum consumables for 3 years	30.000 €

Equipment below 10.000 €

<i>Spinning device setup (self-made) and swelling device</i> - Chip-on-Board (COP) LED Array with monostable multivibrator - Hall Effect Sensor, STM32 controller - Stable motor to minimize vibrations - Solid frame and housing to minimize vibrations	4.500
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4.1.2.2 Travel Expenses

Expenses are needed for the following scheduled travels: - SPP workshops (1 st and 2 nd year, 4 days, both PIs and Ph.D. students) - Advanced SPP school (1 st year, 5 days) - Ph.D. candidate workshop (2 nd year, 4 days) - International (SPP) conference (3 rd year, 5 days) - individual travels 2x per year to partners in Mainz and Münster - participation in Paper Physics conference FRC 2021 in Cambridge	9.000 €
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4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

Prof. Bloch is already enrolled as a Mercator fellow in a parallel DFG funded project (DFG PAK962/1). Hence, during his stay at TU Darmstadt, there will be plenty of time and possibilities to collaborate. No additional funds are requested here.

4.1.2.4 Expenses for Laboratory Animals

not applicable

4.1.2.5 Other Costs

Project specific costs for NMR, SEM and XPS according to DFG-regulations	3.000 €
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4.1.2.6 Project-related publication expenses

Gold Open Access (3 x 750 € in year 2&3 (i.e. a total of 3 publications) will be needed for Gold Open Access fees	2.250 €
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4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

Highspeed Camera pco.1200 hs <i>In order to record the paper strips on the spinning device (Figure 5, WP 2.1) with minimal motion blur, very short exposure times are required. With an exposure time of 50 ns, as provided by the pco.1200 hs highspeed camera, azimuthal displacement of around 2 μm would be achieved on our setup. This low motion blur is required to image fluid transport on and between single paper fibers.</i>	21.400 €
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4.1.3.2 Major Instrumentation exceeding Euro 50,000

not applicable

4.2 Module Temporary Position for Principle Investigator

not applicable

4.3 Module Replacement Funding

not applicable

4.4 Module Temporary Clinician Substitute

not applicable

4.5 Module Mercator Fellows

not applicable

4.6 Module Workshop Funding

not applicable

4.7 Module Public Relations Funding

not applicable

5 Project requirements

5.1 Employment status information

Prof. Dr. Biesalski, Markus, W3 Professor, tenured.

PD Dr. Meckel, Tobias, fixed-term contract until 31.12.2020
(Funding source: base funds and industry funds of Markus Biesalski)

In case of funding of the proposed project within the SPP, Professor Biesalski will secure further funding of Dr. Meckel until the end of the SPP period in 2022)

5.2 First-time proposal data

not applicable

5.3 Composition of the project group

1. Prof. Dr. Markus Biesalski will be responsible for the project and the scientific supervision of the Ph.D. candidate.
2. PD Dr. Meckel will be co-responsible for the project and responsible for the scientific supervision of the Ph.D. candidate (focus on imaging).
3. Dipl. Ing. Heike Herbert (permanent contract on TU base funds) is responsible for technical support with focus on chemical bulk analytics and standard paper characterization in the group of Professor Biesalski. She will in part support the project.
4. Martina Ewald (permanent contract on TU base funds) is responsible for technical support with focus on paper production and chemical synthesis in the group of Professor Biesalski. She will in part support the project.

5.4 Cooperation with other researchers

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

1. Professor Dr. Uwe Thiele, Physics Department, University of Münster;
Generic mesoscopic models applied to wetting of porous paper substrates. Understand and forecast drop-imbibition in paper sheets.
2. Professor Dr. Regine von Klitzing, Department of Physics, TU Darmstadt;
Model systems based on polymeric microgels to understand the influence of pH and charged functions on wetting and swelling.
3. PD Dr. Tatjana Gmabaryan-Roisman, Department of Mechanical Engineering, TU Darmstadt;
Investigation of three-phase contact lines on model-fibers, and application of models to the dynamic wetting of the surface of paper fibers.
4. Professor Dr. Hans-Jürgen Butt and Dr. Rüdiger Berger, MPI for Polymer Research Mainz;
Investigation of wetting processes by high speed imaging of rolling droplets on highly tilted paper substrates.
5. PD Dr. Anita Roth-Nebelsick, Staatliches Museum für Naturkunde Stuttgart
Informative exchange on water transport in cell walls of intact plants. In addition, we attempt to investigate the dynamics of fluid transport as well as the in-situ structure of pits in plant xylem with high temporal and spatial resolution using super-resolution as well as high-speed fluorescence microscopy.

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

- Prof. Dr. Robert Berger, Universität Marburg
- Prof. Jean-Francis Bloch, UT Grenoble, Frankreich
- Prof. Andreas Büter, Hochschule Darmstadt

- Dr. Kevin Land, CSIR, Pretoria, Südafrika
- Prof. Dr. Thaddeus Maloney, Aalto University, Finnland
- Prof. Dr. Frank Miletzky, Papiertechnische Stiftung Heidenau und TU Dresden
- Prof. Dr. Jürgen Rühe, Universität Freiburg
- Prof. Dr. Kai Zhang, Universität Göttingen
- Prof. Dr. Stefan Kleemann, Hochschule München
- Prof. Martin Thuo, Iowa State University, USA
- Prof. Norma Alcantar, Univ South Florida Tampa, USA
- Prof. Dr. Ulrich Hirn, TU Graz
- Prof. Dr. Marie Laborie, Univ Freiburg

5.5 Scientific equipment

- | | |
|--|--|
| <ul style="list-style-type: none"> • Leica Confocal Microscope • Olympus fluorescent microscope • Rapid Koethen Sheet Former • SEC • HPLC • SUMET Coater • Data Physics Contact Angle Instrument including 2 high speed camera systems • Zetapotential • Size press and drum dryer • Inkjet printer & Wax printer • Polyelektrolyte-Titration | <ul style="list-style-type: none"> • Dry-weight balance • Zwick Tensile Measurement • Norm climate laboratory • Wet chemistry labs • Surface analytics laboratory • Cotact Angle Data Phasics incl. 2 High Speed Camera Systems • Size Press & Drum Dryer • Dry-weight balance • Speed-Mixer • Titrator • UV-Illumination Chambers • Freeze-Drying |
|--|--|

Note, a comprehensive list of all equipment in the working group of Professor Biesalski can be found on the webpages of the group.

Available at TU Darmstadt (on demand and by extra billing)

- XRD
- XPS
- SEM/EDX
- HRTEM, EELS
- Solid-state NMR
- Elementaranalyse CNHO

5.6 Project-relevant cooperation with commercial enterprises

not applicable

5.7 Project-relevant participation in commercial enterprises

not applicable

6 Additional information

We do not receive funding and we did not request funding for any project related to imbibition by paper in combination with the here described repression of individual contributions to the process anywhere else. In the event that we submit such a request, we will inform the Deutsche Forschungsgemeinschaft immediately. In submitting a proposal for a research grant to the DFG, we agree to adhere to the DFG's rules of good scientific practice.

Darmstadt, den 15.10.2018

Prof. Dr. Markus Biesalski

Darmstadt, den 15.10.2018

PD Dr. Tobias Meckel