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Bubble Attachment to Cellulose and Silica Surfaces of Varied Surface Energies: Wetting Transition and Implications in Foam Forming

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ABSTRACT: To better understand the complex system of wet foams in the presence of cellulosic fibers, we investigate bubble–surface interactions by following the effects of surface hydrophobicity and surface tension on the contact angle of captive bubbles. Bubbles are brought into contact with model silica and cellulose surfaces immersed in solutions of a foaming surfactant (sodium dodecyl sulfate) of different concentrations. It is observed that bubble attachment is controlled by surface wetting, but a significant scatter in the behavior occurs near the transition from partial to complete wetting. For chemically homogeneous silica surfaces, this transition during bubble attachment is described by the balance between the energy changes of the immersed surface and the frictional surface tension of the moving three-phase contact line. The situation is more complex with chemically heterogeneous, hydrophobic trimethylsilyl cellulose (TMSC). TMSC regeneration, which yields hydrophilic cellulose, causes a dramatic drop in the bubble contact angle. Moreover, a high interfacial tension is required to overcome the friction caused by microscopic (hydrophilic) pinning sites of the three-phase contact line during bubble attachment. A simple theoretical framework is introduced to explain our experimental observations.

INTRODUCTION

Cellulosic microfibrils are versatile biobased materials possessing high strength and relatively low density. They are the reinforcing structural component of plant cell walls, making cellulose the most abundant biomolecule in the biosphere. The use of cellulose fibers in materials such as paper and board makes them easily recyclable and biodegradable. Demand for greener materials is growing fast, and cellulose could be one potential option. Cellulose fibers could be applied, for example, in high-performance materials and products such as soft packaging, air filters, and substrates for biocatalytic conversion.

Foam forming of fibers into paper webs and textile fabrics is a relatively new and versatile modification of papermaking technology. It can be used to produce materials from thick, porous, and lightweight structures to thin fabrics and stratified materials (Figure 1b). In foam forming, fibers are mixed with water and surfactants, and shear forces are applied to create wet foam (Figure 1a). The wet foam is guided onto a wire, and the liquid in the foam is removed by vacuum drainage and drying with heat, leaving a self-standing dry fiber structure. As this technology is relatively new, research has focused on a better understanding of the fundamentals of the wet fiber foam system (drainage rate, bubble size distribution, coarsening rate) and its effects on dry material properties.

Previous studies have shown that even though bubbles do not form clear three-phase contact with fiber surfaces, they are often found weakly attached to the fibers (Figure 1c). Bubbles and fibers both carry a negative charge in aqueous solutions, meaning that the net interaction should be repulsive. Flotation deinking studies have shown that the removal of fibers with froth is mostly dominated by physical entrapment of fibers, and actual bubble attachment to fibers rarely takes place. However, many of the results have been controversial, and the contributions of different forces in bubble–fiber interactions are still unclear.

Bubble attachment and detachment on (from) solid mineral particles are important for the recovery of collected minerals in froth flotation, and the mechanisms underlying bubble–particle interactions have been studied comprehensively. The stability of the wetting film between bubbles and particles dictates whether the bubble forms a three-phase contact with

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the surface. This stability depends greatly on the particle hydrophobicity, charge, and surface tension. In froth flotation, also the kinetics of bubble collision with mineral particles is highly important and usually studied using simple bubble–particle collision systems. The collision kinetics has been studied for several mineral surfaces, such as mica, quartz, Teflon, graphite, and molybdenite. However, there are few studies in which bubble interaction with biopolymers has been addressed.

In general, bubbles readily form a three-phase contact with hydrophobic particles but repel hydrophilic particles, and adsorption of surfactants and polymers can fully reverse this interaction. Therefore, it is also important to study the connection between the bubble contact angle and surface tension of the system and model these phenomena. This can be done using the well-defined theory of wetting and spreading. In the out-of-equilibrium situation, the dynamic contact angle generally depends on physical scale due to large-scale hydrodynamics and microscopic molecular effects. Moreover, impurities, surface roughness, or chemical surface heterogeneity may prevent reaching of the equilibrium state.

Danov et al. studied the adhesion of bubbles on solid surfaces by capillary meniscus dynamometry. They measured the maximal pulling force required to release a bubble from a surface and described it in terms of attractive transversal tension and repulsive disjoining pressure. We apply a similar captive bubble method to smooth thin films of regenerated cellulose and modified silica of different hydrophobicity spin-coated on silica substrates. Regenerated cellulose is a so-called “man-made” cellulose that is produced by converting natural cellulose into a soluble derivative (here trimethylsilyl cellulose, TMSC) and then regenerating it back to cellulose. Model surfaces were immersed in anionic surfactant (sodium dodecyl sulfate, SDS) solutions of different concentrations. Our choice to use SDS stems from the fact that it is a typical reference in the literature, but most importantly, it is commonly used for foam forming with wood fibers. SDS adsorption on the model surfaces and its possible effect on surface wetting were determined using the quartz crystal microbalance with dissipation (QCM-D) technique. The results are interpreted in terms of calculated changes in interfacial energy during bubble attachment. This study, which simplifies the bubble–surface systems, sets a basis for more complex, future exploration of the connections between the properties of wet foams and dry fiber networks.

### Experimental Section

An overview of the experimental setup, including the prepared model surfaces, test solutions, and measurement methods, is shown in Table 1.

#### Materials

All reagents used in the experiments were analytical grade. Anionic surfactant sodium dodecyl sulfate (SDS, purity ≥99%) was purchased from Sigma-Aldrich (Germany) and was used without further purification. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Merk (Germany). Ethanol (EtOH, AA-grade) was purchased from Alfa Aesar (Finland), chlorotrimethylsilane (CTMS) from Sigma-Aldrich (Germany), xylene from Prolabo (France), and toluene from VWR International (France). Diiodomethane (DIM) was obtained from Sigma-Aldrich (India), formamide from J. T. Baker (Holland), and ethylene glycol from Fluka. Water used in the experiments was Milli-Q purified.

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>Surface Code</th>
<th>Contact Angle (θD)</th>
<th>RMS (nm)</th>
<th>Surface Free Energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic surfaces</td>
<td>Hydrophilic silica</td>
<td>Si–OH</td>
<td>5° ± 4°</td>
<td>64.6</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>Si–CellOH</td>
<td>25° ± 5°</td>
<td>60.2</td>
</tr>
<tr>
<td>Hydrophobic surfaces</td>
<td>Hydrophobic silica</td>
<td>Si–CH₃</td>
<td>100° ± 7°</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>TMSC</td>
<td>Si–TMSC</td>
<td>93° ± 1°</td>
<td>21.4°</td>
</tr>
<tr>
<td>Test solutions</td>
<td>SDS at concentrations of 0–8.3 mM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SDS in 0.01 M NaCl at concentrations of 0–8.3 mM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurements</td>
<td>Captive Bubble</td>
<td>QCM-D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Characterization</td>
<td>Sessile Drop</td>
<td>Surface Free Energy</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“TMSC stands for trimethylsilyl cellulose and CellOH for cellulose. RMS values were analyzed from AFM images shown in Figure S3 (area 5 × 5 μm²). Surface free energy of pure Si–TMSC was not measured, but a value of 21.4 mN/m has been reported in the literature.”

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Trimethylsilyl Cellulose (TMSC). TMSC was synthesized from microgranular cellulose by dissolving cellulose in lithium chloride in dimethylacetamide according to the procedure described in the literature. The clear solution was then heated to 80 °C followed by addition of hexamethyldisilazane (HDMS) in nitrogen atmosphere. In the reaction, HDMS substitutes the −OH groups on cellulose and forms TMSC that can easily be regenerated back to cellulose with HCl (Scheme 1). The solution was cooled, and TMSC was crystallized. The TMSC was purified by dissolving in tetrahydrofuran and recrystallizing in methanol followed by filtration, washing several times with methanol, and drying in a desiccator. A degree of substitution (DS) of 2.5 was determined using liquid-state NMR (Bruker Avance III 500). All chemicals were purchased from Sigma-Aldrich, Germany.

Cellulose-Coated Si-Wafers (Si–CellOH). Hydrophobic cellulose and regenerated cellulose model surfaces for the captive bubble experiments were prepared according to a modified procedure previously described in the literature. The model surfaces used in the captive bubble experiments were silicon wafers (Si-wafers, Okmetic, Espoo, Finland). The Si-wafers were first cleaned with a UV- ozone cleaner (Procleaner, BioForce Nanosciences, USA) for 10 min. Then, 3−4 drops of toluene was pipetted onto the wafer and spun for 30 s at 4000 rpm (WS-400BZ-ENPP/Lite, Laurell Technologies, USA). Hydrophobic cellulose surfaces were prepared by pipetting 3−4 drops of TMSC solution (10 g/L in toluene) onto the wafer and spinning for 1 min at 4000 rpm. The wafers were then dried in an oven at 60 °C for 10 min. The TMSC was regenerated back to cellulose by placing the TMSC-coated plates under HCl vapor in a desiccator for 7 min (Scheme 1). The HCl vapor was created by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) in a desiccator for 7 min (Scheme 1). The HCl vapor was created by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) and sealing the lid. Partial regeneration of cellulose can be achieved by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) in a desiccator for 7 min (Scheme 1). The HCl vapor was created by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) and sealing the lid. Partial regeneration of cellulose can be achieved by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) and sealing the lid. Partial regeneration of cellulose can be achieved by placing 200 mL of HCl (3.3 M) into the desiccator (size 200 DN) and sealing the lid.

Hydrophilic and Hydrophobic Modified Si-Wafers (Si–OH and Si–CH2). Surface modification of the Si-wafers was performed according to a modified procedure previously described in the literature. First, the Si-wafers (10 × 10 mm) were cleaned with UV-light for 10 min. The Si-wafers were then hydrophilized by immersion in 2.5 M NaOH for 15 min. The NaOH treatment creates hydroxyl groups on the silica surface, making the surface highly hydrophilic (hydrophilic Si–OH). The slides were then rinsed thoroughly with water and dried with nitrogen gas. The wafers were kept in EtOH until use to avoid contamination.

Hydrophobization was conducted by treating the hydrophilized Si-wafers with a solution of 400 μL of CTMS in 10 mL of xylene overnight. CTMS treatment replaces the hydroxyl groups with dimethylsilyl groups on the silica surface, creating a hydrophobic surface (hydrophobic Si–CH3). After the treatment, the slides were rinsed with xylene and dried with nitrogen gas.

Hydrophilic and Hydrophobic Modified QCM-D SiO2 Crystals. These crystals for the SDS adsorption experiments were prepared in a similar way to the Si-wafers. The quartz cuvette and the hooked needle were carefully washed prior to and after every measurement using Deconex and EtOH and then rinsed with water. The experiments were carried out in a controlled atmosphere of 23 °C and 50% humidity.

Standard deviations (SD) of θB were approximately 6° with pure SDS and 10° with SDS and NaCl addition. The rather large SD is a reported drawback of the captive bubble method. In this study, the needle was retracted and detached from the bubble, which creates a pulling force and stretching of the bubble before detachment. In addition, the needle position in relation to the bubble during attachment contributes to the recorded values, and if the needle is off from the center line of the bubble the contact angles of different sides of the bubble will be different. These factors play a more important role when the surface tension is low. However, the relatively large SD did not hinder the interpretation of the results, as clear trends were observed.

Determination of Contact Angle and Surface Free Energy Using the Sessile Drop Method. An optical Theta tensiometer (Attension, Biolin Scientific, Espoo, Finland) and the sessile drop method were used to measure the contact angle and surface free energy of the modified surfaces. The unit includes a camera and lenses, a light source, and a sample stage. In the sessile drop measurement, a drop (4 μL) of liquid is placed onto a surface, and the shape of the liquid drop is recorded. The droplet contact angle (θL) is defined by the surface and the drop tangent. Under steady state, θ describes the surface wetting by the liquid according to Young’s equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

where $\gamma_{SV}$ is the surface free energy of the solid, $\gamma_{SL}$ is the solid−liquid surface energy, $\gamma_{LV}$ is the liquid surface tension, and $\theta$ is the measured contact angle of the drop. Surface free energy calculations of the model surfaces were carried out by measuring the contact angles with four different liquids: Milli-Q water, D.I. water, formamide, and ethylene glycol. Each contact angle value was the average of three measurements per surface. The experiments were carried out in a

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Figure 2. (a) Captive bubble method for determining the bubble contact angle (θB) against a solid surface: quartz cuvette with solution, hooked needle, model surface, and air bubble. (b) The contact angle is recorded from the outer edge of the bubble cross section.
controlled atmosphere of 23 °C and 50% humidity. Surface free energy was calculated using the OWRK/Fowkes method, which incorporates the contribution of polar $\gamma_p$ and dispersive $\gamma_d$ components in the total $\gamma$:

$$\gamma = \gamma_S + \gamma_L - 2\sqrt{\gamma_S\gamma_L} - 2\sqrt{\gamma_p\gamma_d}$$

When combined with Young’s equation (eq 1), eq 2 can be written as

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S\gamma_L} + 2\sqrt{\gamma_p\gamma_d}$$

The components $\gamma_L$, $\gamma_S$, and $\gamma_d$ are unknown. Thus, at least two liquids with polar and dispersive component need to be used for the calculations. A detailed description of the theory can be found elsewhere.56

Surface Morphology and Roughness. An atomic force microscope (AFM, Analys instruments, afm+) was used to determine the morphology and roughness of the model surfaces. Silicon cantilevers (AppNano, ACTA-10, tip size <10 nm) were used in tapping mode for scanning with a resonance frequency of 200–400 kHz. Measurements were performed in air and at room temperature. Analysis studio software 3.11 was used to calculate surface roughness variation and root means square (RMS).

SDS Adsorption Isotherms. A quartz crystal microbalance with dissipation (QCM-D, Q-sense, Biolin Scientific, Espoo, Finland) was used to determine SDS adsorption on the modified QCM-D SiO$_2$ crystals, including hydrophobic and hydrophilic silica, TMSC, and cellulose. SDS concentrations of 0.7, 7.0, and 70.0 mM were tested. They correspond to values clearly below the critical micelle concentration (CMC) (ca. 8 mM, see Figure S1), close to CMC, and well above CMC. The crystals were first rinsed with water for 500 s as a baseline before injecting the SDS solution into the cell at a flow rate of 0.1 mL/min. The change in oscillation frequency ($\Delta f$) and dissipation ($\Delta D$) caused by SDS adsorption was recorded for 30 min.

In the measurement, a reduction in frequency indicates adsorption, and increased dissipation relates to the structural changes of the adsorbed mass, such as the softening and thickening of adsorbed layers.

The Sauerbrey equation$^{57,58}$ was used as an approximation to determine the apparent adsorbed mass ($\Delta m$) and apparent height ($h$) of the adsorbed layers according to eqs 4–5:

$$\Delta m = -C\frac{\Delta f}{n}$$

$$h = \frac{\Delta m}{\rho}$$

where $C$ is a constant 17.7 ng/Hz$\cdot$cm$^2$, $\Delta f$ is the frequency change, $n$ is the overtone of the oscillations, and $\rho$ is the density of the substance. For SDS, a density value of 1.08 g/cm$^3$ was used in the calculations.$^{59}$ We note that the Sauerbrey equation is more accurate for rigid thin films with low amounts of coordinated water in the structure and low viscoelasticity. Usually, if the dissipation is large compared to the frequency change, the film thickness needs to be determined by modeling; this was not conducted within this study, and the data thus need to be compared on a relative basis.

**RESULTS AND DISCUSSION**

Model Surface Characteristics and SDS Adsorption Isotherms. The surface hydrophobicity, surface free energies, and roughness of the surfaces are listed in Table 1, and AFM images are shown in Figure S3. This includes similar energy values for both hydrophobic surfaces (silica and TMSC) and also for both hydrophilic surfaces (silica and cellulose). Cellulose had a higher dispersive component than hydrophilic silica due to the amphiphilic nature of the cellulose.
molecule. In agreement with earlier measurements, we found a similar difference between dispersive components of hydrophilic and hydrophobic silica. The roughness variation of the surfaces was small, and all other surfaces except the partially desilylated TMSC surface can be considered to be smooth. The RMS roughness was 18.4 nm for the TMSC surface with \( \Theta_D \approx 75^\circ \), and the formation of spherical aggregates of \( \sim 200 \) nm diameter was observed. The effect of roughness is discussed more closely in the section "Pinning of the Three-Phase Contact Line during Bubble Attachment to TMSC".

SDS adsorption on the model surfaces was studied to understand its possible contribution to the bubble–surface interaction. The SDS isotherms for adsorption on the hydrophobic model surfaces (Si–CH\(_3\) and TMSC) are shown in Figure 3, and the calculated changes in mass and height (eqs 4 and 5) of the adsorbed layers are presented in Table S1. With Si–CH\(_3\) at a concentration below the CMC, the changes in frequency and dissipation (Figure 3a, b) were small but detectable. Close to the CMC, the larger SDS adsorption affected both frequency and dissipation, even though the above frequency change was rather small (\( \Delta f \approx -4 \) Hz) when compared to the effect of larger molecules. Above the CMC, the bound water in absorbing SDS micelles caused a much larger increase in dissipation. The stabilization of SDS adsorption was reached within 5 min.

SDS adsorption on the hydrophobic silica surface can be explained by the hydrophobic interaction between the surface and hydrophobic tail of SDS. Figures 3a and 3b agree with previous SDS adsorption studies on other hydrophobic surfaces, where SDS adsorbs as single monomers below 2 mM concentration and as hemimicelles at higher concentrations until the surface is saturated at 7 mM. Thus, the high dissipation measured at 70 mM of SDS indicates that there is micelle formation on the surface but also water coordination on the adsorbed layer.

SDS adsorption on TMSC (Figure 3c, d) differed greatly from the adsorption on hydrophobic silica. At a concentration below the CMC, the SDS adsorption was first seen as a clear decrease in frequency and as an increase in dissipation as expected. However, the subsequent transients could result from slowly diffusing and organizing SDS molecules within the chemically heterogeneous TMSC surface. The mass loss after 800–900 s (\( \Delta f \) increased) suggests that SDS replaced bound water at the surface, where dissipation \( \Delta D \) was still increasing. In other words, a low amount of SDS monomers in the solution seems to cause competitive adsorption of SDS and water molecules on the surface, seen as a simultaneous increase in both frequency and dissipation. Steady state was not reached within the measurement time, which could require several days in this kind of unstable system.

Close to the CMC, SDS adsorption on TMSC was much more stable, suggesting a fairly uniform adsorbed layer, likely comprised of SDS monomers. However, above the CMC, a rapid transient drop in frequency was followed by an increase during the remaining monitoring time. At the same time, the dissipation \( \Delta D \) approached a steady value. This suggests that the SDS micelles released or replaced bound water after adsorption similarly to the earlier case of low SDS concentration. TMSC is a chemically heterogeneous surface with a measured high DS value of 2.5. Thus, even though the surface is mainly hydrophobic (\( \Theta_D \approx 93^\circ \)), there are still free hydroxyl groups that can bind water. This feature is related to the long time (24 h) required for stabilization of the frequency baseline before QCM-D data acquisition.

The SDS isotherms for adsorption on the hydrophilic model surfaces (Si–OH and cellulose) are shown in Figure S4, and the calculated changes in mass and height (eqs 4 and 5) of the adsorbed layers are presented in Table S1. At a concentration below the CMC, the changes in frequency and dissipation were slightly lower than with hydrophobic silica but still detectable. Close to the CMC, SDS adsorption on cellulose was similar to that on hydrophobic silica. In contrast, the adsorption on hydrophilic silica was minor at equal SDS concentrations. Above the CMC, SDS adsorption on both hydrophilic surfaces with a large increase in dissipation. Steady state was reached within 5 min for cellulose, whereas for hydrophilic silica it was reached after 30 min.

Electrostatic repulsion explains the negligible adsorption of negatively charged SDS on hydrophilic silica below the CMC (Figure S4). Increased SDS adsorption with an increase in SDS concentration on a hydrophilic surface could be caused by electrostatic screening of the charges in the presence of counterions (Na\(^+\)) in solution. However, most of the mass gains are explained by the hydration water, which correlated with the observed high dissipation.

**Electrostatic Bubble Repulsion for Smooth Hydrophilic Surfaces.** Bubble interaction with smooth hydrophilic surfaces was investigated using the captive bubble method. The bubbles did not attach to hydrophilic silica or cellulose immersed in water or in SDS solution; i.e., the wetting film between the bubble and hydrophilic surface remained stable (Figure 4). Moreover, the cellulose surfaces were measured both after 10 min and overnight immersion in water. We note that the prolonged immersion did not influence the observed behavior.

![Figure 4](https://dx.doi.org/10.1021/acs.langmuir.0c00682)

Bubble surfaces are negatively charged in water and in SDS solution, and therefore the bubbles strongly repel the fully wetted hydrophilic surface. Despite the amphiphilicity of cellulose, the hydrophilic character dominated the bubble–surface interaction. The presence of hydrophobic domains was indicated by the QCM-D measurements (Figure S4a-d).
showing SDS adsorption on the regenerated cellulose near the CMC. SDS penetrates into the cellulose film and turns it even more hydrophilic as the hydrophobic domains are filled with SDS.73

Critical Surface Tension for Bubble Attachment on Smooth Hydrophobic Surfaces. The wetting film stability and bubble attachment time on smooth hydrophobic silica and TMSC were studied more closely using the captive bubble method (Figures 4 and 5). The aim of these experiments was to determine the critical surface tension for wetting transition by changing the SDS concentration. The effect of the electrolyte was also determined for hydrophobic silica. The addition of 0.01 M NaCl was chosen as it is known to have a moderate effect on surface tension when added with SDS (Figure S1).74 This detectable but not too strong effect enables the production of a controlled surface tension isotherm.63 Theoretical models were used to compare and explain the observed results. We first discuss the results for hydrophobic silica and then for TMSC surfaces, pointing out the mechanisms that explain the observed behaviors.

Bubble Interaction with Hydrophobic Silica, Si–CH3. Figure 5 summarizes the changes in bubble contact angle $\theta_B$ and attachment time as a function of surface tension. The addition of SDS decreased both $\gamma$ and $\theta_B$, while the bubble attachment time increased. Possible scenarios for SDS adsorption on the hydrophobic surface and at the air–liquid interface affecting bubble–surface interaction are presented in Figure 6. At a SDS concentration of 3.5 mM, bubble attachment probability decreased significantly. At this concentration, the air–water interface is almost fully covered with SDS (Figure S2), and hemimicelles form on the Si–CH3 surface (see Figure 6b). No bubble attachment occurred beyond 6.9 mM. This level is roughly the same as the threshold for micelle formation in the solution (see Figure 6c).63,66 The critical surface tension value of $\gamma = 37$ mN/m is not directly explained by the equilibrium spreading coefficient derived from eq 1 but also requires consideration of the friction of the moving contact line, as explained in the next section.
The presence of NaCl (0.01 M) slightly increased the bubble attachment time but did not have a significant effect on $\theta_B$ when compared to a pure SDS solution of similar surface tension. The bubbles no longer attached to the surface when the surface tension was about 40 mN/m. However, the SDS concentration was only 2.8 mM at this point. Both surface tension and CMC decreased with added NaCl (Figure S1) due to the electrostatic screening of negative charges by the positive counterions ($\text{Na}^+$). Essentially, more SDS molecules were able to pack at the air–water interfaces.74

Theoretical Considerations on Wetting Transition on Si–CH$_3$. Here we estimate the energy changes of the immersed hydrophobic silica surface at different surfactant concentrations and compare these to the measured surface free energy of 22.0 mN/m (solid–vapor surface energy, $\gamma_{SV}$) (Table 1). During bubble attachment a new solid–vapor interface is formed, and therefore, the bubble contact angle $\theta_B$ effectively corresponds to the receding contact angle of a drop on the chemically homogeneous surface. A force balance along the solid homogeneous surface leads in this dynamic case to the following equation:75

$$2\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos(\theta_B)$$  (6)

where $\gamma_{SV}$ is the surface free energy of the solid, $\gamma_{SL}$ is the solid–liquid surface energy, $\gamma_{LV}$ is the liquid surface tension, and $\theta_B$ is the measured contact angle of the bubble. The average frictional tension of the moving three-phase contact line during attachment leads to an extra $\gamma_{SV}$ factor on the left-hand side of the equation (compare with eq 1). The somewhat phenomenological eq 6 has earlier been used to explain, surprisingly well, the contact angle hysteresis,76 where nonequilibrium phenomena, like friction, play an important role. In particular, the precursor film near a moving three-phase contact does not seem to alter the above average friction, although this term neglects all nanoscale features of the problem. We apply a similar approach to an attached bubble, omitting finer details arising from a possible thin liquid film between the bubble and the solid surface.43

Using the measured values of surface free energy, surface tension, and $\theta_B$, eq 6 provide us with an estimate of the effective value of $\gamma_{SL}$. The effective $\gamma_{SL}$ of the immersed surface in water is 29.7 mN/m. Figure 7 shows how $\gamma_{SL}$ approaches the surface free energy of 22.0 mN/m near the wetting transition for the pure SDS solution. With added NaCl, there is more scatter in the data near the transition, but the overall trend is similar. The critical value of the surface tension $\gamma \approx 40$ mN/m suggests that the value of the bubble contact angle $\theta_B$ (solved from eq 6) is $\arccos(22/40)$ radians, i.e., 57° at the first-order transition. This estimate agrees well with the result of the captive bubble measurement (Figure 5).

Changes in interfacial and surface energies caused by the bubble attachment and its effect on the total interface energy of the system ($E_{tot}$) can be considered using eq 6 together with simple bubble geometry (see the Supporting Information). The calculated (free) bubble interface energy in water was relatively high, ca. 900 nJ. The total interface energy of the system ($E_{tot}$) is reduced when the bubble attaches to the surface.77 In water, the energy reduction was 208 nJ (Figure S7), and the addition of SDS decreased this value. A steep decrease in $\Delta E_{tot}$ occurred after an SDS concentration of 3.5 mM ($\gamma = 45$ mN/m), which is the concentration where the air–water interface is almost fully covered with SDS, and bubble behavior shifts from clear attachment to more scattered. After $\Delta E_{tot}$ of 45 nJ at $\gamma = 40$ mN/m (close to the CMC of SDS), bubble attachment no longer occurred, and the system reached its energy minimum. No electrostatic forces were considered in these calculations.

Bubble Interaction with Hydrophobic TMSC. The bubble interaction with the hydrophobic TMSC surface in water was similar to that with hydrophobic silica (Figure 5). Using eq 1 and the estimates $\theta_B = 96.8^\circ$ and $\gamma_{SL} = 21.38$ mN/m for the pure TMSC surface,49 we obtain the estimate of $\gamma_{SL} = 30$ mN/m for the solid–liquid surface energy in water. Taking into account the friction of the moving three-phase contact line, these numbers together with eq 6 lead to a predicted $\theta_B \approx 80^\circ$ for an attaching bubble in pure water. For the TMSC surface, the measured contact angle 85° was thus not only close to the predicted value but also very near the measured angle, 79°, for the hydrophobic silica. This is explained by the similar hydrophobicity and dispersive and polar components of TMSC and hydrophobic silica surfaces (see Table 1).

However, contrary to measurements for hydrophobic silica, the addition of SDS had a significant effect on the bubble behavior for TMSC already at very low concentration (Figure 5). At a SDS concentration of 1.0 mM ($\gamma = 64 \pm 2$ mN/m), $\theta_B$ was already rather low, 33 ± 6° (compare with 72° for hydrophobic silica at equal concentration). Due to this low value, it was difficult to clearly observe the rupture of the wetting film. With increased SDS concentration, 2.4 mM, the wetting film remained stable, with no signs of bubble attachment. The critical value of the surface tension was in the range of 50–60 mN/m for the pure SDS solution. This critical value was considerably higher for the TMSC surface than for hydrophobic silica.

A different response to changes in SDS concentration was expected due to the more complex SDS absorption (Figure 3). The above large decay in $\theta_B$ with added SDS and the much higher critical surface tension for amphiphilic TMSC can be explained by a larger frictional tension of the moving contact line on the TMSC surface. The higher frictional tension balances the larger surface tension in an equation similar to eq 6. A more detailed quantitative analysis of this issue is presented in the next section.

Critical Hydrophobicity of Cellulose for Bubble Attachment. Critical hydrophobicity of cellulose surfaces

{fig:7}

Figure 7. Solid–liquid surface energy ($\gamma_{SL}$) of the immersed Si–CH$_3$ surface as a function of surface tension ($\gamma$) estimated based on eq 6. $\gamma_{SL}$ approaches the measured surface free energy ($\gamma_{SV}$) of 22.0 mN/m (dashed line) near the transition for both pure SDS solution (filled dots) and the solution with added NaCl (open dots).
for bubble attachment was determined experimentally using partially regenerated TMSC surfaces with θD of ca. 85°, 75°, 65°, 60°, 50°, and 35°. These values should be compared with θD of 93° for the pure TMSC surface. Fully regenerated cellulose (all methylsilyl groups desilylated to −OH groups) had θD of 35°. Surface contact angles in water and in SDS solution (1.0 mM) were also measured with the captive bubble (θB). The results in Figure 8 show a rather large difference between θB and θD for partially regenerated TMSC surfaces. The 8° difference for pure TMSC in water increased to almost 40° for regenerated TMSC when θD was in the range of 70–85°. The presence of SDS (1.0 mM) increased the difference between θB and θD, up to 50–60° for both partially regenerated and also pure TMSC surfaces. The differences between θB and θD can be explained by a contact angle hysteresis for a chemically heterogeneous surface with pinning sites for the three-phase contact line (see the section Pinning of the Three-Phase Contact Line during Bubble Attachment to TMSC). Bubbles did not attach to the surface when θD was 60–65° or below. However, even in this region, bubbles elongated during the retraction, indicating some adhesion to the surface. Further discussion on this phenomenon is presented in the Supporting Information (Figure S5). In this study, only fully attached bubbles were considered in the theoretical calculations.

Pinning of the Three-Phase Contact Line during Bubble Attachment to TMSC. Gradual regeneration of the TMCS surface creates an increasing number of cellulose −OH groups, which are a source of chemical heterogeneity of the surface. In other words, partial regeneration creates a hydrophobic (1) surface with hydrophilic (2) microscopic domains, as depicted in Figure 9. Earlier Lattice Boltzmann simulations have shown a pinning of the three-phase contact line on such hydrophobic–hydrophilic boundaries. The pinning affects the frictional tension during the initial dewetting of the solid surface required for the bubble attachment. In analogy to eq 6, the threshold to overcome the pinning tension for heterogeneous surfaces can be described by the equation

$$\gamma_{SV,1} + \gamma_{SV,2} = \gamma_{SL,1} + \gamma_{LV}\cos \theta_r$$

(7)

where $\gamma_{SV,i}$ is the surface free energy of the solid of type $i$, $\gamma_{SL,i}$ is the respective solid–liquid surface energy, $\gamma_{LV}$ is the liquid surface tension, and $\theta_r$ corresponds to the receding contact angle (i.e., $\theta_B$) determined by the surface energies on both sides of the pinning site (see Figure 9). We assume in eq 7 that the main friction $\gamma_{SV,2}$ of the moving contact line comes from hydrophilic microscopic domains of type 2 on the otherwise hydrophobic surface (1).

Figure 8. (a) Sessile drop ($\theta_D$) and captive bubble ($\theta_B$) contact angles of pure Si–TMSC and partial regenerated TMSC surfaces with decreasing contact angles described from left to right as the regeneration proceeds. When $\theta_D$ was around 65° the bubbles no longer attached to the surface. (b) Effect of partial regeneration of TMSC on $\theta_B$ and $\theta_D$ measured with water (black diamond), 1.0 mM of SDS (white diamond), and 2.4 mM of SDS (gray diamond). Cases with no bubble attachment are indicated as $\theta_B = 0°$. Orange (SDS) and violet (water) dots show the theoretical predictions of the effects of slight surface regeneration or small SDS addition on the $\theta_B$ change due to pinning of the three-phase contact line.

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Equation 7 was used for the theoretical prediction of the effect of partial regeneration and SDS concentration on the $\theta_B$ of TMSC surfaces. As explained earlier, eq 6 predicted $\theta_B \approx 80^\circ$ for the homogeneous hydrophobic TMSC surface in water. This should be compared with the value of $\theta_B \approx 45^\circ$ obtained from eq 7 for a heterogeneous, partly regenerated surface comprised of estimates of $\gamma_{SV,1} = 21.38$ mN/m, $\gamma_{SL,1} = 30$ mN/m for TMSC and $\gamma_{SV,2} = 60$ mN/m for cellulose. The prediction thus shows a rapid drop in bubble contact angle ($\theta_B \approx 80^\circ \rightarrow 45^\circ$) when moving from a hydrophobic TMSC surface to a slightly regenerated one (Figure 8). This kind of drop was observed experimentally, from $\theta_B \approx 85^\circ$ to $\theta_B \approx 47^\circ$ for a surface regenerated over a short time (2–3 min). Interestingly, the close agreement between the theoretical prediction and our experiment was obtained without the inclusion of a differential Cassie factor $^{27,78}$ in eq 7. The reason could be the pointwise nature of the hydrophilic domains on an otherwise hydrophobic surface so that their total area remains low even when they cover the surface densely.

Equation 7 could also be used to describe the high sensitivity of the bubble contact angle on liquid surface tension. At a SDS concentration of 1.0 mM, eq 7 gives the theoretical value of $\theta_B \approx 36^\circ$ for the hydrophobic TMSC surface using the measured value $\gamma = 64 \pm 2$ mN/m for the liquid surface tension and estimating other surface energies as done earlier. This theoretical prediction compares well with the experimental value of $33 \pm 6^\circ$ for $\theta_B$ (Figure 8). Moreover, we used the same surface energy $\gamma_{SV,2} = 60$ mN/m in eq 7 to estimate $\theta_B$ as earlier in the case of hydrophilic pinning domains caused by regeneration. This suggests that the efficient adsorption of SDS on the hydrophobic TMSC surface (see Figure 3) creates similar hydrophilic pinning sites as the partial regeneration of this surface.

Plotting the effective $\gamma_{SL,1}$ solved from eq 7 for the partially regenerated TMSC surfaces shows (Figure 10) that this energy meets the surface free energy of the fully hydrophilized TMSC surface slightly before the actual wetting transition at $\theta_B = 65^\circ$. This discrepancy could be caused by the fact that Figure 10 neglects the effect of small surface roughness. A RMS roughness of 18.4 nm was found by AFM imaging for the partially regenerated TMSC surface at $\theta_D = 75^\circ$ (Figure S3) due to formation of spherical aggregates (average diameter ca. 200 nm). The observed value of $\theta_B$ is thus slightly smaller than the corresponding intrinsic contact angle. Using Wenzel’s formula $\cos(\theta) = \cos(\theta_B) / r$ to correct this in eq 7 leads to higher estimates of the effective $\gamma_{SL,1}$. The roughness factor $r$ obtained from the measured AFM profile (Figure S3) is rather small, on average 1.002 with a maximal local value of 1.02. Having intersection with the surface free energy 21.4 mN/m at 65° would require a larger value of 1.07 in Wenzel’s formula. Thus, roughness alone is not sufficient to explain why the effective $\gamma_{SL,1}$ crosses over 21.4 mN/m at a larger $\theta_B$ angle. A further reason for the discrepancy could be that eq 7 neglects
the nanoscale wetting film under a bubble, covering partly the pinning sites and thus diminishing their effect.

**CONCLUSIONS**

Bubble attachment on regenerated cellulose and modified silica surfaces of different degrees of hydrophobicity was studied to reveal the key mechanisms involved in complex bubble–fiber interactions. Generally, bubbles immersed in water were subjected to repulsive interactions with hydrophilic silica and cellulose surfaces but were attractive with hydrophobic surfaces. The presence of SDS turned the attractive interaction between hydrophobic silica and a bubble into repulsion when the surface tension was around 40 mN/m, and the attachment tendency showed significant scatter near the transition. Moreover, the critical SDS concentration was affected by the electrolyte concentration. Due to efficient SDS adsorption on hydrophobic TMSC, the critical surface tension was higher at 50–60 mN/m. On the other hand, the transition for bubble attachment in water, at a critical drop contact angle of 65°, was determined by changing the surface energy of TMSC by partial regeneration.

The role of various interaction components was analyzed theoretically in terms of calculated surface and interface energies. This required not only considering the energy balance at the steady state but also that of the dynamics, which includes the moving three-phase contact line of an attaching bubble. Therefore, it was necessary to add frictional tension to the Young’s equation describing the dynamic case. The frictional term differed for chemically homogeneous and heterogeneous surfaces due to pinning of the contact line in the latter. When separating the two cases, we were able to predict the observed dramatic drop in bubble contact angle caused by either regeneration of the TMSC surface or the addition of SDS. In contrast to previous literature, this prediction did not require explicit consideration of electrostatic forces.

Based on the results presented here, smooth cellulose surfaces are not expected to attract air bubbles in wet fiber foams. The surface needs to have a rather high hydrophobic content until a clear attractive interaction occurs, and the presence of surfactants and electrolytes can weaken the interaction considerably. In applications such as textile fabric manufacture, with both natural and man-made fibers, the foam-formed structure is expected to be sensitive not only to the type of fibers used but also to the type and concentration of surfactant. The pinning of bubbles to fibers contributes, among other things, to the coarsening of wet fiber foams and thus to their drainage properties. SDS was shown to adsorb on both hydrophilic and hydrophobic cellulose, which can also affect the dry material properties. The roles of nanobubbles and surface roughness on bubble–fiber interaction remain open questions. Accordingly, the connection between wet foam and dry fiber network properties needs to be investigated. The present findings can be applied to a better understanding of the forming processes with smooth fibers, opening ways to produce new foam-formed fiber materials.

**ASSOCIATED CONTENT**

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00682.

Surface tension isotherms of SDS; calculated SDS adsorption at the air–water interface; model surface characteristics; SDS isotherms for adsorption on the model surfaces; bubble adhesion on partially regenerated cellulose; calculated changes in interface and surface energies due to an attaching bubble for varied surface tension (PDF)

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Notes
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