Membrane emulsification is generally expected to deliver emulsions with narrow drop size distributions. However, the process parameters and the width of the drop size distribution are not clearly linked. This hinders the application of the process in product applications where the uniformity of drops is important. The present work closes this gap by refining the technique of dynamically enhanced membrane emulsification and by linking microscopic phenomena at the membrane surface to the emulsification result.

Drop detachment from membranes was studied in a separate visualization flow cell on lab scale with high-speed imaging. The refinement of the emulsification process in pilot scale was approached by constructing a continuously working experimental setup. In that setup a cone-shaped rotor close (50–100 µm) to the flat membrane surface induced laminar shear flow to detach drops.

Micro engineered membranes were used to specifically study membrane parameters independently. Those were the size of the pores, the inter-pore distance, the wetting properties of the membrane and the pore opening shape. Micro engineered membranes of two types were developed: silicon and silicon nitride membranes with circular pore diameter of down to 12 and 0.4 µm, respectively. The fabrication process was optimized to reduce process costs to a feasible level and the emulsification results were compared to emulsification with commercial membrane types.

The results of this study show that by carefully adjusting the cross flow over the membrane and the membrane properties, the width of the resulting drop size distribution can be reduced. Thereby the regime (dripping or jetting) in which the drops detach is important. This regime depends mostly on the wetting properties of the membrane surface, the applied wall shear stress and the trans membrane pressure. Emulsification with micro engineered membranes improves performance in terms of drop size uniformity compared to other membrane types.
Dynamically enhanced membrane Emulsification using micro engineered Membranes with controlled surface Properties

A dissertation submitted to

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for the degree of

Doctor of Sciences

presented by

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Prof. Dr. Erik van der Linden, Co-Examiner

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We only think when we are confronted with problems.

John Dewey
American philosopher, psychologist, and educational reformer
Danksagung

Hiermit möchte ich mich bei den vielen Menschen bedanken, die während meiner Zeit in Zürich zum Gelingen dieser Arbeit beigetragen haben. Sei es durch fachlichen Rat, technische Unterstützung, Inspiration, unverzichtbare moralischen Beistand oder das Bereiten einer guten Arbeitsatmosphäre. Im besonderen möchte ich folgenden Personen danken.

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ken.

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schung im Bereich Membranentwicklung entdeckt und weitergeführt habe.

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rend der Membranentwicklung danken. Durch seine Offenheit, sein Wissen und Er-
fahrung wurde mir die Arbeit im Reinraum Hönggerberg sehr erleichtert. Die Gute
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derer Arbeit möchte ich nicht missen. Im einzelnen danke ich Pascal Mühlich, Mari-
on Stoob, Laurenz Hürlimann, Katrin Edelmann, Sandra Wieland, Dr. Miguel Angel
Martinez Garza, Romy Conzade, Martina Galler und Vincent Keehnen. Pascals Ba-
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mit ihm zusammenzuarbeiten. Marions Masterarbeit und ihre ruhige und ausdauern-
de Arbeitsweise haben viele Graphen und Ergebnisse in dieser Qualität erst ermög-
liecht. Laurenz danke ich für seinen persönlichen Einsatz während seiner Masterarbeit
im Bereich Microfluidics die ein wichtiger Wegbereiter fürs Membranemulgieren war.
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mit externen Partnern in der Anwendungsstudie von Kosmetikemulsionen für rotie-
rende Membranen im Rahmen ihrer Masterarbeit. Sandras Masterarbeit hat mich
menschlich und fachlich gestählt, für diese Erfahrung möchte ich ihr danken. Miguel
möchte ich für die gute Zusammenarbeit im Bereich Membranemulgieren mit Katrin
und mir danken. Romy danke ich, dass sie mir mit ihrer genauen Hiwiarbeit bei ei-
nigen Experimenten sehr geholfen hat. Ebenso möchte ich Martina für ihre freundige
Hilfe bei einigen langwierigen Experimenten danken.

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der Schuh drückte. Ich erinnere hier beispielhaft an DFG Antragsschriften, Betreuung
von Studenten, rheologisches Knowhow oder nützliche Hinweise zu Publikationen.

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to teilen.

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den nötigen Rückhalt gesichert. Auch freue ich mich über die gute Zusammenarbeit
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tionen, die wir gemeinsam erlebt haben.

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tion bedanken. Seien es z.B. die Zusammenarbeit im NACONU oder MagPro²Life
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und ihren eigenen Experimente im Bereich von Emulgieren mittels rotierender
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der Social Day Rallay als Highlight im Gedächtnis bleiben.

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Kampen, Niederlande, November 2013
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<tr>
<td>$A$</td>
<td>$m^2$</td>
<td>area</td>
</tr>
<tr>
<td>$A$</td>
<td>$\mu m^2$</td>
<td>pore cross shape area</td>
</tr>
<tr>
<td>$B$</td>
<td>m</td>
<td>width of a drop</td>
</tr>
<tr>
<td>$E$</td>
<td>Pa</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$d$</td>
<td>m</td>
<td>characteristic length</td>
</tr>
<tr>
<td>$d_{add}$</td>
<td>m</td>
<td>additional distance between rotor and stator</td>
</tr>
<tr>
<td>$d_{drop}$</td>
<td>m</td>
<td>drop diameter</td>
</tr>
<tr>
<td>$d_{gap}$</td>
<td>m</td>
<td>gap between membrane and rotor</td>
</tr>
<tr>
<td>$d_{pore}$</td>
<td>m</td>
<td>pore diameter</td>
</tr>
<tr>
<td>$D$</td>
<td>-</td>
<td>deformation of a drop</td>
</tr>
<tr>
<td>$D_{chan}$</td>
<td>m</td>
<td>diameter of channel</td>
</tr>
<tr>
<td>$D_E$</td>
<td>m</td>
<td>equivalent diameter</td>
</tr>
<tr>
<td>$D_h$</td>
<td>m</td>
<td>hydraulic diameter</td>
</tr>
<tr>
<td>$D_i$</td>
<td>m</td>
<td>Diameter of inner rotating cylinder</td>
</tr>
<tr>
<td>$D_r$</td>
<td>m</td>
<td>representative diameter</td>
</tr>
<tr>
<td>$f$</td>
<td>-</td>
<td>friction factor</td>
</tr>
<tr>
<td>$F_{\sigma}$</td>
<td>N</td>
<td>interfacial tension force</td>
</tr>
<tr>
<td>$F_r$</td>
<td>N</td>
<td>drag force</td>
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<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{\text{pore}}$</td>
<td>m</td>
<td>height of an etched pore</td>
</tr>
<tr>
<td>$H_{\text{chan}}$</td>
<td>m</td>
<td>height of a channel</td>
</tr>
<tr>
<td>$l_{\text{corr}}$</td>
<td>µm</td>
<td>corrected length</td>
</tr>
<tr>
<td>$l_{\text{meas}}$</td>
<td>µm</td>
<td>measured length</td>
</tr>
<tr>
<td>$l_{\text{mem}}$</td>
<td>m</td>
<td>length of a free standing membrane</td>
</tr>
<tr>
<td>$L$</td>
<td>m</td>
<td>length of a drop</td>
</tr>
<tr>
<td>$L_{\text{chan}}$</td>
<td>m</td>
<td>length of a channel</td>
</tr>
<tr>
<td>$L_{\text{ent}}$</td>
<td>m</td>
<td>entrance length of a channel</td>
</tr>
<tr>
<td>$K$</td>
<td>-</td>
<td>fitting parameter</td>
</tr>
<tr>
<td>$K_{\text{chan}}$</td>
<td>-</td>
<td>shape factor accounting for width-height-ratio of a channel</td>
</tr>
<tr>
<td>$K_{\text{mem}}$</td>
<td>-</td>
<td>membrane constant depending on material properties of the membrane</td>
</tr>
<tr>
<td>$k_x$</td>
<td>-</td>
<td>shape related coefficient</td>
</tr>
<tr>
<td>$n$</td>
<td>s$^{-1}$</td>
<td>number of revolutions</td>
</tr>
<tr>
<td>$q$</td>
<td>Pa</td>
<td>pressure applied to a membrane area</td>
</tr>
<tr>
<td>$q_{\text{max}}$</td>
<td>Pa</td>
<td>maximum trans membrane pressure before burst</td>
</tr>
<tr>
<td>$Q$</td>
<td>m$^3$s$^{-1}$</td>
<td>volumetric throughput</td>
</tr>
<tr>
<td>$P$</td>
<td>m</td>
<td>perimeter</td>
</tr>
<tr>
<td>$Q_0$</td>
<td></td>
<td>cumulative size distribution number based</td>
</tr>
<tr>
<td>$Q_3$</td>
<td></td>
<td>cumulative size distribution volume based</td>
</tr>
<tr>
<td>$q_0$</td>
<td></td>
<td>frequency distribution number based</td>
</tr>
<tr>
<td>$q_3$</td>
<td></td>
<td>frequency distribution volume based</td>
</tr>
<tr>
<td>$q_{\text{max}}$</td>
<td>Pa</td>
<td>maximum pressure load of a membrane before burst</td>
</tr>
<tr>
<td>$r$</td>
<td>m</td>
<td>radius</td>
</tr>
<tr>
<td>$R$</td>
<td>m</td>
<td>outer radius of cone-shaped rotor</td>
</tr>
<tr>
<td>$R_{\text{drop}}$</td>
<td>m</td>
<td>radius of a drop</td>
</tr>
<tr>
<td>$R_o$</td>
<td>m</td>
<td>outer radius</td>
</tr>
<tr>
<td>$R_i$</td>
<td>m</td>
<td>inner radius</td>
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<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>m</td>
<td>gap height between cylinders</td>
</tr>
<tr>
<td>$t_{mem}$</td>
<td>m</td>
<td>membrane thickness</td>
</tr>
<tr>
<td>$t_{sidewall}$</td>
<td>m</td>
<td>layer thickness on a pore side wall</td>
</tr>
<tr>
<td>$t_{top}$</td>
<td>m</td>
<td>layer thickness on the top of a substrate</td>
</tr>
<tr>
<td>$\bar{v}$</td>
<td>m s$^{-1}$</td>
<td>average velocity</td>
</tr>
<tr>
<td>$v$</td>
<td>m s$^{-1}$</td>
<td>local fluid velocity</td>
</tr>
<tr>
<td>$V$</td>
<td>m s$^{-1}$</td>
<td>fluid velocity</td>
</tr>
<tr>
<td>$V_{disp}$</td>
<td>m$^3$</td>
<td>volume occupied by the disperse phase fluid</td>
</tr>
<tr>
<td>$V_{cont}$</td>
<td>m$^3$</td>
<td>the volume of the continuous phase fluid</td>
</tr>
<tr>
<td>$w_o$</td>
<td>m</td>
<td>membrane deflection</td>
</tr>
<tr>
<td>$W_{chan}$</td>
<td>m</td>
<td>width of a channel</td>
</tr>
<tr>
<td>$X_{50,i}$</td>
<td>m</td>
<td>50 % quantile of a size distribution ( = median)</td>
</tr>
<tr>
<td>$X_{10,i}$</td>
<td>m</td>
<td>10 % quantile of a size distribution</td>
</tr>
<tr>
<td>$X_{90,i}$</td>
<td>m</td>
<td>90 % quantile of a size distribution</td>
</tr>
<tr>
<td>$y$</td>
<td>m</td>
<td>distance from the middle of a channel</td>
</tr>
<tr>
<td>$z$</td>
<td>nm</td>
<td>height position measured from bottom of a pore</td>
</tr>
</tbody>
</table>

### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>rad or °</td>
<td>tilting angle of a sample</td>
</tr>
<tr>
<td>$\beta$</td>
<td>°</td>
<td>contact angle</td>
</tr>
<tr>
<td>$\delta$</td>
<td>m</td>
<td>measure accounting for the distance between rotor and plate in a rheometer</td>
</tr>
<tr>
<td>$\delta_p$</td>
<td>m</td>
<td>distance between plates in a plate-plate-shear cell</td>
</tr>
<tr>
<td>$\delta_c = R \cdot \theta$</td>
<td>m</td>
<td>$\delta$ as defined for a cone-plate setup</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pa</td>
<td>pressure drop</td>
</tr>
<tr>
<td>$\Delta_{int}$</td>
<td>Pa</td>
<td>pressure drop caused by the the Laplace pressure</td>
</tr>
<tr>
<td>$\Delta_{total}$</td>
<td>Pa</td>
<td>total pressure drop (over a membrane during emulsification)</td>
</tr>
</tbody>
</table>

continued on next page
### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{cont} )</td>
<td>Pa s</td>
<td>dynamic viscosity of the continuous phase fluid</td>
</tr>
<tr>
<td>( \eta_{emulsion} )</td>
<td>Pa s</td>
<td>dynamic viscosity of an emulsion</td>
</tr>
<tr>
<td>([\eta])</td>
<td>-</td>
<td>intrinsic viscosity</td>
</tr>
<tr>
<td>( \phi_{emulsion} )</td>
<td>- or %</td>
<td>volume fraction of an emulsion</td>
</tr>
<tr>
<td>( \dot{\gamma} )</td>
<td>s(^{-1})</td>
<td>shear rate</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>-</td>
<td>viscosity ratio ( \eta_{disp}/\eta_{cont} ), or wavelength in nm</td>
</tr>
<tr>
<td>( \omega )</td>
<td>s(^{-1})</td>
<td>angular velocity</td>
</tr>
<tr>
<td>( \omega_i )</td>
<td>s(^{-1})</td>
<td>angular velocity of outer cylinder</td>
</tr>
<tr>
<td>( \omega_o )</td>
<td>s(^{-1})</td>
<td>angular velocity of inner cylinder</td>
</tr>
<tr>
<td>( \omega_0 )</td>
<td>s(^{-1})</td>
<td>angular velocity of rotor</td>
</tr>
<tr>
<td>( \rho )</td>
<td>kg m(^{-3})</td>
<td>density</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>N m(^{-1})</td>
<td>interfacial tension</td>
</tr>
<tr>
<td>( \sigma_{bend} )</td>
<td>Pa</td>
<td>bending stress</td>
</tr>
<tr>
<td>( \sigma_{tensile} )</td>
<td>Pa</td>
<td>tensile stress</td>
</tr>
<tr>
<td>( \sigma_{total} )</td>
<td>Pa</td>
<td>total stress</td>
</tr>
<tr>
<td>( \theta )</td>
<td>°</td>
<td>cone angle of a rotor</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Pa</td>
<td>stress</td>
</tr>
<tr>
<td>( \tau_{int} )</td>
<td>Pa</td>
<td>interfacial tension related stress</td>
</tr>
<tr>
<td>( \tau_{shear} )</td>
<td>Pa</td>
<td>shear related stress</td>
</tr>
<tr>
<td>( \tau_{wall} )</td>
<td>Pa</td>
<td>wall shear stress</td>
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### Indices

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i )</td>
<td>distribution index, ( i = 0 ), number based; ( i = 3 ), volume based</td>
</tr>
<tr>
<td>( cont )</td>
<td>continuous phase liquid</td>
</tr>
<tr>
<td>( disp )</td>
<td>disperse phase liquid</td>
</tr>
<tr>
<td>( sol )</td>
<td>solid surface</td>
</tr>
</tbody>
</table>

continued on next page
Symbol | Meaning
--- | ---
x, y, z | across-, up- and down- channel directions

### Dimensionless Numbers

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca$</td>
<td>Capillary number</td>
</tr>
<tr>
<td>$Ca_{cr}$</td>
<td>critical Capillary number</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$Re^*$</td>
<td>gap Reynolds number of cone-plate geometry</td>
</tr>
<tr>
<td>$Re_o$</td>
<td>Reynolds number of outer moving cylinder</td>
</tr>
<tr>
<td>$Re_i$</td>
<td>Reynolds number of inner rotating cylinder</td>
</tr>
<tr>
<td>$Re_{gap}$</td>
<td>gap capillary number in a cylindrical geometry</td>
</tr>
<tr>
<td>$Ta$</td>
<td>Taylor number</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number</td>
</tr>
<tr>
<td>$We_{cr}$</td>
<td>critical Weber number</td>
</tr>
</tbody>
</table>

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>fps</td>
<td>frames per second</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low Pressure Chemical Vapour Deposition</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapour Deposition</td>
</tr>
<tr>
<td>PEG</td>
<td>polyethylene glycol</td>
</tr>
<tr>
<td>ROMER</td>
<td>Rotating Membrane Extruder</td>
</tr>
<tr>
<td>Span i</td>
<td>width of a size distribution defined as: $\frac{X_{90,i} - X_{10,i}}{X_{50,i}}$, $i = 0$, number based; $i = 3$, volume based</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>SPG</td>
<td>Shirasu Porous Glass</td>
</tr>
</tbody>
</table>
Summary

Emulsification is widely used in food-, pharmaceutical-, and chemical industry. The process allows dispersing immiscible liquids to achieve certain techno-functional product properties. In applications targeting a controlled release of active ingredients such as drugs or nutrients emulsions with a narrow drop size distribution are of special interest, because the release depends on the size of the resulting drops or particles. Membrane emulsification is generally expected to deliver emulsions with narrow drop size distributions. In this process the disperse fluid phase is pushed through a membrane into a cross flowing continuous liquid. Drops form at the membrane pores and are detached and carried away by the cross flow. The drop size can be well controlled by the cross flow. However, the method is limited by the amount of disperse phase emulsified in time per membrane area, because size of the drops and continuous liquid phase throughput are coupled. To overcome this issue Dynamically Enhanced Membrane Emulsification has been introduced and studied in the Food Engineering group at ETH Zurich. The method overcomes the limitation in conventional membrane emulsification by introducing a shear field across the membrane surface. This shear practically decouples the resulting drop size from the continuous liquid throughput. However a clear link between the process parameters and the width of the drop size distribution is missing. This hindered the application of the process in product applications where the uniformity of drops is important.

The present work closes this gap by refining the technique of dynamically enhanced membrane emulsification and linking microscopic phenomena at the membrane surface to the emulsification result. Therefore drop detachment from membranes was studied in a separate visualization flow cell on lab scale at flow conditions similar to the pilot scale. The refinement of the emulsification process in pilot scale was approached with a new experimental setup (ROMER II). A laminar flow above the membrane was maintained by choosing a cone-plate geometry with a narrow shear gap (50 – 100 µm). Rotational speeds were limited to achieve gap Reynolds numbers in the laminar flow domain. Further the setup enabled the use of flat micro engineered membranes. Micro engineered membranes were used to specifically study membrane parameters independently. Those were the size of the pores, the inter-pore distance, the wetting properties of the membrane and the pore opening shape. The fabrication and design of the membranes was part of this work because commercial
membranes with precise control over the membrane properties were not available, and the membrane properties determine to a large extent the emulsification result.

Micro engineered membranes of two types were developed: silicon and silicon nitride membranes. Fabrication was performed by lithographic techniques followed by a sequence of dry and wet etching steps. It was possible to fabricate membranes for the lab scale cell and the pilot scale setup, with sufficient mechanical stability against the trans membrane pressure. Circular pores were etched in the size range down to 0.4 µm for silicon nitride membranes and down to 12 µm for silicon membranes. The fabrication process was optimized to reduce process costs to a feasible level. This optimization included the reduction of the etching time through selecting an optimum membrane thickness for silicon membranes and to optimize lithographic exposure parameters in electron beam lithography for silicon nitride based membranes. The dependency of the feature size on the etching rate was studied for both membrane types. As expected, small structures etched slower, which required the adaptation of the pore etching process. The sequence of fabrication steps was critical for the fabrication of silicon nitride based membranes. This sequence was therefore ordered to achieve functional membranes and increased the yield of the fabrication process. A comparison of different silicon nitrides as membrane materials was carried out. As a results, the etching process was switched from silicon nitride from plasma enhanced chemical vapor deposition (PECVD) to silicon nitride from low pressure chemical vapor deposition (LPCVD). This increased the yield and the stability of membranes but the pore shape accuracy was compromised. Both membrane types were applicable in lab scale drop formation experiments. Silicon membranes were successfully implemented as membranes in the pilot scale process. Contrary, silicon nitride membranes had a reduced stability in the pilot scale process compared to silicon membranes. Nevertheless, in lab scale this membrane type was appropriate to study emulsification with different pore sizes and shapes and a proof of principle study was successfully carried out at pilot scale. Visualization experiments revealed that the disperse phase wetted the membrane when the membrane surface was not sufficiently altered hydrophilic, which hindered proper emulsification. This result was supported by comparative experiments between hydrophilic and more lipophilic membranes in the pilot scale setup.

From lab and pilot scale investigations it was confirmed that the wall shear stress was the governing factor to influence drop detachment, if the membrane was not wetted by the disperse phase liquid. Increase of the wall shear stress generally decreased the drop size. The drop size correlated with the pore size at a given wall shear stress. The opening aspect ratio had a minor influence on the drop detachment characteristics. However some results suggested that a high pore opening aspect ratio (length/width) coupled with a high pore aspect ratio (height/width) could induce spontaneous drop detachment as reported in literature.
In lab scale visualization commercial membranes from ceramics and metals were harder to study compared to micro engineered membranes, because of their poor optical surface properties. This issue was partly overcome by switching to fluorescence microscopy which increases the optical contrast between the drops an the membrane surface. When the pore size was too large, the control over the regime of drop detachment was poor. This poor control was caused by a change in drop detachment already for small changes of the trans membrane pressure. Drop detachment from sintered mesh membranes was less controlled, when a supportive mesh on the membrane surface hindered the continuous phase flow and caused turbulence. The inter pore distance on sintered membranes was dependent on the pore size. If the inter pore distance was too small, coalescence and wetting of the disperse phase on the membrane resulted. Drop detachment from micro engineered membranes and also from sintered ceramic membranes was well controlled when the pores were sufficiently apart. Contrary, the rough surface of sintered metal membranes lead to formation of slug-like disperse phase reservoirs sticking in the cavities of the membrane surface. From these reservoirs drop detached in a dripping or jetting state. A sintered metal membrane was applied in pilot scale emulsification. There, drop formation was less controlled compared to the use of micro engineered membranes.

Drop detachment morphology was classified in two different regimes: dripping and jetting. A transition from dripping to jetting was induced when the wall shear stress and/or the trans membrane pressure exceeded a critical threshold. This threshold depended on the membrane properties (mainly the pore size and membrane thickness). In studies with micro engineered membranes it was found that increasing the wall shear stress generally widened the width of the resulting drop size distribution. However a minimum threshold of the wall shear stress had to be exceeded to reach homogeneous drop detachment across the membrane area. Hence the recommended regime for achieving narrow drop size distributions was the dripping state. However, a decrease in drop size distributions width was observed from intermediate to large wall shear stresses which suggested that also in the jetting regime the width of the drop size distribution can be controlled to a certain extent.

The results of this work showed, that by carefully adjusting the cross flow over the membrane and the membrane properties, the width of the resulting drop size distribution can be reduced. Further studies should be performed towards the application of the method to products. There the dependence of the emulsification result on the material properties of the continuous and the disperse phase liquid should be included. To benefit from the control over the drop size distribution width and to push forward the process development, also the structure-property relationship between the drop size and e.g. the release of encapsulated active ingredients should be studied. Further work should also consider the membrane fabrication processes to produce membranes applicable up to industrial scale.
Zusammenfassung


Zusammenfassung


Visualisierungsexperimente zeigten, dass die Dispersphrase die Membran benetzte,
wenn die Membranoberfläche nicht hydrophil eingestellt war, was eine geordnete Emulgierung verhinderte. Dieses Ergebnis wurde in vergleichenden Experimenten im Pilotmassstab bestätigt.


Zusammenfassung

Verbreiterung der Tropfengrössenverteilung führte. Allerdings musst ein minimale Grenze der Wandschubspannung überschritten werden, um eine gleichmässige Tropfenablösung über die Membranfläche zu erreichen. Daher war das empfohlene Regime um enge Tropfengrösseverteilungen zu erreichen das Drippingregime. Jedoch wurde beim Übergang von mittlerer zu grossen Wandschubspannung wieder eine Verkleinerung der Tropfenverteilungsbreite beobachtet, was nahelegt, dass auch im Jetting die Breite der Tropfengrössenverteilung in einem bestimmten Rahmen gesteuert werden kann.

Part I

Micro engineering of porous membranes for dynamically enhanced membrane emulsification
1 Introduction

In membrane extrusion processes, the product structure is determined by the membrane properties. Key structural properties of membranes are (i) the pore size, (ii) the pore size distribution, (iii) the pore distance, (iv) the pore shape, (v) the surface roughness and (vi) the surface chemistry. Also the structural properties influence the stability and the efficiency during processing, e.g. (vii) membrane material, (viii) thickness, (ix) porosity as well as the (x) structure of the membrane support.

This work aims to control the drop formation of tailored membranes on lab- and pilot scale (with membrane areas up to $\approx 50 \text{cm}^2$). Demands on the membranes were (a) the ability to choose the membrane pore size between 400 nm and several micrometers, at practically mono-sized pores on one membrane and (b) the ability to freely choose inter pore distance, (c) the ability to produce different pore shapes (circular, rectangular, free forms), (d) flat membrane surface with controlled surface properties.

Micro engineering offers unique opportunities to structure materials down to a submicrometer level. Micro engineered membranes, made of nickel alloys and silicon nitride, were commercially available [5, 80], however choice of different membrane structures and sizes was insufficient. Therefore, the development of membranes specifically designed for the needs of the drop formation experiments became part of this work.

In this work, two types of membranes were developed, using lithographic techniques and high aspect ratio etching processes:

1. Silicon based membranes
2. Silicon nitride based membranes supported by silicon frames

Silicon is the most prominent material in engineering of micro mechanical systems (MEMS) and has already been shaped to form micro channels [6], complex microfluidic devices [104] and emulsification membranes [46]. For membranes based on silicon nitride, prove of principle for the functioning for filtration and emulsification was carried out in the work of Geerken et al. [27].
1 Introduction

1. Silicon membranes. The BOSCH process is a well established process to etch structures into silicon, which can be down to submicrometer in size. The process combines dry etching with a deposition of a fluorocarbon film in cycles, inhibits horizontal etching and promotes vertical etching. This leads to an anisotropic etching profile, which is necessary to achieve high aspect ratios (depth/width). Aspect ratios > 15 for trenches can be easily reached. Based on this process characteristics, the opportunity was identified to adapt this well established etching procedure to fabricate flat micro engineered membranes with mono-sized pores and free adjustability of the membrane design.

Challenges anticipated for the use of silicon as membrane material and the BOSCH process as patterning for pores were (a) the fragility of silicon as mechanical material, (b) to reach a high aspect ratio (depth/width) during etching of circular structures and (c) to macroscopically create a membrane shape and dimension useful for a pilot scale apparatus.

2. Silicon nitride based membranes supported by silicon frames. The possibility was seen to fabricate membranes with pore sizes down to 200 nm diameter. Fabrication of membranes from silicon nitride appeared feasible, because similar types of membranes had been developed. Furthermore, a process was already available for the pore etching, which is the most critical step in membrane fabrication. Additional steps to form membrane samples were established procedures in micro engineering.

A process originally developed for etching circular structures into silicon nitride to finally form photonic-crystals in an indium phosphite substrate [38] was adapted for pore etching of membranes. The structural demands for etching of circular pores, to finally form photonics crystals, and the pore etching for emulsification in this work, are similar. In both cases the aim is to etch circular (and other) structures of aspect ratios above 3 into silicon nitride, while guaranteeing high reproducibility among the pores. The demands of photonic crystals to the pore accuracy was higher compared to emulsification membranes. However, much more pores had to be produced on one sample for a larger area of emulsification membranes. Additionally, in the photonic crystals application the silicon nitride layer is alway supported by a substrate. In membrane emulsification the active membrane layer is free standing and is only supported at the sides. This increases the demand on mechanical stability of the membrane layer compared to the application of such a layer in the fabrication of photonic crystals. When the layer is not stable enough, this can lead to failure during the application of the membrane, but also to stability issues during fabrication. Therefore several challenges in adapting the process appeared. Apart from pore etching, other process steps to create a membrane sample had to be identified and further developed. A large number of pores had to be patterned by electron beam lithography. As this technique is expensive, the process had to be optimized to meet acceptable process
costs. For free standing membranes, silicon nitride with low internal stress had to be used to avoid spontaneous shivering after release of membrane squares. It had to be revealed, if the silicon nitride produced by in-house deposition, was sufficiently strong and possessed low enough internal stress. Similar to the silicon membranes the challenge to scale-up the process to fabricate macroscopically ring-shaped membranes had to be solved.

**The research questions** for the development of micro engineered membranes were:

- Are the selected fabrication processes feasible for producing membranes with aimed structural properties, and which process steps have to be applied or modified?
- Do the (mechanical) membrane characteristics allow the application of the membranes for structure formation (drops or vesicles)?

A product development approach was chosen to answer both questions. First, the basic process steps were identified, separately tested and implemented. Where necessary, process-structure relationships were investigated to optimize the process. After proof of principle, the membrane process was scaled up to wafer based fabrication while implementing the optimizations.

At the beginning of the result section, the processes developed for the fabrication of the two membrane types are described and briefly commented. Following this general description, the results of important aspects of the process characteristics and the membrane characteristics are presented.

The etching depths and the pore uniformity that could be reached with the existing etching process for a given structure and membrane material was important for both membrane types. Etching trials followed by microscopy of the etched structures were used to evaluate this point. Also lithographic parameters were evaluated by imaging of the achieved structures. Thus, the morphology of the fabricated structures was correlated to process parameters like exposure dose, feature type and size, development time and type of resist.

In the background of this part, general aspects of membranes are discussed and a brief guide on micro engineering is provided.
2 Background

2.1 Membranes

2.1.1 Influence of membrane structure on product structure

Typical applications of membranes are the separation of solid-liquid-, solid-solid-, gas-gas- or colloidal material systems. In membrane emulsification or vesicle extrusion, they are used as an array of orifices to create a specific structure. This application is the focus of this work. Key properties of membranes, which influence largely the product structure and the process characteristics, are explained in the following text.

(i) Membrane pore size. The size range of drops or vesicles are directly correlated to the membrane pore size. Schröder and Schubert [72] showed this correlation in membrane emulsification by sintered ceramic membranes. In the work of Frisken et al. [24] and Mayer et al. [53] the size of extruded vesicles was proportional to the pore size for the final extrusion step through polycarbonate membranes. Similar trends were found in other investigations about membrane emulsification [7, 12, 59, 60, 81, 99], drops detaching from capillaries of different sizes [74] and microfluidic investigations [42].

(ii) Pore size distribution. Investigations of pore size distribution and pore area density influence on the droplet size in membrane emulsification are rare. This is probably because the control over the pore size and the membrane porosity in a narrow range is not given for most of the membrane fabrication processes. The work of Schröder [74] indicates that the width of the drop size distribution is wider compared to the width of the pore size distribution of the membrane. They tested tubular ceramic membranes with median pore sizes of 0.1, 0.2, 0.8 and 1.4 µm and a span of ≈ 0.5. The corresponding emulsions had span values of ≈ 0.7–3.1 \(^1\). A similar trend was also observed by Williams et al. [99], who also tested tubular ceramic membranes in a pilot scale apparatus. Wagdare et al. [96] used micro sieves made of

\(^1\)Span values were derived from the \(Q_3\) distributions given in their work
2 Background

silicon nitride to emulsify vegetable oil in water with different surfactants. Narrow droplet size distributions were achieved with span values around 0.6 using membranes with practically uniform circular pores of 5 µm diameter.

(iii) Inter pore distance. Small distances between neighbor pores in membrane emulsification leads to contact of drops still in the stage of expansion. This can cause coalescence of drops and reduces the drop size control. Abrahamse et al. [1] performed numerical simulation on growing drops at membranes with circular pores of 5 µm under cross flow conditions. From the results, a pore distance of >10 times the pore diameter in the direction of flow was proposed. It avoids steric hindrance of neighbor drops and coalescence. Once the drops are sufficiently stabilized against coalescence, they deform when they touch each other, causing additional force contributions to the detachment, as shown theoretically and experimentally in Kosvintsev et al. [47]. Drops shield each other from the continuous cross flow, when they are close together, besides steric hindrance. Schadler and Windhab [70] used membranes with inter pore distance of 12 times the pore diameter in order to prevent coalescence at the membrane in dynamically enhanced membrane emulsification.

(iv) Pore shape. The influence of pore shape on the detachment of droplets was investigated experimentally by Kobayashi et al. [44]. They found that the slot aspect ratio influences the droplet detachment mechanism. They also claimed that a length-to-width pore ratio larger than 3 is required to induce spontaneous drop formation independent of the cross flow velocity. Rayner et al. [69] developed a simulation using a Matlab algorithm around the surface Evolver package to investigate the influence of the mass transfer of surfactants to the drop interface on the drop detachment. Their results support a dependency of drop detachment from the shape of the pore. The pore shape can serve as a control parameter of the drop detachment from pores. Because of that a membrane fabrication process where the pore shape can be adjusted is preferred.

(v) Surface chemistry. The surface chemistry is the most important parameter to control the wetting of the membrane surface. If the disperse liquid phase wets the membrane, a well controlled drop formation and detachment is not feasible. This was shown by Geerken et al. [26] by drop formation of water in hexadecane at a pore array of a silicon nitride membrane. When the membrane was hydrophobized with a silane coating, they observed stable droplet formation at each pore; if it was not treated wetting occurred and drop formation was uncontrolled. Therefore the membrane material should be selected in a way that the surface chemistry can be easily adapted to the material used for emulsification.
(vi) **Surface roughness.** Roughness promotes the onset of secondary flows and may disturb the cross flow which detaches the drops in membrane emulsification. Roughnesses which are big compared to the drop size may lead to shielding of the drops from the continuous liquid phase flow. This leads to a reduced hydrodynamic force acting on the drop. Roughnesses on the nanometer to micrometer scale may lead to a different wetting behavior compared to an ideal flat surface [77]. In order to control drop detachment, a flat membrane surface is consequently preferred.

(vii) **Membrane material.** The membrane material selected for membrane fabrication influences the mechanical and chemical resistance of the membrane. Membranes from ceramics, silicon or glass are more fragile than membranes made from metal, if exposed to an uneven stress e.g. caused by the mounting procedure or different thermal expansion of the membrane and its holder. Metal membranes and polymers would undergo plastic deformation before breaking whereas the other materials would break immediately. However, ceramics and silicon may be mechanically stronger than most metals. For stoichiometric silicon nitride ($Si_3N_4$) the yield strength is more than six times, the knob hardness is more than five times and the Young’s modulus is almost two times bigger than for stainless steel [66]. The chemical resistance differs as well. Polymer membranes are often unstable against solvents, such as acetone or hexane. Metals and ceramics are stable in most solvents. Metals undergo corrosion when exposed to acidic conditions. Silicon is etched by strong alkaline fluids.

Finally, the material selection determine the membrane fabrication process. Etching methods for silicon and silicon nitride are standard procedures in micro engineering labs, which can be adapted for pore etching. Metal etching however is not straightforward. There, other techniques like laser ablation have to be considered to form pores in a sufficiently thick metal substrate. Some materials might not be adequate for the application. E.g. in food or pharmacological applications membranes made of nickel could be critical, because nickel ions are considered as toxic.

If the membrane should be mounted in such a way that the upper surface is free from any support structure (which would disturb the fluid flow over the flat surface), glueing it to a support showed to be an appropriate solution [27]. For low energy surfaces such as polyethylene, it is a challenging task to determine a bonding procedure and to find an appropriate glueing material, to establish a well sealed and stable connection between the membrane and the holder without blocking a large portion of the pores.

(viii) **Membrane thickness.** Along with the material, the thickness of the membrane is important for its mechanical stability. Van Rijn et al. [94] showed through calculations and experiments that the burst pressure of a membrane of silicon nitride
Background

increases linearly with its thickness and its (unsupported) width. The membrane thickness influences the pressure drop, whenever a liquid phase is pushed through the pores. Considering the pores as cylindrical channels, the pressure drop for a given fluid at a given throughput scales linearly with the membrane thickness [63]. Therefore, especially for small pores a thin membrane is preferred, because the pressure drop caused by interfacial tension adds significantly to the working pressure. Depending on the membrane material, the optimal thickness is a compromise between pressure drop, membrane stability and membrane fabrication process.

(ix) Porosity. The porosity of a membrane is the volume fraction of pores. For a flat membrane with cylindrical pores, the porosity is equal to the area occupied by pores divided by the membrane surface area. It determines the throughput of disperse liquid phase per membrane area for a given pore size and a given transmembrane pressure. The porosity is dependent on the inter pore distance, since a large distance between pores automatically leads to a low porosity. Typical porosities of sintered membranes are > 15%, whereas a micro engineered membrane with circular pores and inter pores distance of 10 times the pore diameter has a porosity of 0.8%. In the study of Wagdare et al. [96], the porosity of the micro sieves was 30% caused by a small pore distance of 1.6 times pore diameter. The main achievement of their work was a well controlled drop detachment despite of the high porosity, by finding the best combination of surfactants for the fluid and membrane material.

(x) Structure of membrane support. In most cases the active layer of a membrane with the finest pores is not self supportive and therefore needs – usually more coarse – support structure. Sintered membranes are often constructed in a way that the outmost layer is supported by a coarse structure of the same material. Sintered mesh membranes use coarser meshes to support the finer ones. Thin silicon nitride membranes are usually fabricated as square arrays with membrane squares of more than 100 µm width supported by silicon. Polymer membranes are available without any support structure. In practical application like filtering or extruding, the membranes are mounted on a fine support mesh which increases pressure resistance. In dynamically enhanced membrane emulsification, the upper membrane surface should be maintained free of any support structure, to avoid perturbations of the cross flow.

2.1.2 Micro engineered membranes versus other types

Micro engineered membranes can be designed with pores in defined position and size. Thickness and pressure drop over the membrane area can be well controlled, and the surface can be smooth. In the following, typical examples of commercially
Figure 2.1: Electron microscopy pictures of commercial membrane surfaces. Images are taken from top of the surface (if not stated). A: Sintered metal membrane SIKA R AX 0.5 (GKN); B: Sintered mesh with support structure on top (Bopp, Absolita); C/D: Nickel membrane (Stork Veco), D: Side view of one membrane pore; E/F: Sintered ceramic membrane of alumina oxide; E: Side view of a broken sample; G: Track etched polycarbonate membrane
available membranes are presented and some comments are made regarding possible advantages or disadvantages for their application. Some electron microscopy pictures of commercial membranes are shown in Figure 2.1.

**Commercially available membranes** inherit their micro structure mostly from bulk processing of more macroscopic structures. The difference between membranes and sieves, which are e.g. used to separate materials, is only defined by the application. Indeed most of the porous materials considered for membrane emulsification are originated from sieving applications.

**Sintered membranes** are commercially available made from different metals (e.g. stainless steel, brass, titanium) and ceramics (e.g. alumina oxide). A support structure is formed from coarse particles which are sintered at specific temperatures and pressures. Typically this structure is some millimeters in thickness. The active membrane layer is formed either in a single sintering step together with the support or by successive application of fine particles. The pores of the membranes are the voids between the sintered particles. The paths of the pores are interconnected, so the liquid can move within the membrane in all directions. In application, the membrane has to be sealed, to force the flow of the disperse phase through the fine pore structure. Nominal pore diameter down to \(0.1 \mu m\) can be reached with ceramic membranes of such a type.

Sintered metal membranes have typically pore sizes an order of magnitude bigger (down to \(\approx 1 \mu m\)). The nominal pore size is usually derived from bubble point measurements or filter tests. These measurements depend on the pore channel width within the porous structure. The openings on the membrane surface may be larger than the nominal pore size suggests, which is important for drop formation. The inter pore distance is mostly linked to the pore size which is disadvantageous for membrane emulsification. Another drawback is the rough surface structure and the irregular pore shape originated from the sintering of the particles.

These membranes are cheaper than micro engineered membranes and can be purchased in many different shapes. Most studies on membrane emulsification were carried out with tube-shaped sintered membranes made of ceramics. Due to their thick support, the membranes are stable against pressure. They resist most solvents and cleaning agents. The support structure adds to the minimum trans membrane pressure and is susceptible to fouling which is disadvantageous for applications.

**Sintered mesh membranes** are produced from woven stainless steel threads. The pores consist of the voids between the threads. To reduce pore size and increase stability, the mesh is compacted. When the membrane should be self supportive, coarser meshes are sintered together to form a rigid base. Characteristic length scale of the pore opening is in the order of several micro meters and goes down to \(\approx 2 \mu m\).
Unfortunately the smallest pores sizes are only available with a coarser support mesh on top for protection, which would prevent the direct access of a cross flowing fluid.

**Thin, not self-supportive membranes** are made of $\geq 7\,\mu m$ thick foils from many different materials like Teflon, polyethylene, polycarbonat, cellulose. The pore size ranges from micrometers down to nanometers. As a standard in vesicle extrusion, track etched membranes of polycarbonate are used, which have the advantage of a narrow pore size distribution. Pores are formed by bombardment of the membrane foil with ions followed by wet etching, which leads to a widening of the ion tracks to open channels. The pore size can be controlled by the etching step. The pore density can be controlled by the exposure intensity and duration to the ion source. The distribution of the pores is arbitrarily scattered which gives no control over the distance between individual pores. This leads to partial overlap of pore openings, which reduces the control over the pore shape of the otherwise nearly circular pore openings. Since the membranes are thin, they have to be supported during use. Usually this is achieved by supporting the membrane by a fine metal mesh which absorbs most of the force applied during processing and leaves only small areas of the membrane free standing. This is disadvantageous for membrane emulsification, because the support structure prevents direct access of the cross flowing fluid to the pores.

**Micro engineered membranes of nickel alloys** are produced by metal deposition on a negative pattern of pores. Standard materials with flat surface can be purchased up to several $100\,cm^2$ per piece with pore diameters of several hundred of micrometers down to $2\,\mu m$. The pore pattern is originally produced by photolithography and the inter pore distance and pore size can be freely adjusted. Standard membranes, are available only with fixed inter pore distances. The membranes are $\approx 70\,\mu m$ thick and are designed in such a way that a support grid is already formed on the backside of the membrane during the electrodeposition step. Pore diameters are almost monosized. The membranes have to be supported, but are much more stable compared to not self-supportive membranes. These micro engineered membranes have already been used with further modifications in projects dealing with dynamically enhanced membrane emulsification [70]. Some issues to mount and seal this membrane type on a cylindrical membrane holder remains unsolved, but nevertheless, most of the properties required for membrane emulsification are fulfilled.

**Silicon nitride based micro sieves** consist of typically $1\,\mu m$ thin silicon nitride membranes which are supported by a silicon substrate. Relatively small samples with active membrane areas of several square millimeters are commercially available with pore sizes down to $\approx 300\,nm$. Since small membrane areas are supported by the substrate material, the membrane samples are self supporting and resist moderate trans membrane pressures and contact to many chemicals. Membranes with the dimension needed for a pilot scale process were not commercially available.
2 Background

2.1.3 Pressure deflection and burst pressure of a membrane

Membranes have to resist the trans membrane pressure applied during processing (e.g. emulsification, filtration, vesicle extrusion). Especially for thin membranes, the free standing (unsupported) membrane area has to be optimized. Further, it is important that the membrane deflection is small compared to the gap size in which they are used.

The maximum deflection in the middle of a square shaped membrane is given in [94]:

\[ w_0 = 0.318l \sqrt[3]{\frac{q_{\text{mem}}}{Et_{\text{mem}}}} \]  \hspace{1cm} (2.1)

where \( t_{\text{mem}} \) is the thickness of the membrane, \( E \) is the Young's modulus of the material, \( q \) is the pressure applied and \( l_{\text{mem}} \) is the membrane length.

Van Rijn et al. [94] developed a semi-empirical equation to correlate the total stress through bending and expansion of the membrane material to the pressure \( q \) applied and membrane parameters \( l, t_{\text{mem}} \) and \( E \):

\[ \sigma_{\text{total}} = \sigma_{\text{tensile}} + \sigma_{\text{bend}} = 0.29(1 + 1.47/0.37) \sqrt[3]{\frac{q^2l_{\text{mem}}^2E}{t_{\text{mem}}^2}}. \]  \hspace{1cm} (2.2)

Rearrangement of the equation leads to:

\[ q = \frac{t_{\text{mem}}}{l_{\text{mem}}} \cdot \sqrt[3]{\frac{\sigma_{\text{total}}^3}{(0.29(1 + 1.47/0.37))^3E}} \]  \hspace{1cm} (2.3)

So, for a given material system, taking \( E \) as a constant and replacing the total stress at a pressure \( q \) by a constant \( \sigma_{\text{max}} \), the equation 2.3 yields for the maximum pressure load \( q_{\text{max}} \):

\[ q_{\text{max}} = \frac{t_{\text{mem}}}{l_{\text{mem}}} \cdot K_{\text{mem}} \]  \hspace{1cm} (2.4)

with

\[ K_{\text{mem}} = \sqrt[3]{\frac{\sigma_{\text{max}}^3}{(0.29(1 + 1.47/0.37))^3E}}. \]  \hspace{1cm} (2.5)
2.2 Micro engineering in a nutshell

The term micro engineering covers a wide field of fabrication processes for sensors, actuators, flow channels, analytical instruments on micrometer scale. MEMS is the field of micro electronical mechanical systems. Although not containing any mechanical moving parts, the fabrication of microfluidic channels or membranes designed for emulsification in this work belong to this field [3].

Chemical engineers, food scientists or process engineers are usually not familiar with some of the MEMS techniques like deposition, patterning and etching on the micro- and nanoscale. The following few sections are provided for those who would like to get some basic information on MEMS technology and their practical challenges. A more detailed introduction can be found in literature [3]. Useful and free hands-on guides on silicon wafers, photolithography and troubleshooting can be ordered from MicroChemicals GmbH (Ulm, Germany) [54–56]. A useful website collecting information on some standard techniques is the website of the Brigham Young University (Provo, USA)\(^2\).

As an introductory example patterning of the membrane support structure used for silicon nitride membranes is shortly explained and illustrated in Figure 2.2. In 1. a silicon wafer is coated with silicon nitride (a ceramic like material) from both sides. 2. One side is coated with a photoresist (spin-coating and baking step). 3. The

\(^2\)http://www.cleanroom.byu.edu

Figure 2.2: Cartoon of a simple example for patterning one side of a silicon wafer by photolithography, pattern transfer to a hard mask of silicon nitride and wet etching steps.

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\(^2\)http://www.cleanroom.byu.edu
Background

(photoresist is patterned by exposing the selected parts of the wafer with UV light. Typically squares of several hundred micrometer size aligned to the crystal plane of the silicon wafer are exposed. Exposed resist is washed away by an alkaline developer. 4. The sample is dry etched, so unprotected areas are etched away and the pattern is copied from the resist to the layer of silicon nitride. 5. The remaining resist is washed away with solvents, because it may lead to contamination in the following steps. 6. The sample is wet etched by KOH solution. KOH etches silicon, but not silicon nitride. The crystal plane \( <100> \) etches faster than the others, therefore the etched profile is anisotropic with the characteristic angle of the slower etched crystal plane. Vertical etching stops when all silicon is removed until reaching the silicon nitride layer on the back of the wafer. The results are free standing membrane areas framed by the remaining silicon substrate.

Similar to this example, patterning and etching of several materials is possible. Thereby the process has to be developed for a specific application, taking into account the properties regarding their functionality in the final device and their resistance or ability to be etched in the processes available. Etch rates and lithographic processes decide about the material selection and their thickness.

2.2.1 Substrate material

The most prominent material in MEMS is (still) silicon. Silicon crystals grow from a melt by the Czochralski method. Crystal growth is initiated at a small seed crystal. The final result after crystallisation is a long rod of crystalline silicon (single crystal), which then is cut into slices. Those slices (called wafers) are further grinded and polished to finally achieve the specified thickness and smoothness. Typical thicknesses are \( 200 - 500 \mu m \) at a diameter of 3, 4, 8” and surface roughness of a few nanometers. It is important that the single crystal is sliced into wafers along one of the crystal planes. This alignment can be used during fabrication, because the etching speed depends on the crystal plane orientation. Electrical properties are adjusted by doping the wafers with ions, which are integrated into the crystal. The crystal plane and the type of doping is indicated by reference marks on each wafer. Crystal planes are named according to the Miller index.

2.2.2 Patterning of substrates

Litography  As explained by Figure 2.2, lithographic techniques are used to pattern the resist. Further, the pattern is transferred to the substrate by etching. The lithographic process and the resist have to be chosen according to the etching process and the feature size to be achieved.
For classical photolithography, Kresolresins with added fotoninitiators are used as photoresists. These are coated to the sample, hardened by baking and exposed to UV light. A designed mask is printed on a polymeric film at high resolution or is transferred to a chrome mask which has higher resolution than polymeric films. This mask is then used in the photolithography. Where the mask is transparent the substrate is exposed with UV light, nontransparent areas are protected.

Depending on the type of photoresist, the exposed areas of the resist become more soluble (positive resist) or less soluble (negative resist). For negative resist usually an additional baking step is necessary after exposure, because the UV-light only initiates the polymerization of the resist and it has to be further promoted by the heat treatment.

Photolithography can be easily carried out for sizes down to 5 µm. With deep UV and special precautions, the minimum feature size can be extended down to about 500 nm. For smaller structures, a typical method is electron beam lithography. There the pattern is exposed onto special resists by an electron beam. Different from photolithography, every feature has to be written dot per dot, similar to a inkjet printer. The resist has to be bombarded by the focused electron beam in order to transfer the pattern. A typical resist for electron beam with high resolution is polymethylmethacrylat (PMMA). Similar to photolithography, the sample is developed after the exposure and can then be used for etching steps. Feature sizes which can be exposed range from several nanometers to hundreds of micrometers. The process costs scale with the area and the number of features, because every feature has to be exposed one-by-one. This often limits the application of the method. The resist is usually an order of magnitude thinner compared to photolithography, because the power that is transferred to the resist is lower. Therefore the following etching time is limited. To overcome this limitation, often a hard mask is introduced, which is a layer applied to the sample before the electron beam resist. By changing the etching chemistry between the transfer of the pattern to the hard mask and the later etching of the substrate, the selectively towards the substrate can be high enough to protect a thick layer by a thin hard mask. For hard masks often metals are used but also silicon nitride as in Figure 2.2 or silicon oxide are typical mask materials.

2.2.3 Plasma processes

Clean room processes like chemical vapor deposition, sputtering, plasma cleaning and dry etching apply gas plasma under under low pressure (≈ 100 Pa absolute pressure). In a plasma, the gas is ionized by energy, which leads to a typical plasma glow. In practical applications this can be achieve by many ways such as the application of electromagnetic fields at radio frequencies (RF) of e.g. 100 kHz or 13.56 MHz at powers of e.g. 100 W. Ions in the plasma can induce chemical reactions. This induced
reaction can be used to deposit material, as in plasma enhanced chemical vapor deposition (PECVD), or to remove material. Physical and chemical interactions of the ions with surfaces are used in dry etching methods. In such processes, the sample is placed on one of the electrodes in the plasma chamber. In the plasma, due to different mobilities of electrons and ions in the oscillating electromagnetic field, part of the electrons are absorbed by the walls and the electrode. This causes a potential between the electrode (with the sample) and the ions near the electrode (DC-bias). This potential leads to a perpendicular acceleration of the ions towards the surface. When the acceleration is large enough, ions interact with the surface physically and sputter material away. Additionally ions react with the surface chemically. Plasma processes are very complex and the etch rate and selectivity are influenced by many physical processes which also can be influenced by the design of the chamber and the electrodes, the pressure inside the chamber, the choice of etching gases and their throughput as well as the applied plasma type and power. A comprehensive discussion on plasma processes has been published by Franz [23].

2.2.4 Deposition processes

Spin-coating is one of the standard processes to coat flat substrates with liquids as photoresists. The sample is clamped (usually by vacuum) onto the chuck of a rotor. An amount of resist is placed in the middle of the sample (or the whole sample is covered). Then the sample is spun. The centrifugal forces act on the liquid and spreads it on the sample. Excess liquid separates. Theoretically and practically it can be shown, that the thickness of a (Newtonian) fluid layer is equal over the whole sample. It depends on the viscosity of the resist, the rotational speed and on spinning time, but changes only negligible for long spinning times (e.g. 60 s) [61, chap. 5, p. 136 ff.]. During spinning solvent also evaporates, so it is difficult to calculate the exact resulting thickness. In practice, a spin-curve is recorded for each resist, by spinning several samples at different speeds and same spinning times and measure the layer thickness. With such a calibration spin coating delivers reproducible results. Depending on the resist and application resist thickness applied by spin coating is in the range of 100 nm to 300 µm.

The thickness of the layer can be determined by measuring at a trench in the resist with a surface profilometer. Such a trench can be created by exposure and development of a sample, or simply by making a scratch into the resist with tweezers. The width of this trench should be at least 10 µm wide.

Plasma enhanced chemical vapor deposition (PECVD) and Low pressure chemical vapor deposition (LPCVD) In plasma deposition a material is deposited onto
2.2 Micro engineering in a nutshell

a substrate by inducing a chemical reaction of gases at the surface of the substrate. To enable the reaction between gases, energy has to be applied to the etching chamber, by heating it or by additionally initiating a radio frequency plasma. In such a case, the temperature can be lower. Typical examples for such processes are the deposition of silicon nitride, silicon oxide or poly silicon. E.g. silicon nitride ($SiN_4$) can be deposited in plasma enhanced chemical vapor deposition at 300 $^\circ$C from silane ($SiH_4$) and ammonia ($NH_3$). Depending on the process conditions stoichiometric silicon nitride or silicon nitride which contains hydrogen or (more) nitrogen is formed. If thick layers are deposited (> 100 nm), intrinsic compressive or tensile stresses are created within the deposited layer, which cause bending or even fracture of the substrate. These intrinsic stresses can be controlled by combining low frequency and high frequency plasma in chemical vapor deposition. A low stress layer is necessary, if free standing membrane areas or cantilevers are fabricated. Layers by LPCVD have usually less pin hole defects, are denser and more resistive against etching. Deposition rates are between 1 and 20 nm/min. For comparison of both methods see [79]. The thickness of the deposited film can be determined optically by ellipsometry. An approximation of the thickness can be already derived from the color of the layer. A color chart for silicon nitride and silicon oxide can be found online\(^3\).

**Electron beam evaporation**  Samples can be coated by electron beam evaporation with different metals, like titanium, gold, copper, platinum, nickel and others. This layers can be used as hard mask, electrodes, alignment marks or to promote adhesion between different layers. The metal to be evaporated is placed in a crucible inside a vacuum chamber. The sample is typically in the same chamber, but separated from the crucible by a shutter. The electron beam is directed into the crucible, which transfers energy to the metal. The metal melts and evaporates. When the evaporation reaches a steady state, the shutter to the sample is opened and material is deposited onto the sample. The evaporation is monitored by an quartz crystal balance sensor, which measures the thickness deposited on a separate crystal in the chamber by correlating the resonance frequency of the crystal to the thickness. When the thickness is reached, the shutter is again closed, to stop deposition onto the sample. The deposition is unidirectional, so any obstacle between the vapor source and the sample, will avoid deposition of material. The sample can be rotated to increase homogeneity of the deposition. Flexibility of the methods to deposit many different materials and the reliability to achieve thicknesses with accuracy to a few nanometers are advantages of the method. Typical thicknesses deposited are between 10 and 300 nm at a rate of 0.01–0.5 nm/s. For thicker layers other methods, such as metal plating from liquid solutions, should be considered.

\(^3\)http://www.cleanroom.byu.edu/color_chart.phtml
2 Background

**Sputtering** In a sputtering process a plasma is ignited in a chamber at a low pressure. Reactive ions are accelerated towards the surface of the target, which is the source of deposition material. By the impact of the ions, atoms are forced from the target into the gas phase and deposit on the sample mounted opposite to the target. A typical example is the deposition of a few nanometers of gold in an argon plasma, to generate a conductive surface. This helps to reduce charging of samples during electron microscopy.

2.2.5 Etching

Etching processes transfer the pattern created in lithography to a substrate. Etching is also used to completely remove sacrificial layers from a substrate or to clean samples from contaminants. A vast number of different processes and etching recipes are available and have been tested in literature [97, 98]. The etching process has to be selected according to the target material and its of structure. Etching can happen isotropically (in all directions) or anisotropically (only in one direction), see Figure 2.3. The selectivity of the etching is very important for a possible application. It can be expressed as the ratio of the etch rates between the substrate and the passivation layer (resist layer). A selectivity of >200 is certainly beneficial, but there are also processes successfully applied, where the selectivity is around 1.

![Figure 2.3: Cartoon illustration the difference between isotropic and anisotropic etching.](image)

**Wet etching** Wet etching is usually performed by immersing the sample into an etching solution. The process is carried out with standard lab equipment, unless it requires precise control over temperature, agitation or contains extremely hazardous material (like HF). The etchant transfers the material into soluble or gas by chemical reaction. E.g. the reaction of silicon with potassium hydroxide can be written as $Si + 2H_2O + 2KOH_{aq} \rightarrow [SiO_2(OH)_{2}]^{2-} + 2K^+ + H_2 \uparrow$. 

![](image)
2.2 Micro engineering in a nutshell

Wet etching is usually isotropic for amorphous materials and can be anisotropic if crystalline substrates such as silicon are used. When trenches are etched into silicon $<100>$, the side walls are tapered at an angle of $54.74^\circ$ from the plane. Because of the different etch rates for different crystal planes, the shapes that can be etched with $<100>$ planes are limited to rectangular shapes aligned with their sides to the wafer flat. For instance, a rectangular structure not aligned properly would etch larger to a rectangle aligned to the crystal plane. In practice the shape would fray at the sides due to the uneven access of etchant to the substrate. Simulation and experiments on silicon etching for complex shapes can be found in [71]. Typical examples for wet etching are silicon etching with KOH to achieve free standing silicon nitride windows, removal of oxide layers on wafers with hydrofluoric acid, removal of contaminants by piranha solution (mixture of $H_2SO_4$ and $H_2O_2$) or removal of a titanium hard mask with a mixture of $HF$, $H_2O_2$ and water.

**Dry etching** In dry etching, the etchant is a gas. Inside a vacuum chamber a plasma is created by applying an electromagnetic field between two electrodes. Typically, the sample is placed on one of the electrodes. As briefly explained in Section 2.2.3, a DC bias forms, which accelerates ions towards the sample, causing etching of the substrate. The depth of etching is usually controlled by the process duration, where the etch rate has to measured through test runs. Automatic systems for detecting etching depths online exist but are still not widely used. Etching depths can also be controlled by introducing a layer that is resistive to etching. An example are SOI (silicon on insulator) wafers, where a thin layer of silicon oxide inside the wafer stops etching for a silicon specific process.

During etching, ions (and also non-charged species) react with the sample surface chemically and physically. Pure chemical interaction would lead to isotropic etching. Physical etching causes an anisotropic etching profile perpendicular to the sample surface. Adjusting etching parameters such as the gases, pressure, temperature and plasma power temperature, influences the selectivity, etch rate and the ratio of physical and chemical etching. Anisotropy can be promoted by side wall passivation. Etching and passivation is alternated. During the passivation step a polymer layer is deposited onto the sample homogeneously (also inside the already etched structures). This film protects the substrate mostly against chemical etching. Physical impact of ions leads to etching of the material, but only vertically. Chemical etching (horizontal and vertical) is inhibited, the result is an anisotropic etch profile. The BOSCH process, which was used for silicon etching in this work, uses this mechanism by alternating between an plasma with sulfur hexafluoride ($SF_6$) to etch silicon and a plasma with octafluorocyclobutane ($C_4F_8$) to passivate. A similar mechanism was also employed in this work when etching anisotropically into silicon nitride. There, a protective film of fluorocarbon forms during the etching step in a plasma with triflu-
oromethane (\(CHF_3\)). This film is removed through an etching step with an oxygen plasma. By balancing the length of these two steps straight (untapered) side walls can be achieved.

Dry etching requires specialized equipment, but can be used to etch anisotropically into amorphous and crystalline substrates, which distinguishes it from wet etching methods. Many different types of dry etching equipment are available. Often reactive ion etching (RIE) is supported by an additional plasma generation unit, which leads to a higher density of reactive ions and increases the etch rate. Such a device is then called ICP-RIE which stands for inductive coupled plasma reactive ion etching. Such a configuration is usually used for the Bosch process.
3 Material and method

3.1 Material

**Silicon and silicon nitride** Silicon wafers were purchased from Si-Mat, Kaufering, Germany and Active Business Company GmbH, Brunnenthal (Munich), Germany. See Table 3.1 for the specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Relevance for application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>4&quot;</td>
<td>processability, membrane size</td>
</tr>
<tr>
<td>Thickness</td>
<td>300 ± 10 µm</td>
<td>stability and etching duration</td>
</tr>
<tr>
<td>Wafer quality</td>
<td>Prime</td>
<td>not clear</td>
</tr>
<tr>
<td>Dopant</td>
<td>p/Bor</td>
<td>not relevant</td>
</tr>
<tr>
<td>Cristallographic orientation</td>
<td>&lt;100&gt;</td>
<td>wet etching trench shape</td>
</tr>
<tr>
<td>Manufacturing method</td>
<td>Czochralski process</td>
<td>not relevant</td>
</tr>
<tr>
<td>Front- and backside</td>
<td>polished</td>
<td>processing and usage</td>
</tr>
<tr>
<td>Flat</td>
<td>SEMI Std.</td>
<td>not relevant</td>
</tr>
<tr>
<td>Total thickness variation (TTV)</td>
<td>&lt;5 µm</td>
<td>membrane usage</td>
</tr>
<tr>
<td>Wafer bow (BOW)</td>
<td>&lt;10 µm</td>
<td>membrane usage</td>
</tr>
<tr>
<td>Electrical resistance</td>
<td>1 – 30 Ω·cm</td>
<td>not relevant</td>
</tr>
</tbody>
</table>

Silicon nitride wafers consist of a silicon wafer coated by low pressure chemical vapor deposition (LPCVD) on both sides with 1000 nm silicon nitride ($SiN_x$). They were purchased from Siegert Wafer GmbH, Aachen, Germany. The specifications of the silicon substrate are the same as specified in Table 3.1. According to the manufacturer, the internal stress of the silicon nitride layer was < 250 MPa and its refractive index 2.2±0.5.

For some preliminary etching tests 5 mm, square shaped silicon samples coated with silicon nitride by LPCVD were purchased from Silson Ltd (Northampton, United Kingdom).
3.1.1 Lithography materials

Photolithography chemicals  The positive photoresists AZ4562 and AZ6632 were used.
An 1:4 aqueous solution of AZ351 and AZ726MIF based on tetramethyl-ammonium-
hydroxide aqueous solution (2.4%) were used for developing the AZ resists.
Developers and resists were purchased from Clariant GmbH, Wiesbaden, Germany.

Electron beam lithography chemicals  Two positive electron beam resists were used: PMMA (Polymethylmethacrylat) 950 K 4% in Ethyllactat, Allresist GmbH, Strausberg, Germany, and ZEP-520, Polystrene Copolymer in Anisol, Marubeni, Tokyo, Japan. Methyl isobotyl ketone (MIBK) mixed with isopropanol was used for development of samples after electron beam lithography. An 1:3 mixture was used for PMMA and 9:1 for ZEP.

Masks for photolithography  High resolution emulsion film masks were used for all exposures in photolithography, except the pore exposure. The mask was designed in CAD program (Vectorworks 2012, Nemetschek Vectorworks, Inc., Columbia, USA) and transferred from a DGF file to polymer film at JD Photo-Tools, Lancs, United Kingdom, by laser exposure (resolution of 64000 dpi). The masks where cut and assembled with scotch tape to a 12 cm wide square-shaped glass plate. This assembly is the photo mask of the mask aligner. For the exposure of circles with a diameter of 10 µm and a distance of 100 µm, a high resolution chrome mask was purchased from JD Photo Tools. For highest flexibility regarding the support structure and membrane shape, the mask was designed as a regular lattice of $10^8$ circles. Such a large number of features is not feasible to digest with a CAD program. Consequently a small array of circles was drawn in a mask software (KIC, Whiteley Research Inc., Sunnyvale, USA). The source file was edited with a text editor to increase the number of circles. This file was opened in KIC again and exported as GDS file to be sent to the mask manufacturer.

3.2 Processing

3.2.1 Clean rooms

The membrane fabrication, except the wet etching of silicon, was carried out in clean rooms of the FIRST lab at ETH Zurich (FIRST = Frontiers in Research: Space &
3.2 Processing

Photolithography was mostly carried out in clean room CLA B, the plasma etching of silicon in clean room CLA A. All other fabrications steps related to silicon nitride based membranes were carried out in FIRST clean room. Relevant specifications of the clean rooms are listed in Table 3.2.

Table 3.2: Clean room specifications

<table>
<thead>
<tr>
<th>clean room</th>
<th>temperature</th>
<th>rel. humidity</th>
<th>particle specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRST</td>
<td>21.5 ± 1°C</td>
<td>45 – 50%</td>
<td>ISO 5</td>
</tr>
<tr>
<td>CLA A/B</td>
<td>21 ± 1°C</td>
<td>45%</td>
<td>ISO 7 / Photolitho ISO 5-6</td>
</tr>
</tbody>
</table>

3.2.2 Spin-coating

Silicon membranes Before the spin-coating step in silicon membrane fabrication, wafers were cleaned for 10 min in a plasma asher (TePla PP300E, PVA TePla AG, Wittenberg, Germany) in an oxygen plasma at 0.95 mbar and a generator power of 600 W. After, the wafers were baked at 100 – 120°C for 5 min. To improve resist adhesion the samples were coated with hexamethyldisilazan (HMDS) by chemical vapor deposition in a dedicated chamber with a mixture of N₂ and HMDS for 30 s. About 3 ml of AZ4562 were placed in the middle of the wafer with a pipette. Spin coating was carried out with open spinner chamber. To distribute, the resist spinning was carried out for 3 s at 700 rpm. To achieve a thickness of 10 µm the final spinning step was carried out for 35 s at 1700 rpm. The acceleration between steps was set to 1000 rpm/s. After spin-coating, the wafer was baked for 10 min at 100°C on a hot plate, supported by an aluminum wafer tray. After cooling the wafer to room temperature, it was used for photolithography.

Silicon nitride membranes Silicon nitride membranes required the same spin-coating process to pattern the support structure on the back and to align the marks at the front of the sample. Back and front side were spun with AZ4562, according to the described procedure, but with shorter baking time of the first coated side (5 min). Wafer baking and treatment with HMDS was left out. A spinner module (Suss RC 5 GYRSET, SUESS Microtec, Garching, Germany) was used to coat the silicon nitride membranes with electron beam resist. Thickness of electron beam resist was set to 650 nm. When using PMMA, the resist was spun
twice at 2000 rpm with a baking step of 10 min at 180 °C after the first spinning and 15 min after the second spinning step. When ZEP was used the resist was spun two times at 3000 rpm with a baking step of 2 min at 170 °C after each spinning step.

3.2.3 Photolithography

Photolithography was carried out with a mask aligner Type MA6 from SUESS MicrcoTec, Garching, Germany, equipped with a backside alignment module. The exposure was carried out in constant power mode (lamp). The intensity of the light was measured before exposure by a UV intensity meter, model 100, SUESS Microtec, Garching, Germany, which detects wavelengths of 405 nm. The time of exposure was calculated based on the intensity and the exposure dose. Standard exposure dose was 700 mJ/cm² for all structures, except for pore exposure, where the standard dose was 350 mJ/cm². The time was split into equal intervals of maximum 30 s with interrupts of 10 s.

3.2.4 Electron beam lithography

Electron beam lithography was carried out with a Raith150TWO system from Raith GmbH, Dortmund, Germany. For prototyping, the design and position list required for the exposure were prepared manually using the Raith150-TWO software (Version 5.0 SP 11). For more complex designs, especially for the pilot scale silicon nitride membranes, a separate line in the position list was created, for each square filled with pores. A script (SH_get_rect_coordinates.txt) within the mask drawing software (Vectorworks) was used to export the positions of all squares of the membrane support structure. The script provides the lines for the position list. These lines were copied to a position list created in the Raith software by a text editor (Smultron by Peter Borg, Version 3.8.4). The file was saved as text file (line endings as CRLF (Windows style)). Exposure was carried out with a beam voltage of 30 kV. Other parameters are mentioned with the corresponding results.

3.2.5 PECVD deposition of silicon nitride

Silicon nitride deposition was used to fabricate membranes and hard masks to be used in wet etching. It was performed with plasma enhanced chemical vapor deposition, Plasmalab System80+PECVD, Oxford Instruments, Oxfordshire, United Kingdom. The deposition was carried out at a pressure of 300 mtorr, a plate temperature of 300 °C and gas flows of 400 and 30 sccm for silane (2.5% SiH₄ in N₂) and NH₃, respectively. The low frequency plasma generator was alternated between 17 s on
and 10 s off. The high frequency generator was always on. Both generators were set to 30 W forward power.

Before deposition, wafers were treated for 5 min in an oxygen plasma (Technics Plasma 100-E, PVA TePla AG, Wettenberg, Germany) at a pressure of 700 mtorr and a forward power of 200 W.

3.2.6 Deposition of titanium

Titanium hard mask was deposited by electron beam evaporation using a Plassys system from Plassys-Bestek, Marolles-en-Hurepoix, France, at a deposition rate of 0.2 nm/s. Before deposition, samples were treated for 3 min in an oxygen plasma (Technics Plasma 100-E, PVA TePla AG, Wettenberg, Germany) at a pressure of 700 mtorr and a forward power of 100 W.

3.2.7 Wet etching of silicon

Silicon <100> was wet etched by a 20% KOHaq at approximately 80 °C. For membrane fabrication, the frontside of the samples was protected by sealed sample holders, which were tailor-made by AMMT GmbH, Frankenthal, Germany for the sample dimensions. In Figure 3.1 A–C drawings of the two sample holders are shown. The etching assembly consisted of two glass beakers, a magnetic stirrer and self-made covers to reduce evaporation (3.1 D). The small sample holder exposed an area of 14 x 31 mm of the sample to the etching solution. The larger holder exposed a ring shaped area with inner diameter 40 and outer diameter 66 mm. The maximum sample diameter that can be mounted is 75 mm. Holders are designed for a sample thickness of 300 µm. Samples mounted on the holder were heated up in deionised water in a separate beaker before transferring them to the etching bath. This procedure is necessary to maintain good sealing between the holder and the sample. Sudden temperature changes may lead to leakage of etching solution through the seal. After etching, the holder was transferred again to the separate bath, which was then slowly rinsed and cooled down with fresh deionized water.

3.2.8 Wet etching of titanium

After pore etching, residual titanium was removed from the membrane by wet etching in a solution of H$_2$O : H$_2$O$_2$ : HF (100 : 4 : 1). Prior to etching, the solution was prepared by mixing 50 ml of hydrofluoric acid (concentration 1:50 in water) with 2 ml of H$_2$O$_2$ (concentration $>$ 30%) in a flat teflon bath. The sample was immersed into
3 Material and method

the solution with the titanium surface placed upwards. After removal of the titanium layer, the sample was kept in the solution for another $5 - 10\text{ s}$. Etching was stopped by transferring the sample to a second bath with water, and then to a third one for $1\text{ min}$, where it was rinsed. Finally the samples were dried with an air gun.

40 66
A
B
C
D

Figure 3.1: Drawings of sample holders for front side protection during wet etching and photograph of etching setup. A: small sample holder for prototyping, B/C: sample holder for large ring-shaped membranes, B: vertical cut through the holder, dimensioning in drawings are in millimeters. C: Sketch to visualize how the holder was assembled (with membrane sample). D: Photograph of etching setup. Drawings are printed as received from AMMT GmbH with slight modification.

3.2.9 Dry etching of silicon

An inductive coupled plasma reactive ion etching (ICP-RIE) machine, STS Multiplex from Surface Technology Systems, Newport, United Kingdom was used for dry etching of silicon membranes. Etching was carried out with the BOSCH process, where steep sidewalls are achieved by alternating between $16\text{ s}$ etching and $6\text{ s}$ passivation. Passivation protected the sidewalls from etching. The process was carried out at a plate temperature of $15\text{ ºC}$. Etching was performed at a pressure of $20\text{ mtorr}$, at a RF coil power of $1000\text{ W}$, a platen power of $10\text{ W}$, with gas throughput set to 40, 130 and $13\text{ sccm}$ for $C_4F_8$, $SF_6$ and $O_2$, respectively. The deposition was performed at a pressure of $10\text{ mtorr}$, RF coil power of $800\text{ W}$, platen power switched off, with gas throughput set to $100\text{ sccm}$ for $C_4F_8$. 

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3.2 Processing

3.2.10 Dry etching of silicon nitride and titanium

An reactive ion etching machine, PlasmalabRIE80+, Oxford Instruments, Oxfordshire, United Kingdom was used for etching of silicon nitride and titanium.

The electrode, which carried the sample, was tempered to 18°C. For large areas of silicon nitrite (e.g. for mask etching of the support structure of silicon nitride membranes), the samples were etched at a pressure of 100 mtorr, generator power of 100 W and with gas flow rates of 80 and 20 sccm for CF₄ and O₂, respectively.

For pore etching, a multistep etching protocol was used. Based on the work presented in Kaspar et al. [38]. To transfer the pore pattern from the resist layer to the titanium hard mask underneath it, the etch step was carried out at a chamber pressure of 30 mtorr and gas flow of 40 sccm SF₆ and 10 sccm N₂. The DC bias was set to 255 V and automatically matched by the control software within a range of ±5 V by adjusting the plasma generator power.

To etch the pore pattern through the layer of silicon nitride, the etching plasma alternated between oxygen and CHF₃ plasma. The former removes deposits of fluorocarbons, the latter etches silicon nitride. By controlling the magnitude of etching and deposition, a steep etching profile is achieved. In the CHF₃ plasma step, chamber pressure was set to 30 mtorr and gas flows were adjusted to 40 and 10 sccm for SF₆ and N₂, respectively. The DC bias was set to 260 V. In the oxygen plasma step, the chamber pressure was set to 200 mtorr, oxygen flow to 100 sccm and DC bias to 100 V. The two steps were alternated applying 100 s silicon nitride etching with CHF₃ followed by 15 s oxygen plasma etching. Typically 70 of such cycles were applied.

When etching was carried out after a mask renewal step (see Section 3.2.11) then the oxygen step was omitted.

3.2.11 Mask renewal for high aspect ratio pores in silicon nitride

The etch rate becomes critically low and mask thickness has to be increased to prolong etching, for high aspect ratios etching. To allow longer etching without increasing the initial mask thickness, the so called Self-aligned mask renewal technique was developed in Kaspar et al. [39]. A scheme of the process principle is shown in Figure 3.2. After a first etching run, the mask (e.g. titanium) is almost sacrificed. To protect the upper surface during further etching, the hard mask is renewed by angular deposition of the mask material. In Kaspar et al. [39] a formula for the thickness
3 Material and method

3.1.2 Thickness determination of membranes

The silicon membrane thickness was determined by measuring the etching depth of the support structure by a mechanical surface profiler, Carycompare from Cary, Le Locle, France. The membrane thickness was calculate by subtracting etching depth from the thickness of the wafer.

Silicon nitride layer thickness was determined optically using an ellipsometer, SE850 from Sentech instruments GmbH, Berlin, Germany.
3.3 Analytics

3.3.2 Depth measurements of structures larger 10 \( \mu m \)

During process optimization, depths of the structures fabricated larger than 10\( \mu m \) were measured in order to determine resist thickness or the depth of etching. This depths were measured with a surface profiler, Dektak XT, Billerica, USA.

3.3.3 Pore size determination of silicon and silicon nitride membranes

For morphological studies of the pore shape and pore size, scanning electron microscopy (Ultra 55 from Carl Zeiss GmbH, Oberkochen, Germany) was used. Before examination, samples were coated with a thin layer (\( \approx 10 \) nm) of gold-platinum alloy with a sputter system (SCD-050, BAL-TEC AG, Liechtenstein) to alter the surface of the samples conductive. This reduces the loading of the samples with electrons and thus the artifacts during imaging.

Membrane pore size distributions were determined by image analysis of scanning electron microscopy taken perpendicularly to the surface. Images were analyzed with the software ImageJ (Wayne Rasband, National Institutes of Health, USA, version 1.47k, http://rsbweb.nih.gov/ij/) by the analyse particles function implemented in the software. The process was automatized by programming a macro script (SH_pore analysis SEM images 3.txt). The obtained list of pore areas was used to calculate the size distribution tables. The corresponding data and indices were determined using Matlab (MathWorks, Inc., USA, version R2010a) with a user defined function (semanalyzer_table_mac.m) or with a similar algorithm (SHareasToPSD2.R) programmed in R (R.app GUI 1.43 (5989 Leopard build 32-bit), S. Urbanek and H.-J. Bibiko, R Foundation for Statistical Computing, 2011). It was assumed that the pore shape is circular and therefore the diameter of a pore is given as:

\[
d_{pore} = \sqrt{4 \frac{A_{pore}}{\pi}},
\]

where \( d_{pore} \) is the pore diameter and \( A_{pore} \) is the measured pore area.

3.3.4 Pore size determination after photolithography

Width and depth of pores in photoresist were evaluated using a white light interferometer (ZYGO New View 5020, Zygo, Middlefield, USA)). An interferogramm was
recorded and the resulting 3D-images were evaluated manually by placing a measurement line to read the structure width and height. An example of an image and the measured profile at the line is given in Figure 3.3.

![Figure 3.3: Measurement of width and height of a structure in a photoresist layer. Example of placing a measurement line within control software of the white light interferometer.](image)

### 3.3.5 Determination of etching depth

Silicon etching depths for features with a cross shape smaller than 1 mm$^2$ were determined by cutting the sample with a wafer saw (ESEC 8003) and examining the cut by optical microscopy. The etching depth was determined by image analysis, by calibrating the pixel to length ratio, giving that the wafer thickness is known. An example of a cut through a wafer is given in Figure 3.4.

Etching depths in silicon nitride were determined by cleaving the sample with a wafer cleaver (Ritzer III, Micro-controle, Evry Cedex, France) and examining the cleaved area by surface electron microscopy. The samples were mounted with a fixed angle (typically 20°). Therefore the length measured from the pictures had to be corrected by using the formula

$$l_{corr} = \frac{l_{meas}}{\cos \alpha}, \quad (3.3)$$

where $l_{corr}$ is the corrected length, $l_{meas}$ the measured length from the micrograph and $\alpha$ the tilting angle of the sample.
Figure 3.4: Example of two light microscopy images of a silicon wafer cut with circular structures of 50 µm (left) and 10 µm diameter (right) after etching with the BOSCH process. Images were taken after 300 cycles of etching and removal of photoresist.

3.3.6 Determination of pressure resistance of membranes

Pressure resistance of membranes was determined by burst tests. Membrane samples were glued onto a membrane holder and pressurized by pumping water or oil into the cavity underneath the membrane. The pressure built up was measured by a transducer (ED 510/354.241/075 0..10 bar, Haenni, Switzerland) and recorded by the LabView software. The maximum pressure recorded before burst was taken as the burst pressure. Additionally, the breakage morphology was noted, especially when the supporting silicon structure broke.
4 Results

4.1 Final fabrication process for membranes with 10 µm pore diameter based on silicon

An overview of the process steps for silicon based membrane fabrication is depicted in Figure 4.1.

Figure 4.1: Process steps of the fabrication of membrane based on silicon.

**Step 1 to 4 - support structure.** 1. A clean silicon wafer is spin-coated with photoresist (AZ4562 – 10 µm thickness) and baked at 100°C for 10 min. 2. The pattern of the support structure is exposed by UV light through a photomask with 700 mJ/cm². After exposure, the pattern is developed in alkaline developer (AZ 351 1:4) for 3 min. The sample is rinsed with water for 30 s and dried. 3. Areas which...
are not protected by photoresist after patterning, are etched during plasma etching.
4. The photoresist is removed in an ultrasonic bath with acetone and isopropanol.

The etched depth and thus the thickness of the membrane is determined by the number of etching cycles performed in the BOSCH process. Typically, photolithography and the etching parameters are designed to form hundreds of membrane areas of 100\,\mu\text{m} thickness and approximately 1.5\,\text{mm}^2. The remaining material between the thin membranes is necessary for mechanical support and to guarantee the macroscopic stability of the sample.

**Step 5 to 8 - Pore formation and cutting out membrane.** 5. Photoresist is spin-coated to the front side of the sample. 6. Two patterns are exposed after each other. First the pore structure is exposed (typically spherical pores of 10\,\mu\text{m} diameter) with 350\,\text{mJ/cm}^2. Afterwards the overall membrane boundary shape with 700\,\text{mJ/cm}^2 is exposed with a second mask. 7. Etching results in straight-through pores in the membrane areas and a release of the ring-shaped membrane from the silicon wafer. 8. Finally, the resist is removed by rinsing with acetone and isopropanol in an ultrasonic bath.

### 4.2 Final fabrication process of silicon nitride based membranes

An overview of the process steps for the fabrication of silicon nitride based membranes is depicted in Figure 4.2. 1. A clean silicon wafer is coated with silicon nitride on both sides either by LPCVD or PECVD. For the final process, silicon nitride from LPCVP was used. On the backside, the layer is used as etch mask for the wet etching of silicon, which occurs later in the process. The front layer forms the membrane. A thickness of 1\,\mu\text{m} was chosen (or 2\,\mu\text{m} in case of silicon nitride from PECVD).

2.-3. By photolithography (using AZ4562 as a resist), the pattern of the membrane squares is transferred to the backside of the wafer. Alignment marks and the final shape (e.g. ring-shape) are transferred to the front side of the wafer. During photolithography, the back and front pattern are aligned by the the mask aligner.

4. Subsequently, the photolithography patterns from both sides are transferred to the silicon nitride layer by reactive ion etching (RIE) with a mixture of \textit{CF}_6 and \textit{O}_2 as etching agent.

5. The overall membrane sample is cut out of the wafer by ICP etching utilizing the BOSCH process.
4.2 Final fabrication process of silicon nitride based membranes

6. The membrane sample is stripped from photoresist by rinsing with acetone and cleaned with isopropanol and oxygen plasma treatment.

7. The sample is etched in KOH solution (20%, 80 °C). Etching takes place only where silicon nitride was etched away previously. Front side and the edges are additionally protected by mounting the sample on a sealed holder, specifically designed for the sample shape. Free standing square-shaped membrane areas are the result of the wet etching procedure.

In the following, the pore pattern is created and etched into the membrane squares:

8. The front side of the membrane is coated with titanium by electron beam evaporation (typically a layer of 140 – 210 nm).

9. Afterwards, electron beam resist (ZEP, typically a layer of 650 nm) is spin-coated onto the sample and hardened by baking.

10. By electron beam lithography, the pore pattern is transferred to the sample followed by development in a solution of MIBK in isopropanol.

11./12. Reactive ion etching is conducted in a multi-step process. The pore pattern is transferred from the layer of electron beam resist (soft mask) to the titanium layer. This titanium layer serves as an hard mask for the etching of silicon nitride. The transfer from the soft to the hard mask is carried out by etching with \(N_2\) and \(SF_6\). After the patterning of titanium, silicon nitride etching is performed by applying a cyclic etching process. During this process the etching gas is alternated between \(CHF_3\) and \(O_2\) typically 55–70 times. \(CHF_3\) etches silicon nitride whereas \(O_2\) removes the fluorocarbon film, which forms during the etching with \(CHF_3\). Further details can be found in [38].

If the pore size is smaller than 1 µm, a renewal of the hard mask is necessary (not shown in Figure 4.2). Therefore the sample is again coated with titanium by electron beam evaporation. To deposit only on the surface of the membrane and on the top of the pores, leaving the bottom of the half-etched pores free for further etching, the sample is mounted at a certain angle during deposition. Further details to this process can be found in [39].

After mask renewal, the RIE etching is continued. The oxygen step is omitted since it does not have a measurable impact on the etching result when the pore aspect ratio is high. Nevertheless the loop structure of the recipe is maintained.

13. After the etching, some residual titanium remains on the membrane, which is removed by immersing the sample into a solution of \(H_2O : H_2O_2 : HF (100 : 4 : 1)\) for a few seconds. This process step should be as short as possible, because the solution also attacks the membrane layer of silicon nitride.
Figure 4.2: Process steps of the fabrication of membrane based on silicon nitride.

1. Deposit SiN$_x$ on Silicon wafer (both sides)

2. Spincoat with Photoresist (both sides)

3. Photolithography, marks on front aligned with marks on the back

4. Etch big structures into layer of SiN$_x$ (both sides), RIE, CF$_4$

5. Etch macroscopic shape of membrane (cut out from wafer by etching), ICP, Bosch process

6. Clean membrane from resist

7. Etch backside to release membrane areas from silicon support, KOH, 20 %, 80 °C

8. Deposit titanium hard mask on membrane

9. Spincoat electron beam resist

10. Expose by electron beam lithography and develop

11. First membrane etch: transfer pore pattern from soft mask to hard mask, RIE, SF$_6$, N$_2$

12. Second membrane etch: transfer pore pattern from hard mask to silicon nitride membrane, RIE, alternate O$_2$ and CHF$_3$

13. Remove titanium, wetetch HF, H$_2$O$_2$, H$_2$O
4.3 Fabrication characteristics for silicon based membranes

4.3.1 Feature size vs. exposure dose

The pore pattern of silicon membranes was transferred to the sample by photolithography. The diameters of >1000 circles on the chrome mask were measured by optical microscopy and image analysis. The resulting average diameter was $10.0\,\mu m$ with a standard deviation of $0.39\,\mu m$. Feature size using standard exposure conditions lead to bigger pore diameters of about $12 - 14\,\mu m$ compared to the mask feature size. To optimize the exposure dose, it was varied in four steps from 120 to 700 mJ/cm$^2$.

After two minutes development, the resulting pore size in the resist was evaluated by measuring a few pores by light microscopy. Additionally, the width and depth of the pores were measured at 5 to 7 pores by white light interferometry. The result is illustrated in Figure 4.3. Both measurement techniques show differences in the evaluated pore size. For the interferometric measurements, a significant increase in pore size can be seen between an exposure dose of 350 and 700 mJ/cm$^2$. For low doses, especially at 120 mJ/cm$^2$, the measurements in the white light interferometer showed a rough surface on the bottom of the pore, indicating residues of undeveloped resist. Because of this, and since there was no significant difference in pore width up to 350 mJ/cm$^2$, this dose was further used.

4.3.2 Etching depth in BOSCH process as a function of feature size and shape

To fabricate straight through pores of a membrane, it was necessary to study the etch depth versus the number of etching cycles. The distance that can be etched through silicon determined the maximum possible thickness of the membrane. It was necessary to study also the dependency of the etch rate on the feature size, to determine the smallest pore size, which can be etched through the membrane layer. Additionally, information on the etch rate for different feature sizes and shapes helped to reduce etching time. By adapting membrane thickness from 250 to 100\,\mu m, the etching time was reduced from 3 : 20 h to 2 : 20 h. The contour width for cutting out the overall shape was adapted to the process. By this adaptation pores and contour etching was completed with the same number of etching cycles and was therefore carried out simultaneously. At both locations the sample was etched through, in spite of the different thicknesses of active membrane and support structure.
Figure 4.3: Pore width in photo resist AZ4562 vs. dose of exposure. The samples were developed 2 min and measured by white light interferometry and light microscopy. The lines were drawn to guide the eye. Error bars show the standard deviation of the measured values. The grey area represents the pore size measured on the chrome mask by light microscopy.

Three feature sizes were etched on a silicon wafer, to determine etching characteristics of the BOSCH process in the ICP machine for silicon. Two different feature types (line and circle) were evaluated by etching three wafers with 100, 200 and 300 etching cycles and measuring the etching depth at 9 to 25 sites. The result is shown in Figure 4.4. It is obvious that smaller features etched slower than bigger features. Etch depths were in general deeper for line features than for circle features with the same nominal size (taking the width of the line and the diameter of the circle). The average etch rate decreased when more cycles were performed. This can be seen from the decline of slope of the connecting lines. The effect is more pronounced towards smaller feature sizes. For example, the etch rate for the smallest circular feature (10 µm diameter) decreased from $0.80 \pm 0.03 \mu m/\text{cycle}$ (for 0 to 100 etching cycles) to $0.34 \pm 0.11 \mu m/\text{cycle}$ (for 200 to 300 etching cycles). In contrast, the etch rate stayed nearly constant for a 50 µm line feature ($1.15 \pm 0.01$ and $1.04 \pm 0.04 \mu m/\text{cycle}$).

### 4.3.3 Etching morphology of pores etched into silicon

A silicon membrane cut is shown in Figure 4.5. The pores are cylindrical from top to the bottom of the membrane. In the top area, the inner surface of the pores were smooth, apart from some regular edging resulting from the etching cycles. Towards
4.4 Membrane characteristics of silicon based membranes

4.4.1 Pore size distribution of silicon based membranes

The pore size of the silicon membranes were analyzed by electron beam microscopy and image analysis. The cumulative distribution function \( Q_0 \) of 325 pores is shown in Figure 4.6.
4 Results

Figure 4.5: Micrographs of silicon membrane. A: Single pore viewed from top, B: cut through membrane square and support viewed from approximately 20° side/top, C: Closeups of one single pore viewed from approximately 20° side/top.

4.4.2 Pressure resistance of silicon based membranes

The stability of silicon membranes against pressure load was tested as a function of the support structure at the back of the silicon membranes. The holder for the membranes consisted of 25 sections as shown in Figure 4.8. The dependency of the maximum pressure before burst on the unsupported membrane area on one section is given in Figure 4.7. The highest pressure resistance was measured for membrane samples with the largest supported (and smallest unsupported) membrane area.

4.5 Fabrication characteristics for silicon nitride based membranes

4.5.1 Exposure dose determination and influence of development time on lithography result

During electron beam lithography, the exposure dose has to be sufficient to expose the resist along the height of the layer. Too high dose lead to overexposure and to an increase of the size of exposed features. Doses too low resulted in insufficient solubility of the resist, which lead to residues of resist after development. Such residues inhibit etching. The clearing dose is the minimum dose for sufficient development. To determine this dose trenches or squares of at least 20 µm were exposed with different doses ranging from 30 to 60 µQ/cm². The samples were developed and the depth of the
4.5 Fabrication characteristics for silicon nitride based membranes

Figure 4.6: Cumulative pore size distribution (number based, \( Q_0 \)) of a micro engineered silicon membrane used for emulsification. The result is based on image analysis of 325 pores. The 10, 50 and 90 % quantiles are given in the plot.

structures was measured with a mechanical profilometer. A sufficient dose is reached, when the depth of the edge measured is the same as the resist thickness. This dose was determined to be 60 \( \mu \)Q/cm\(^2\) for a ZEP layer of 650 nm spun on titanium.

Additionally, the duration of development influences the lithography. The minimum duration also depends on the size of the structures. In Figure 4.9 the influence of the development time on the lithography result is illustrated. When developed for 3 min, the large area dose of 60 \( \mu \)Q/cm\(^2\) is sufficient to clear the resist exposed for a rectangular shape of 20 \( \mu \)m. When the size of the structures is decreased, 3 min are not sufficient to fully develop the structures and clear the ZEP layer down to the titanium surface. It was sufficient to increase the development time from 3 to 6 minutes and to maintain the large area dose at 60 \( \mu \)Q/cm\(^2\) (4.9).

4.5.2 Influence of exposure dose in electron beam lithography on pore diameter

The pores size after etching was calibrated to the dose applied in electron beam lithography. Therefore dots and circles were exposed. Then, etching was performed as described in 4.2. Pore size was measured for two repetitions of the process, at two process stages: after electron beam lithography and after silicon nitride etching. The average values for dots and circle features are plotted versus the dose in 4.10.

The pore morphology for the steps in pore etching are depicted in Figure 4.11. For dots, pictures of different exposure doses are given. For circles, a change of the dosis
4 Results

Figure 4.7: Pressure before burst as a function of membrane area of one membrane segment (out of 25). The included graphics show the silicon support design used.

between 60 to $114 \text{µQ/cm}^2$ did not influence the morphology of the pores, therefore, only pictures from one dose are shown.

4.5.3 Optimization of electron beam lithography process

The electron beam exposure is one of the most time consuming and expensive process steps in the membrane fabrication process. Since every pore is exposed individually, the exposure time scales with the number of pores exposed. To reduce the processing time for one sample, exposure parameters were optimized. For circular pores, several sets of exposure parameters were tested. Additionally, the electron beam resist was changed from PMMA to ZEP during the optimization procedure. A lower clearing dose is needed for ZEP at similar resolution of the resist, resulting in shorter exposure. The dose for circles and dots for matching similar pore sizes after etching was calibrated in an experiment. The time needed to expose $10^4$ pores in a 200 µm write field was determined by the Time simulation feature in the Raith software for different parameter sets. These showcases are depicted in Table 4.2. Only one parameter was changed for each set going from left to right. The parameter changed is marked. If two parameters are marked, they depend on each other, e.g. reducing the aperture size automatically reduces the beam current passing the aperture. Only one write field with closely packed pores was used for this evaluation to exclude the influence of the write field stitching time and stage waiting time. In practice, stitching of write-
fields was avoided, by exposing one write field to each membrane square. The *Stage wait* parameter was reduced to 0.5 s from the default value of 3 s, which reduced the exposure time for a membrane design with 1000 write fields by 42 min.
4 Results

Figure 4.9: Result of ebeam exposure at 60 $\mu$Q/cm$^2$ versus the development time. Structures in 650 nm ZEP resist on 210 nm titanium layer on silicon nitride after ebeam exposure and development in MIBK:IPA, 9:1 viewed in an 20° angle after cleaving. A, B: 500 nm trench, C: 780 nm circle, D: 20 $\mu$m trench.

Figure 4.10: Dependency of pore size on dot dose (left) and area dose for circle features (right) applied in electron beam lithography. The pore size was accessed for two different stages of the process. A linear function was fitted to the data of the dot exposure. Regression parameters of the fit are depicted in Table 4.1. Error bars represent the minimum and maximum values of the two measurements.
Table 4.1: Regression parameters measured pore size vs. dot dose used in electron beam lithography.

<table>
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<th>Process step</th>
<th>Regression parameter</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>1st step, after ebeam lithography</td>
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<td>3rd step, after silicon nitride etch</td>
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</table>

Figure 4.11: Pores viewed from top in SEM after fabrication steps in pore etching. Pictures for each step are shown for dots exposed with five different doses and for one circle of 780 nm in the design with the given large area dose. Pores are etched in LPCVP silicon nitride (Siegert), ebeam resist (ZEP) thickness was 690 nm, initial titanium thickness was 210 nm, titanium etch was 5.75 min and 75 cycles were performed in the silicon nitride etch.
Table 4.2: Exposure time for different sets of parameters used for electron beam lithography, as calculated from the Raith software for the parameters given. The exposure simulation was carried out for 10000 pores in one writefield. Reading the table from set 1 to set 5, the adjusted parameters are marked.

<table>
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<th>Parameter</th>
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<th>Set 3</th>
<th>Set 4</th>
<th>Set 5</th>
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<td>ZEP</td>
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<td>Beam current [pA]</td>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2.7</td>
</tr>
<tr>
<td>Area dose [μQ · cm⁻²]</td>
<td>420</td>
<td>420</td>
<td>420</td>
<td>73</td>
<td>NA</td>
</tr>
<tr>
<td>Dwelltime [s]</td>
<td>766.0</td>
<td>622.8</td>
<td>536.3</td>
<td>9.5</td>
<td>73.5</td>
</tr>
<tr>
<td>Settling time [s]</td>
<td>1207.5</td>
<td>238.4</td>
<td>238.4</td>
<td>239.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Total exposure time [s]</td>
<td>1984.5</td>
<td>866.4</td>
<td>779.9</td>
<td>254.1</td>
<td>78.6</td>
</tr>
<tr>
<td>Total exposure time [%]</td>
<td>100</td>
<td>44</td>
<td>39</td>
<td>13</td>
<td>4</td>
</tr>
</tbody>
</table>
4.5.4 Wet etching characteristics

Squared membranes have to be etched from one side (selectively removing silicon) to create free standing squares. This step was carried out by a selective wet etch step in KOH (20 %) at 80 °C. There are two approaches for the sequencing of etching steps: etching the pores before or after the release of the membrane squares by wet etching. The selectivity of silicon compared to silicon nitride is good (comparing etch rates for both material from Table 4.3). Therefore it is possible to etch silicon (masked with silicon nitride) by entirely immersing samples in the etch solution without extensively reducing the thickness of the silicon nitride layer (which forms the membrane). If wet etching was performed after pore etching (without removing the titanium hard mask before), the membrane pores were blocked and therefore not suitable for drop detachment experiments. A sponge-like structure on and in the pores, was observed in electron microscopy, see Figure 4.12. This structures were formed by the remaining titanium. When immersing the entire sample, the yield of intact membrane squares was low. Furthermore, the edge of the etched squares was often not even. By temporarily glueing the membrane side onto a holder and thereby protecting it from KOH, the wet etching characteristics was clearly improved. The yield of intact membrane squares was nearly 100 % and the edges of the membrane squares was well defined. Typical examples of an immersed sample and one that was covered from one side are depicted in Figure 4.13. The protection of one side was implemented by acquiring a commercially available tailor-made sample holder made of PEAK (see Section 3.2.10 for further information).

When wet-etching was performed before pore etching and before titanium deposition, the protection of one side of the sample was not absolutely necessary. However, the etching with a sealed wafer holder implies the protection of the sample sides. Therefore, front side protection was applied for pilot scale membrane samples even when not absolutely necessary, to prevent degradation of the macroscopic shape of the membranes due to etching of the silicon substrate from the side.

4.5.5 Comparison of silicon nitride deposited by PECVD and LPCVD regarding wet- and dry etching

Differences between silicon nitride layers from PECVD (deposited in ETH labs) and LPCVD (commercially acquired) were detected during fabrication. Layers from LPCVD were more resistive against KOH (higher selectivity towards silicon during wet etching). Silicon nitride from PECVD frequently showed small defects, which lead to arbitrary etching under the layer. This resulted in reduced yield of intact membrane squares. Defects were practically absent in silicon nitride deposited by
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Figure 4.12: Result of wet etching without removal or protection of the titanium layer. Left: Light microscopy image showing a membrane square after etching in KOH and the exfoliation of titanium and defects in membrane. Middle and right: SEM images of the membrane surface after KOH etching, middle: pores partly covered and blocked by a sponge-like titanium layer, right: single pore blocked by sponge-like titanium deposition.

LPCVD. Therefore, the whole membrane process was finally transferred to the use of silicon nitride from LPCVD as membrane and masking layers.

In dry etching, the etch rate of silicon nitride deposited by LPCVD turned out to be much lower compared to silicon nitride from PECVD. In Figure 4.14 pictures of etched trenches are shown to visualize these finding. Etch rates in the silicon nitride pore etching was up to a factor of 2.6 lower for silicon nitride from LPCVD compared to etching of silicon nitride from PECVD. Etching rates in the titanium removal step and silicon nitride mask etching were 16.6 and 3.7 times lower (see also Table 4.3 for the etch rates).

### 4.5.6 Mask renewal for high aspect ratio pores in silicon nitride

For circular pores sizes smaller than 1 µm the *self-aligned mask renewal* technique was applied. An example of this process is shown in Figure 4.15. After the first silicon nitride etch, the titanium hard mask is almost sacrificed. To further protect the silicon nitride from etching, the titanium hard mask is renewed by angular deposition of titanium. The depth, to which material is deposited, can be adjusted by the angle of deposition (Figure 4.15). Using the formula from [39], the maximum depth to which titanium is deposited can be calculated. Performing deposition at a 400 nm pore with and an initial height of 1700 nm, the height can be calculated where deposition starts. Depending on the deposition angle of 13 or 25°, the corresponding heights from the bottom of the pore are 33 or 842 nm. This heights corresponds well to the experimental results (Figure 4.15 third and forth picture from the left).
4.5 Fabrication characteristics for silicon nitride based membranes

![Figure 4.13: Left: membrane square after KOH etch, front side of sample not protected. Right: membrane square after KOH etch with opaque titanium layer on membrane side, protected by covering front side of membrane.](image)

The protected pore was further etched. After the second etching, more depth is gained for the pore protected from titanium deposited at an angle of $13^\circ$. For the pore deposited at $25^\circ$, no further increase in depth was measured. Instead, horizontal etching leading to a wider pore was observed. Both parameter sets, however, lead to overetching of the pores. From the pictures and the etch rates assumed for silicon nitride, it was estimated that about 10 cycles before the end of etching, the titanium layer at the top was exhausted. Without titanium, the silicon nitride layer was no longer protected. This led to a complete degradation of the mask and the typical crater-like pattern.

### 4.5.7 Etch rates

Table 4.3 gives a summary on the etch rates accessed during this work. For structures smaller than 20 µm etch rates were calculated by dividing the depth of the structure etched by the time or the numbers of etching cycles. The depth of small structures was measured with electron microscopy after cleaving the sample. For wet etching of silicon, masked by silicon nitride, the reduction in thickness of silicon nitride was measured by ellipsometry before and after etching. Only an average etch rate can be given, because the rate varies due to a change of the aspect ratio of the structure during etching. The depth was measured only at two points: before and after etching. In in Figure 4.16 the etch rate for silicon nitride from PECVD is plotted versus the pore diameter. It decreases with the pore diameter. At pore diameters $> 1$ µm the etch rate stays constant.
Figure 4.14: SEM pictures from a 0.5 µm trench etched into titanium and silicon nitride from PECVD and LPCVD masked with electron beam resist. PECVD (in-house deposition ETH), material 1 (LPCVP deposition company Silson), material 2 (LPCVP deposition company Siegert). Initial titanium layer thickness and titanium etch time: 70 nm, 2 min for left/middle, 170 nm, 4.5 min for right pictures.

4.6 Membrane characteristics of silicon nitride based membranes

4.6.1 Pressure resistance of silicon nitride based membranes

In Figure 4.17 the maximum pressure load before burst is shown for unperforated membranes made of silicon nitride. The lines reflect a fit of Equation 2.4. The maximum pressure load applicable is strongly dependent on the size of the membrane square and the type of silicon nitride used. Considering the application, a suitable size was selected for further trials. For membranes made of silicon nitride from PECVD and LPCVD, a square size of 125 µm and 250 µm was chosen, respectively. According to the fitted curves at this sizes the pressure resistance of the membrane is expected to be above 8 and 10 bar.
4.6 Membrane characteristics of silicon nitride based membranes

4.6.2 Pore size distribution and pore morphology of silicon nitride based membranes

The pore sizes of a membrane sample were generally uniform. Pore uniformity was checked by SEM images from the top surface and evaluating pore size by image analysis. The result of these measurements for pores exposed as dots with 2.7 pAms are shown in Table 4.4. Membranes were fabricated out of LPCVP silicon nitride (Siegert) with a hard mask titanium layer of 210 nm and a ZEP resist thickness of 690 nm. Etching of pores in RIE was carried out using 5:45 min titanium etch and 75 cycles SiNx etch. Some pictures made of LPCVD silicon nitride membranes are shown in Figure 4.18. For membranes with pores of 2μm distance at the edge region, a decrease in pore size was found. In Figure 4.18, visual impressions of silicon nitride membranes made from PECVD silicon nitride are shown.

Figure 4.15: SEM pictures of the *Self-aligned mask renewal* process steps. Samples were cleaved and observed at a 20° angle. Arrows indicate the deposition of titanium inside the pore.
4 Results

Figure 4.16: Average etch rate in RIE silicon nitride etching step versus the pore diameter for pores etched into silicon nitride (PECVD). 70 cycles were carried out. Embedded pictures show pores from the side with a 20° angle after etching and cleaving.

Figure 4.17: Maximum Pressure load before burst as a function of membrane square length for three types of silicon nitride membranes. Thickness of the membrane and the deposition method is shown in the legend. The lines represent a fit to equation 2.4. The grey line represents the model introduced in van Rijn et al. [94] with the material constants given in their paper for silicon nitride.
Table 4.3: Etch rate for different layers and process steps in etching of membranes based on silicon nitride.

<table>
<thead>
<tr>
<th>Process step</th>
<th>Material</th>
<th>Average etch rate</th>
<th>Unit</th>
<th>Etch test, comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium etch</td>
<td>Titanium</td>
<td>43 ± 3.6</td>
<td>nm/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>164</td>
<td>nm/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZEP</td>
<td>88 ± 6.8</td>
<td>nm/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(^{1} \text{SiN}_x)</td>
<td>≈ 400</td>
<td>nm/min</td>
<td></td>
</tr>
<tr>
<td>(^{2} \text{SiN}_x) etch</td>
<td>Titanium</td>
<td>&lt; 2.8</td>
<td>nm/cycle</td>
<td>500 nm trench, 15 cycles</td>
</tr>
<tr>
<td></td>
<td>(^{1} \text{SiN}_x)</td>
<td>32</td>
<td>nm/cycle</td>
<td>480 nm pore, 70 cycles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>nm/cycle</td>
<td>720 nm pore, 70 cycles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29</td>
<td>nm/cycle</td>
<td>1110 nm pore, 70 cycles</td>
</tr>
<tr>
<td></td>
<td>(^{2} \text{SiN}_x)</td>
<td>12</td>
<td>nm/cycle</td>
<td>500 nm trench, 15 cycles</td>
</tr>
<tr>
<td></td>
<td>(^{3} \text{SiN}_x)</td>
<td>14</td>
<td>nm/cycle</td>
<td>500 (\mu)m trench, 15 cycles</td>
</tr>
<tr>
<td>2(^{nd}) step (^{1} \text{SiN}_x) etch</td>
<td>(^{1} \text{SiN}_x)</td>
<td>≈ 7</td>
<td>nm/cycle</td>
<td></td>
</tr>
<tr>
<td>Titanium wet etch</td>
<td>Titanium</td>
<td>≈ 10</td>
<td>nm/s</td>
<td>large area</td>
</tr>
<tr>
<td></td>
<td>(^{1} \text{SiN}_x)</td>
<td>≈ 25</td>
<td>nm/s</td>
<td>large area</td>
</tr>
<tr>
<td>RIE (^{3} \text{SiN}_x) mask etch</td>
<td>AZ6632</td>
<td>≈ 150</td>
<td>nm/min</td>
<td>&gt; 100 (\mu)m squares</td>
</tr>
<tr>
<td></td>
<td>(^{1} \text{SiN}_x)</td>
<td>≈ 370</td>
<td>nm/min</td>
<td>&gt; 100 (\mu)m squares</td>
</tr>
<tr>
<td></td>
<td>(^{3} \text{SiN}_x)</td>
<td>100±26.7</td>
<td>nm/min</td>
<td>&gt; 100 (\mu)m squares</td>
</tr>
<tr>
<td>KOH wet etch</td>
<td>Silicon</td>
<td>1.1</td>
<td>(\mu)m/min</td>
<td>750 (\mu)m squares</td>
</tr>
<tr>
<td></td>
<td>(^{1} \text{SiN}_x)</td>
<td>≈ 0.6</td>
<td>nm/min</td>
<td>large area</td>
</tr>
<tr>
<td></td>
<td>Titanium</td>
<td></td>
<td></td>
<td>sponge like swelling of layer</td>
</tr>
</tbody>
</table>

\(^{1}\)PECVD deposition in FIRST lab, \(^{2}\)LPCVD from Silson, \(^{3}\)LPCVD from Siegert.
4 Results

Table 4.4: Pore size evaluation of silicon nitride membranes made of LPCVD silicon nitride. Image analysis was performed on membranes sputtered with approx. 10 nm of Pd/Au after removal of titanium.

<table>
<thead>
<tr>
<th>Pore distance µm</th>
<th>Membrane side</th>
<th>(X_{50.0}) nm</th>
<th>(X_{50.3}) nm</th>
<th>Span 0 –</th>
<th>mean diameter nm</th>
<th>standard deviation nm</th>
<th>number of pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>front</td>
<td>1136</td>
<td>1138</td>
<td>0.077</td>
<td>1086</td>
<td>19.6</td>
<td>3497</td>
</tr>
<tr>
<td>6</td>
<td>front</td>
<td>857</td>
<td>858</td>
<td>0.030</td>
<td>822</td>
<td>8.8</td>
<td>360</td>
</tr>
<tr>
<td>20</td>
<td>front</td>
<td>874</td>
<td>874</td>
<td>0.035</td>
<td>835</td>
<td>68.3</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>back</td>
<td>1085</td>
<td>1085</td>
<td>0.030</td>
<td>1148</td>
<td>38.4</td>
<td>789</td>
</tr>
<tr>
<td>6</td>
<td>back</td>
<td>820</td>
<td>820</td>
<td>0.025</td>
<td>860</td>
<td>13.8</td>
<td>327</td>
</tr>
<tr>
<td>20</td>
<td>back</td>
<td>842</td>
<td>843</td>
<td>0.056</td>
<td>879</td>
<td>18.5</td>
<td>57</td>
</tr>
</tbody>
</table>

Figure 4.18: SEM pictures of the top surface of a silicon nitride membrane with pores of 2 µm distance (from center to center) fabricated of silicon nitride from LPCVD (Siegert). Closeup pictures represent characteristic spots at the edge and somewhere in the middle of the pore field.
Figure 4.19: SEM pictures of silicon nitride membranes fabricated of silicon nitride from PECVD. Membrane squares were broken to get an inside view of the pores. Left: membrane square broken viewed with a 20° angle, middle: closeup picture of the membrane and a pore, right: closeup picture of a single pore viewed from top. Not the exact spot is viewed on the different images, positions represent the characteristic spot, only.
5 Discussion

5.1 Fabrication characteristics of micro engineered membranes

5.1.1 Relevance of exposure dose in optical- and electron beam lithography

The solubility of a positive resist in a developing agent increases in photolithography when it is exposed to UV light. The same is true when exposing electron beam resist to electron radiation. During exposure, the dose transferred to the resist can deviate significantly through diffraction, scattering and backscattering as a function of the resist and material underneath, layer thickness and the radiation source. Even though the entire layer of resist might be exposed to radiation, the dose along the height and the width of the structure might vary, which leads to different degrees of solubility. Within this work the resist type and its thickness was adapted in electron beam lithography. At this process it was shown, that the development time had to be increased from 3 to 6 min, when structures of 500 nm width (circles and trenches) and a resist thickness of 650 nm were exposed. However, the standard clearing dose was sufficient and was not changed. Increase in exposure dose for trenches slightly increased their width after exposure. It is assumed that the insufficient development after 3 min was not caused by insufficient exposure, but by the slow solubilization of the resist due to its thickness increase compared to the standard recipe. This can be explained, when considering that in electron beam lithography – in contrast to optical lithography – the thickness of the resist layer is less important. Most of the electrons pass through the layer and only a very small portion looses its energy during the interaction with the resist.

For the exposure of dots into electron beam resist, the pore size increased for pores closer to each other, even though the dot dose was equal for all pores exposed. This can be explained by the proximity effect. During exposure, through backscattering of electrons, resist is also exposed in the adjacent region. However, the dose is not sufficient to dissolve resist during development. When many structures are close to each other, the pattern of the back-scattered electrons overlap and more resist is
dissolved. This effect caused an increase of the pore size from 0.8 to 1.1 µm, when the pore distance was changed from 6 to 2 µm (Table 4.4). The influence of the proximity effect can also be seen on the edges of a pore field with small pore distance. The pores at the edge of the membrane field are smaller, because they have fewer structures in their vicinity compared to pores in the middle of the field. Therefore the pores receive less dose resulting in a smaller diameter (Figure 4.18). If the pore size shall be kept constant, a proximity correction factor for the exposure dose at the edges would have to be introduced. For this purpose software simulation tools can be used, which have to be calibrated to the material system used, or a fully empirical approach has to be chosen.

For the formation of pores in optical lithography, a dependency on exposure dose and achieved feature size was shown. This fits to the assumption, that overdosing leads to exposure of a wider area through one or more of the effects mentioned above. The measurements performed with light microscopy or white light interferometry deviated significantly. The pores size measured varied between the two methods between 7 and 57 %. Routine checks by light microscopy during membrane fabrication revealed pore sizes between 10 and 13 µm, resulting in average pore size after etching of 12 µm. Therefore it is assumed, that the optical microscopy reflects the width of the pores better. In optical microscopy it was not see, whether the pores were exposed sufficiently down to the wafer surface. The interferometric measurements showed some roughness for low doses. Therefore in spite of their inaccuracy regarding the pore size, the interferometric measurements might have prevented the use of too low dosage. A further reduction of the pore size towards the actual size of the pores on the mask might be achievable by reducing the dose and adjusting development time to guarantee the entire development of the resist forming the pores.

5.1.2 Etching depth depending on feature type and characteristic size

The feature size and its shape have an impact on the etching rate. Thus, it limits the maximum depth that can be achieved during etching. For example, differences were shown for etching circles or trenches into silicon using the BOSCH process. Small features etched slower and circles etched at a lower rate than trenches. A similar relationship was found to pores etched into silicon nitride, as shown in Figure 4.16. The etch rate dependency on the feature size is well known and one of the issues discussed in plasma etching under the acronym ARDE (Aspect ratio dependent etching). According to [23, page 478ff] several mechanisms leading to the dependency are discussed. Etching is determined by the transport of reactive species to the etched surface. As the aspect ratio increases, this process is more and more hampered. Depending on plasma composition, the ions accelerated towards the surface are more
5.1 Fabrication characteristics of micro engineered membranes

or less aligned perpendicular to the substrate. The more the trajectory of the ions differ from the ideal alignment, the smaller the probability is to reach the bottom of the structure. Hence, these ions are partly absorbed by the side walls, or they cause horizontal instead of vertical etching. A similar effect is true for non-charged etching species (atoms or radicals), which interact chemically with the surface to be etched. Due to reactions with the surface the concentration of the etchant is locally depleted. The flow of etchant to and from the site of etching therefore becomes relevant. Because of the confinement of a small structure, this flow is slowed down. Additionally, reactions may occur also at the sidewalls of the structures which reduces the amount of etchant reaching the bottom. Since the specific side wall area is bigger for high aspect ratios, this effect is also more pronounced for small structures.

Since the aspect ratio increases during etching, the actual etching rate changes over time. Therefore, etching rates are denoted as average etch rates in this work, because they were measured at the end of etching and divided by the cycles or time used for it. For silicon etching, this dependency can be derived from Figure 4.4, where the slope of the curve depth versus etching cycles decreases towards longer etching, especially for the smallest structures tested.

5.1.3 Comparison of silicon nitride types and silicon as membrane materials

In this work, micro engineered membranes were fabricated from silicon and silicon nitride (on a silicon support). Two silicon nitride types were tested for membrane fabrication: silicon nitride from PECVD and from LPCVD. Silicon nitride from LPCVD was more resistant during dry- and wet etching than silicon nitride from PECVD. The burst pressure for square-shaped membranes was higher even when the silicon nitride layer was thinner. Similar observations were found in literature. Stoffel et al. [79] reviewed LPCVD and PECVD and discussed the properties of silicon nitride layers from both methods. At a high deposition temperature like in LPCVD, hydrogen is included into the amorphous silicon nitride structure. This generally leads to a denser structure with stronger resistance against all kind of etchants. At the same time, internal stresses of the material increase which can lead to more spontaneous crack formations during processing and applications. In PECVD, temperatures of < 300 °C lead to a material quality not acceptable especially for masking during wet etching. However, PECVD deposition can be controlled by pulsing high and low frequency plasma towards low internal stress, and can be deposited at lower temperatures compared to LPCVD. This two facts make the material from PECVD in some cases the best choice. However, LPCVD material characteristics are otherwise more desirable, the authors in [79] conclude to use LPCVD whenever possible and PECVD whenever necessary.
5 Discussion

Implications for the etching process when using different silicon nitride types.

Silicon nitride from LPCVD was used, because of increased reliability mainly of the wet-etching steps, compared to silicon nitride from PECVD. In this way, bigger membrane areas with more than 1000 membrane squares could be fabricated. However, a compromise between this achievement and the pore etching step had to be made. As shown in this work, the etching of LPCVD silicon nitride is slower compared to PECVD silicon nitride. Therefore the etching takes longer and consequently the thickness of the mask material had to be increased. In spite of that, it was still possible to produce pores (circular or other shapes) with a good reproducibility. However, the contour accuracy initially achieved with silicon nitride from PECVD was not achieved when switching to LPCVD. In general, the masking material should be as thin as possible to achieve a good transfer of the applied pattern. The thicker the material, the more the result of exposure, development and etching varies between the top and the bottom of the layer. A thicker resist layer e.g. is more likely to exhibit a larger radius of curvature towards the surface of the sample. The structure will widen up over time during etching, because the etch rate depends on the angle of the surface to the etching direction [23, page 468]. Therefore, increasing the thickness of the masking layer leads to a more heterogeneous etching result.

Beyond issues directly related to layer thickness, other indirectly related issues may occur. The SEM images revealed that depositing a thicker titanium layer by electron beam evaporation leads to a bigger grain size. Locally, the presence of larger grains leads to a rougher surface. The results suggest that this might also be a cause for more frayed shapes. Cai et al. [9] studied the grain size of titanium deposition with atomic force microscopy (AFM) dependent on film thickness and deposition rate. They found an increase of grain size from \(\approx 30\) to \(40\) nm when the thickness of the layer was increased from 100 to 200 nm at a deposition rate of 0.1 nm/s. Furthermore, they showed an increase in grain size with deposition rate. E.g. the grain size increased from \(\approx 40\) to 60 nm when increasing the deposition rate from 0.1 to 0.5 nm/s. These results corresponded well to the estimated grain size of 60 nm from SEM images in experiments of this work, which were obtained for a layer thickness of 210 nm and a deposition rate of 0.2 nm/s.

5.2 Characteristics of micro engineered membranes

5.2.1 Pressure resistance versus membrane design

A large specific membrane area is beneficial for the application of the membrane. However, the membranes have to be supported to withstand the applied pressure. The supported part of the area cannot be used for drop formation in membrane
5.2 Characteristics of micro engineered membranes

emulsification. To optimize the ratio of support structure to usable membrane area, burst tests were performed for silicon and silicon nitride membranes. It was shown that the maximum pressure before burst for a given membrane material with a given thickness depends on the free standing area of the membrane. The smaller the area the more stable the membranes are against applied pressure.

For silicon membranes, the final support design was based on purely empirical investigations. For square-shaped membranes – especially for silicon nitride – van Rijn et al. [94] developed a semi-empirical equation to predict the membrane stability (Equation 2.2). From the maximum total stress (bending and tensile) that a material can resist and its Young’s modulus, the maximum pressure load can be calculated for a given size and thickness. The model mentioned in van Rijn et al. [94] fits perfectly the data from LPCVP silicon nitride, when the material constants for silicon nitride given in their paper are inserted. For silicon nitride from PECVD, the pressure resistance is much lower compared to silicon nitride from LPCVD. Among PECVD silicon nitride membranes, silicon nitride with tensile stress was slightly more stable compared to a membrane with compressive internal stress. The compressive membrane showed corrugations after fabrication. Presumably, these corrugations reduce the stability of the membrane, because it has space to deform when pressure is applied. Such bending may induce breakage of the membrane. When the internal stress is more tensile the membrane bends less, which leads to smaller bending stresses applied to the material.

The Young’s modulus and the yield strength could be derived by measuring the deformation of a membrane (or of a micro bridge or cantilever) by force application. A comparison of different silicon nitride materials tested in literature can be found in Table 5.1. The yield strengths are higher for silicon nitride from LPCVD compared to silicon nitride from PECVD, leading to higher burst pressure for the former. This general trend fits well to the results obtained in this work.

Knowing the material parameters for Equation 2.1, the maximum deflection of a membrane square under pressure can be calculated. This was done for the square sizes of 140 and 280 µm, typically used in this work for silicon nitride membranes from LPCVD nitride. The deflection in the middle of the membrane would be 2.8 and 7.0 µm, respectively, assuming a Young’s modulus of 290 GPa and a pressure load of 5 bar. For membranes of silicon nitride from PECVD and a thickness of 2 µm with the same sizes, assuming a Young’s modulus of 150 GPa leads to a deflection of about 2.7 and 6.9 µm, which is very similar. For applications in a shear cell it is interesting to know, that the deformation is relatively low compared to a shear gap height over the membrane of 50 µm as it is was used later in this work.

The results and the discussions on the membrane deflection and its pressure resistance was based on unperforated membranes. When the membranes are perforated, material properties change. Van Rijn et al. [94] measured a pressure resistance dropping of
about 50% comparing unperforated to perforated membranes. The perforated area was about 25%. In experiments performed in this work, pores occupied typically only around 0.8% (silicon membranes) and 0.5% (silicon nitride membranes) of the area. Tong et al. [89] claim in their paper on circular membranes that base on [94] the maximum pressure before burst scales with the non perforated area. Following this assumption here, the measured pressure (with unperforated membranes) would deviate from the burst pressure for perforated membranes of such low porosity less then +1%. Therefore the measurements performed with unperforated membranes are assumed to be a good measure for the pressure resistance of the membrane.

Table 5.1: Mechanical properties of silicon nitride

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Yield strength (GPa)</th>
<th>Test setup</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon nitride from PECVD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-rich, 250°C</td>
<td>112</td>
<td>0.39</td>
<td>bulge test</td>
<td>[10]</td>
</tr>
<tr>
<td>N-rich, 250°C</td>
<td>163</td>
<td>0.42</td>
<td>bulge test</td>
<td>[10]</td>
</tr>
<tr>
<td>330°C pulsed frequencies</td>
<td>143</td>
<td>1.13</td>
<td>bulge test</td>
<td>[25]</td>
</tr>
<tr>
<td>330°C 13.56 MHz</td>
<td>170</td>
<td>1.47</td>
<td>bulge test</td>
<td>[25]</td>
</tr>
<tr>
<td>Silicon nitride from LPCVD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>stoichiometric, 770°C</td>
<td>278</td>
<td>2.56</td>
<td>bulge test</td>
<td>[25]</td>
</tr>
<tr>
<td>Si-rich</td>
<td>290</td>
<td>4</td>
<td>bulge test</td>
<td>[76, 94]</td>
</tr>
<tr>
<td>Si-rich</td>
<td>295</td>
<td>5.5</td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>5.87</td>
<td>bulge und microbridge</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>6.9</td>
<td>microcantilever</td>
<td>[13]</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>288</td>
<td>11.2</td>
<td>bulge test</td>
<td>[103]</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>385</td>
<td>14</td>
<td>Bulk</td>
<td>[88, 94]</td>
</tr>
<tr>
<td>Deposition at 840°C</td>
<td>325</td>
<td>6.4 (7.1)</td>
<td>bulge and microbridge</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>203</td>
<td></td>
<td>microbridge</td>
<td>[106]</td>
</tr>
</tbody>
</table>

Selection of support structure. A compromise has to be made between a large membrane area and a high membrane stability. The pressure resistance is an important but not the only criterium to predict the stability of a membrane. The stability during membrane fabrication, handling and assembling of the device has to be taken into account as well. For instance, thin silicon nitride membranes might resist several bars in pressure but are susceptible against other mechanical impacts like scratching. In that case the force is less homogeneously applied to the surface than pressurizing
5.3 Optimization of the fabrication process of micro engineered membranes

In Table 5.2 relevant properties of membranes produced in this work are qualitatively related to their structure and the corresponding process. The stability and the pore morphology are two of the main properties for the development.

5.3.1 Optimizing membrane stability

The property of membrane stability can be subdivided into three categories.
(i) The stability during fabrication. Contamination and scratches can occur during all steps of fabrication. Good lab practice can reduce, but not totally avoid such defects. Typically damages occur during vacuum clamping on spin coaters, loading and unloading procedures into equipment. Contamination by particles on the wafer leads to damages in deposited layers, which can lead to defects in the membrane during etching.

(ii) Stability during handling is important when the membrane sample is stressed mechanically. This happens during assembling procedure into a device, coating procedure of the membrane or during characterization.

(iii) Stability during usage refers mainly to the pressure resistance during the application of the membrane, the resistance due to other mechanical stresses like the scratching or tensile stresses induced by differences of thermal expansion of holder and membrane. Also the chemical stability against cleaning agents is of importance, however it was not treated experimentally in this work.

As summarized in Table 5.2, the stability can be improved by choosing a thicker membrane, a stronger material and increasing the supported area. Reasonable membrane stability for small membrane samples was achieved when using silicon nitride from PECVD with a thickness of 2 µm. For larger membranes, the stability during fabrication was only acceptable when choosing silicon nitride from LPCVD. This conclusion was mainly triggered by achieving zero defects during wet etching of silicon, masked with LPCVD nitride, in contrast to many defects for PECVD nitride. A thickness larger than the 1 µm used with LPCVD nitride would be theoretically beneficial. The availability of low stress silicon nitride films from LPCVD was not given. Additionally, the etching process would have to be significantly adapted to deal with the stronger and thicker material. For silicon membranes a thicker membrane of 100 µm was chosen, because very thin membranes break easily and the pore etching process was capable to etch through even thicker layers.

Consequences for the fabrication process when increasing membrane stability. If a more stable membrane is achieved by increasing the thickness of the membrane, longer pore etching times have to be taken into account. The selectivity between mask and etched materials for the attack of silicon nitride membranes was between 2 and 11. Because the selectivity of the process is poor, the thicknesses of the masking materials have to be increased with the membrane thickness. Thicker masking material lead to less accurate transfer of the pore pattern to the actual membrane. The same is true when a stronger membrane material is chosen, namely silicon nitride from LPCVD instead from PECVD. Therefore, a compromise between membrane stability and
pore accuracy had to be accepted. Since the membrane etching process was initially developed for the etching of PECVD silicon nitride, 2\(\mu\)m of this material could be etched well, which led to a good shape accuracy. For silicon nitride from LPCVD, the dry etching recipe in pore etching was applied without further adaptation, because it proved to give reliable and reproducible results. This etching procedure could be adapted to improve the pore accuracy also for the more stable material. However, etching process development is seldom straightforward and would consume significant resources.

For silicon based membranes the processing allows to choose from a wide range of thicknesses (up to > 250\(\mu\)m for 12\(\mu\)m pores), because the mask to silicon selectivity was good (>200). In the etching process it was possible to handle aspect ratios above 20. However, the membrane thickness was reduced to 100\(\mu\)m, aiming shorter process time and lower pressure built up during emulsification. The etch rate for the larger support structure from the back is roughly twice as big compared to the pore etch rate. Therefore, the etching time was reduced from 3 : 20 h to 2 : 20 h by reducing the active membrane thickness from 250 to 100\(\mu\)m. A further reduction by about 30 min was achieved by starting with a wafer of 300 instead of 400\(\mu\)m thickness.

### 5.3.2 Optimization of pore morphology

The pore morphology was the second main criterion during process development and can be subdivided into three aspects.

(i) **The contour accuracy** is the shape of the pore at the edge to the membrane surface compared to the design exposed during lithography. As already discussed above, this accuracy is linked to the thickness of the mask materials and this has to be chosen according to the thickness of the membrane material. An increase of the hard mask titanium thickness effects the etching result in two ways: 1) the initial aspect ratio of the structure during etching increases. This leads to a less accurate transfer of the structure to the mask, because small arbitrarily occurring variations propagate more when a thicker layer is etched through. 2) Deposition of thick titanium layers lead to larger grain size of the titanium. Those larger grains may also effect locally the accuracy of the etching into the titanium layer. With deceasing size of structures transferred to the resist layer by electron beam lithography or photolithography the demands on the lithography accuracy increases. For 10\(\mu\)m pores the use of a polymeric film mask was still reasonable for feasibility studies, but had to be replaced by a high resolution chrome mask to increase the shape accuracy. For the structures of the backside, lithographic masks base on polymeric film where utilized. Electron beam lithography was capable to create pores with a high accuracy
down to 200 nm. The cost of the different lithography methods changes by orders of magnitude. Therefore the appropriate patterning mechanism should be selected, for the length scale needed. However, for rapid prototyping even for features of the size of several micrometers electron beam lithography can be used in a cost efficient way, since photomasks for photolithography have to be repurchased if the design is changed. For electron beam lithography the cost scales with the beam time, which may be much lower than designing and buying a new mask.

Contour accuracy in etching of silicon membranes was overall acceptable and homogeneity over the membrane was good. In some cases horizontal overetching of pores was observed, visible as etched spot(s) around the pores (see also Figure 4.5), even when the the resist seemed to be in good condition. Since that occurred occasionally and not systematically over the membrane area, the reason is speculative. It could be caused by insufficient binding of the resist to the wafer surface forming micrometer sized gas pockets under the resist around the pores. Insufficient binding of the resist is a common issue in photolithography. It was avoided by plasma cleaning the wafers and a HDMS treatment before spin coating. Monolayers of water can also decrease the binding of photoresist, which can be reduced by baking the wafer before use. Baking of 5 min at 100 – 120°C may have been too short in our experiments to completely avoid this effect.

(ii) the side wall steepness was initially optimized by Kaspar et al. [38] for silicon nitride from PECVD. The sidewall steepness was similar for silicon nitride from LPCVD. For membrane emulsification, this parameter is not critical, because mainly the outlet of the pore is relevant to the formation of drops. It is more important that the shape of the openings is homogeneous over the membrane area to avoid variation in pressure drop (and thus pore throughput) over the membrane area.

For silicon membranes, very steep side walls were achieved along a third of the pore depth. Further down, the pore widened slightly and the inner surface of the pore was rough. Secondary etching effects caused by inhomogeneous bombardment of ions at a certain aspect ratio could be the cause. Also a change in the etching gas composition due to consumption of the etchant and insufficient transport of gas in and out of the pore may explain the observation. Again, for membrane emulsification, mostly the upper part of the pore was considered as relevant for the emulsification process and an overall homogeneity over the membrane area, therefore no further adaption of the etching process was carried out.

(iii) The smallest pore size achievable in etching, together with the membrane material properties are critical for the application of the membrane. The etch rate is dependent on the aspect ratio of the structure and also the material etched. A thicker
or more etch resistant membrane needs longer etching for the same pore size. E.g. the smallest pore size achievable for a 100 μm thick silicon membrane was limited to about 12 μm. On one hand side, a reduction in the membrane thickness to 10 μm pore sizes down to 1.2 μm would have been possible. On the other hand concessions regarding the membrane stability had to be made.
6 Conclusion

Two etching processes were chosen to fabricate membranes of silicon and of silicon nitride with circular pores. The BOSCH process and one originally developed for photonic crystals were adapted and successfully applied to membrane fabrication.

For the fabrication of silicon membranes, several aspects of the fabrication process were studied. These were: the dependency of the etch rate on feature size and shape, the optimal exposure dose in photolithography and the dependency of the pressure resistance on the unsupported membrane area. With this information a protocol was developed to fabricate ring shaped silicon membranes with circular pores of 12 µm, etched through an active membrane thickness of 100 µm. The support structure thickness was 300 µm. The knowledge of the etch rate dependency helped to optimize the process as such that membranes were fabricated by only two photolithographic steps and two etch runs. By optimization of the membrane thickness the overall etching time was reduced to below 3.30 h. Membrane pores were nearly mono-sized. The inner wall of the pores were smooth until about one third of the depth. When etching deeper, the etching morphology became less controlled leading to a rough inner surface and to widening of the pores. This was assumed not disadvantageous for the application in membrane emulsification. The etch rate dropped significantly towards smaller pores. Therefore, it is assumed that the process had to be adapted when it is intended to etch circular pores smaller than 10 µm with the BOSCH process into silicon. A clear stability increase against transmembrane pressure was measured when the active membrane area was reduced.

Fabrication of silicon nitride membranes were produced with circular pores down to 400 nm diameter. The process was more complex compared to the silicon membrane process, because support structure and pores were etched by different methods and the minimum pore size chosen required electron lithography as a patterning method. The process was developed by studying process-property relationships for the various process steps. These were: the dependency of pore size and the process duration on the parameters of electron beam lithography; the etch rates for the process steps for mask and substrate materials; the dependency of the etch rate in silicon nitride on the pore size and the kind of silicon nitride material; and the wet etching characteristics influenced of the sequence of applied process steps and the kind of silicon nitride material. A proof of principle was carried out to increase the maximum depth during pore by applying the self-aligned mask renewal technique.
The electron beam time for the fabrication of circular pores of 1 μm was reduced to 4% of the original time, by replacing PMMA with ZEP as a mask material and exposing dot features instead of circles. It was shown that wet etching of the silicon support structure in KOH was feasible to carry out before pore patterning. If performed after, etching through the pores lead to uncontrolled etching and shivering of membrane squares. Also, remaining titanium (from the hard mask in pore etching) swelled in KOH and blocked pores irreversibly. Both issues were avoided by protecting the pore side during etching with a sealed wafer holder. However, it was more reliable to avoid the issues by etching pores after the wet etch. This had also the advantage, that the most expensive process step (pore patterning and etching) was shifted towards the end of the process chain. The process step with the most issues regarding defects (the wet etching) could be shifted towards the beginning. Samples which were defective during wet etching therefore were sorted out before the patterning, which made the process more efficient.

Silicon nitride from LPCVD proved to be the better material regarding stability during wet-etching and handling, compared to silicon nitride from PECVD. However, this material was also very stable against the pore etching process which lead to slower etching rates and a less defined pore shape. The latter was mainly linked to the necessary increase of the hard mask thickness.
Part II

Dynamically enhanced membrane emulsification – from lab to pilot scale
7 Introduction

Emulsions are widely used in the food-, pharmaceutical-, chemical- and cosmetics industries. The goal is to tailor the emulsion microstructure such that the product quality with respect to e.g. texture, rheology color and stability is optimized.

Generally, the mean drop size and the drop size distribution are the major characteristics of emulsions with direct impact on their stability [22, 37] and functionality. When emulsion drops carry functional components, a narrow drop size distribution is mandatory to control the release [102]. Only in such case one can claim tuning the release kinetics by tailoring the drop size.

A specific emulsification example is the production of magnetic micro particles for the application in bio separation. Such particles are produced from emulsions by solidifying a lipid dispersed phase by temperature quenching. The development of those particles was one task within the European Union’s Seventh Framework program (FP7/2007-2013) under grant agreement number 229335 and the present work was conducted within these project. The movability of the particles in a magnetic field is dependent on their size, which relates to the efficiency and reliability of separating the particles from a continuous fluid phase. Accordingly, the development of a process to control drop size and produce emulsions with a narrow drop size distribution is relevant.

Membrane emulsification is generally expected to deliver emulsions with narrow drop size distributions. The process was first introduced by Nakashima et al. [60], in which a disperse liquid phase is pressed through the pores of a membrane into a continuous cross flowing fluid phase. Drops form at the pore outlet and are detached by the hydrodynamic force induced by the flow of the continuous liquid phase. Main advantages of membrane emulsification from a processing perspective are (i) low energy input resulting in a gentle treatment of the components, (ii) good scalability, and concerning the material characteristics, the adjustability of (iii) the mean drop size and the (iv) narrow drop size distribution width.

In membrane emulsification, conventionally, the membrane remains static. A pressure driven flow of the continuous phase is directed along the membrane surface and its mean velocity directly correlates to the size of the resulting drops. The production of smaller drops requires higher continuous phase throughputs, which in general results in a lower disperse phase volume fraction, limiting the use of such conventional
membrane emulsification. To overcome this, in 2006 the group of Food Process engineering at ETH Zurich developed a patented a dynamic membrane emulsification process [100]. In this process, a shear field is induced above the membrane surface using two different configurations: 1) a cylindrical membrane rotating within an outer cylinder and 2) a rotor moving above the membrane [57, 70].

Depending on the process parameters and membrane type, the morphology of drop formation may vary, which will influence the structure of the emulsion produced. E.g. in numerical simulations of drops detaching from a single pore Feigl et al. [21] found a transition from a dripping to a jetting regime when the gap capillary number was increased. Schadler and Windhab [70] found for dynamically enhanced membrane emulsification a sudden drop in drop size, when increasing the rotational speed of the membrane. The hypothesis supported by Taylor number calculations was that the drop was linked to Taylor vortices formed in the gap. However the mechanism of drop detachment for the different regime was not possible to observe with their setup. Visual access to drop formation morphology can help to better understand the principles of membrane emulsification. However in most applications it is difficult to implement such visualization tools. Flow cells of different complexity were introduced to study the mechanisms of formation and detachment of drops from membrane pores [2, 26, 44, 70]. All of these studies visualized drops at low continuous fluid phase velocities ($\leq 0.6 \text{m/s}$), mostly due to limitations of the imaging technique or the pumping mechanism used. Geerken et al. [27] studied the influence of the surface properties of micro sieves on the contact angle at the drop formation sites, thereby demonstrating on lab scale experiments the importance of adapting the membrane surface chemistry to the emulsion formulation. They also demonstrated, by using membranes with hydrophilic surfaces, that the watery disperse phase wetted the membrane without forming drops at the pore outlets, whereas drops formed when using a more hydrophobic surface. More recently, Wagdare et al. [96] published results on emulsification of sunflower oil utilizing micro engineered membranes. They empirically determined a significant effect of surfactants and co-surfactants on the membrane wetting behavior ranging from strong wetting to good droplet formation.

The flow over and through the membrane, the membrane to liquid interfacial interaction, as well as the membranes themselves are the key to control membrane emulsification. Studies performed in microfluidic devices with single drop formation sites of a T-shaped junction showed that drop formation and detachment were reproducible and drops produced at the same conditions had all the same size [34, 101]. Drop detachment from a membrane pore is very similar to the microfluidic case. However, the drop sizes obtained in membrane emulsification are not mono-disperse. Even when membranes with nearly uniform pore size and controlled inter pore distance were used, the obtained drop size distributions were not mono-dispers and often not even narrow [70]. The discrepancy between these cases leads us to the research questions of the present work, which are summarized below.
• Which are the main process factors in membrane emulsification leading to polydispersity? And hence . . .

• To which extent can polydispersity be controlled by adjusting these process factors?

• Is it possible to scale up the process to a pilot device and adjust process conditions to produce emulsions with narrow drop size distributions?

• Can the process conditions in small scale devices be transferred to large scale devices?

Drop formation in microfluidic devices can serve as a benchmark process for membrane emulsification in terms of drop size reproducibility. E.g. drops produced in a T-shaped micro channel are nearly mono-dispers. Similar to membrane emulsification, drops are produced from a pore under cross flow conditions. But what are the differences between the two processes?

• There is less control over the dimension of pore and gap in membrane emulsification compared to microfluidics.

• Continuous phase liquid flow conditions differ. Reynolds numbers of the continuous liquid phase are usually smaller in microfluidics.

• There is less confinement during drop growth in membrane emulsification compared to microfluidics.

• In membrane emulsification several drops form simultaneously.

The impact on membrane emulsification of two process factors: 1) membrane properties and 2) flow conditions were analyzed in this work. Fluids model systems were chosen with similar properties compared to oil-in-water emulsions used in industrial applications. To have a good control over membrane properties, a micro engineering process was developed (see part I) to design and fabricate membranes for this work. This development opened up the possibility to vary pore size, pore shape, pore size distribution and membrane surface properties. Drop formation and detachment from membranes was studied by means of a flow cell and high-speed imaging. The cell was designed to have a good control over the flow state of the continuous liquid phase and enabled optical access.

In parallel, a new pilot scale setup was designed and built in close collaboration with Bühler AG (Uzwil, Switzerland). The design consisted of a cone-plate shear flow cell used for continuous emulsification. The membrane for emulsification was integrated into the plate, to establish a shear flow on top of the membrane. The gap dimensions were designed to best control the flow conditions in the gap. This was mainly achieved by choosing a small cone angle, and low tolerances in surface roughness and distance adjustment between plate and cone.
Combining visualization of drops in the separate device and emulsification in the pilot scale setup, enabled the correlation of drop detachment morphology to the emulsification result.

The results from the visualization of drop detachment from membranes are presented in chapter 9. Drop detachment from micro engineered membranes was evaluated by studying drop size, size distribution width and drop detachment morphology as a function of size, shape and distance of pores as well as flow through and on top of the membrane.

The reproducibility of the findings in chapter 9 was evaluated at the pilot scale and the results are shown in chapter 10.

Part of this work has been published in Holzapfel et al. [33].
8 Background

8.1 Emulsions and their applications

Emulsions are liquid-liquid dispersions of at least two immiscible liquids. They are thermodynamically unstable, which leads to the challenge in tailoring the stability against sedimentation, coalescence and Ostwald ripening for specific applications.

Emulsions are widely applied. Table 8.1 gives some examples of emulsions and their application, by far not being exhaustive, nevertheless illustrating their importance.

<table>
<thead>
<tr>
<th>Category</th>
<th>Product</th>
<th>Emulsion type</th>
<th>Continuous liquid</th>
<th>Disperse liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food</td>
<td>salad dressing</td>
<td>O/W</td>
<td>watery suspension</td>
<td>vegetable oil</td>
</tr>
<tr>
<td></td>
<td>mayonnaise</td>
<td>O/W</td>
<td>lecithin rich watery suspension</td>
<td>vegetable oil</td>
</tr>
<tr>
<td></td>
<td>clinical nutrition</td>
<td>O/W</td>
<td>milk protein solution</td>
<td>vegetable oils</td>
</tr>
<tr>
<td></td>
<td>butter</td>
<td>W/O</td>
<td>milk fat (solid)</td>
<td>water</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>whitening lotion</td>
<td>O/W</td>
<td>watery solution</td>
<td>castor oil, silicone oil</td>
</tr>
<tr>
<td></td>
<td>sunscreen</td>
<td>O/W</td>
<td>dispersion of TiO₂ particles</td>
<td>castor oil</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>parenteral nutrition</td>
<td>O/W</td>
<td>watery solution</td>
<td>purified vegetable oil</td>
</tr>
<tr>
<td></td>
<td>intravenous drugs</td>
<td>O/W</td>
<td>watery solution</td>
<td>lipophilic drug solution</td>
</tr>
<tr>
<td>Chemicals</td>
<td>herbicides</td>
<td>O/W</td>
<td>watery solution</td>
<td>lipophilic solution of actives</td>
</tr>
<tr>
<td></td>
<td>magnetic wax particles</td>
<td>O/W</td>
<td>watery solution</td>
<td>dispersion of magnetide in wax</td>
</tr>
<tr>
<td></td>
<td>crude oil</td>
<td>W/O</td>
<td>hydrocarbons</td>
<td>water</td>
</tr>
</tbody>
</table>

8.1.1 Structure and properties of emulsions

Volume fraction and rheology The volume fraction $\phi_{\text{emulsion}}$ of an emulsion is the part of the emulsion occupied with disperse phase fluid:


\[ \phi_{\text{emulsion}} = \frac{V_{\text{disp}}}{V_{\text{disp}} + V_{\text{cont}}}, \]

where \( V_{\text{disp}} \) is the volume of the disperse phase fluid and \( V_{\text{cont}} \) the volume of the continuous phase fluid. The viscosity of an emulsion \( \eta_{\text{emulsion}} \) depends on its disperse volume fraction. For low disperse phase fractions the viscosity can be approximated by a linear model. This model is expressed by the well-known Einstein equation. Originally it was developed for solid-liquid suspensions but can also be used to describe emulsions:

\[ \eta_{\text{emulsion}} = \eta_{\text{cont}} \cdot (1 + 2.5\phi_{\text{emulsion}}), \]

where \( \eta_{\text{cont}} \) is the viscosity of the continuous fluid phase. For higher phase volume fractions the viscosity of emulsions follows a non-linear dependency of the phase volume fraction. Other models have to be used, to describe \( \eta_{\text{emulsion}} \), e.g. the Krieger-Dougherty equation which is also commonly used for dispersions:

\[ \eta_{\text{emulsion}} = \eta_{\text{cont}} \cdot \left(1 - \frac{\phi_{\text{emulsion}}}{\phi_{\text{max}}} \right)^{-[\eta]\phi_{\text{max}}} \]

\([\eta]\) denotes the intrinsic viscosity of the disperse phase particles, \( \phi_{\text{max}} \) is the maximum volume fraction, which depends on the size distribution and shape of the particles. For mono-disperse solid spheres the theoretical maximum volume fraction is \( \phi_{\text{max}} = 0.637 \). For poly-disperse particles it is higher, because the space can be occupied more effectively as smaller particles can be placed in the voids between larger particles. Extremely high maximum volume fractions of up to 0.96 (96% disperse phase volume) are possible when drops are stable against coalescence. At such high volume fractions drops deform and are only separated by thin films of continuous liquid phase [52].

**Drop size distribution and its representation** Drop size is one of the most important characteristics of an emulsion, because it has a large influence on emulsion properties, such as stability and appearance. Drop size is usually measured by optical methods such as microscopic image analysis or laser diffraction and scattering. In laser diffraction and scattering measurements a laser beam penetrates the (transparent) sample and the diffraction/scattering pattern is recorded. Mathematical models based on the Fraunhofer-theory help to correlate the diffraction pattern with the drop size. For scattering patterns the Mie-theory delivers an appropriate approximation. Parameters that have to be available are the refractive indices of the continuous and disperse fluid phases (for the Fraunhofer model only of the continuous fluid phase). It is assumed that the particles are spherical.

Drop size can be plotted as cumulative distributions or as frequency distributions. For emulsions and particles it is common to have a log scale on the size axis, having
in mind that typical results for a dispersion process follows a log-normal distribution. Drop size distributions can be number-, area-, or volume-weighted. In volume based distributions, small particles are less represented while larger particles will be enhanced. In case of number distributions it will be opposite. The choice of a representation depends on the application. For encapsulation purposes the amount of encapsulate in the few bigger drops might exceed the amount of encapsulated material in many small particles, because the amount that is in one capsule depends on its volume. If the total amount delivered by a size fraction is relevant one would chose the volume based representation. Common rules on how to plot drop and particle size can be found in [36]. Useful hints on avoiding clangers while dealing with size distributions are given in [75].

To compare different drop size distributions, some distinct drop sizes are derived from the distributions. Commonly, the quantiles \( X_{10}, X_{50}, X_{90} \) are used, indicating the sizes of drops for which 10, 50 or 90 % of the total considered amount (e.g. number, volume, mass) of the sample is delivered by drops smaller or equal in diameter. The median diameter \( X_{50} \) is often chosen as representative drop size. For example \( X_{50,3} = 50 \mu m \) indicates that 50 % of the volume of the drops in the sample consists of drops with diameters 50 \( \mu m \) and smaller. The index "3" indicates the volume based distribution. A "0" refers to a number based- and a "2" to an area based distribution. The Sauter diameter \( s_{2,3} \) which is a specific area based average value, is also often selected. To characterize the width of the distribution the span of the distribution can be calculated. It is defined as:

\[
span = \frac{X_{90,i} - X_{10,i}}{X_{50,i}} (i = 0...3)
\]  

Another measure for the width of the distribution is the standard deviation of the drop diameter, often given as deviation in percent from the average value of the number based distribution.

8.2 Emulsion formation and drop breakup

8.2.1 Drop breakup under different flow conditions

Drops can be deformed and broken up under different flow conditions. Interfacial tension stabilizes the spherical drop against deformation.
**Interfacial tension** \( \sigma \) is the specific interfacial area physical work \( W \) needed to expand the interfacial area \( A \) (e.g. during the deformation of an oil drop dispersed in a flowing watery continuous liquid phase.)

\[
\sigma = \frac{\Delta W}{\Delta A} = \left[ \frac{N \cdot m}{m^2} \right] = \left[ \frac{N}{m} \right]
\]  

(8.5)

The interfacial tension between two pure liquids is the result of the affinity between the molecules of the two liquids (affinity within each of the liquid phases and between them). The strength of the affinity is determined by physical and chemical interaction of the liquid phases. Because such interactions can be manyfold it is hard to predict the interfacial tension between two fluids. Even though, for pure materials it is possible to approximately calculate the interfacial tension from material constants characterizing their potential of interaction. In practice the interfacial tension is determined experimentally. A typical approach to determine it uses a drop in a surrounding fluid. Forces acting on the drop under static and/or defined dynamic conditions result in its deformation. When the forces acting on the drop are known, from the deformation of the drop the interfacial tension can be derived. E.g. in a pendant drop experiment, a drop is formed at a capillary tip within another immiscible liquid. When the density of the drop phase is larger than the continuous liquid phase, gravity leads to deformation of the drop to an elongated shape. The appropriate model equations (e.g. the Young-Laplace-equation) can be fitted numerically to the drop shape, to determine the interfacial tension between the two liquids.

**Laplace Pressure** The pressure difference \( \Delta p \) between inside and outside of an interface, depends on its curvatures and the interfacial tension \( \sigma \). Such pressure is called Laplace pressure and is given by the Young-Laplace equation:

\[
\Delta p = \sigma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

(8.6)

\( R_1 \) and \( R_2 \) are the two curvature radii of the interface. For an undeformed drop \( R_1 = R_2 \) and the equation Laplace pressure gets a function of the drop radius:

\[
\Delta p = \frac{2 \cdot \sigma}{R_{\text{drop}}}
\]

(8.7)
### 8.2 Emulsion formation and drop breakup

**Interfacial tension stabilizing drop shape**  A drop with large interfacial tension is more stable against deformation induced by mechanical forces. Thus, higher force (compared to a drop with low interfacial tension) is needed to deform a drop and break it into smaller ones. This counteraction and related impact factors can also be well illustrated using the dimensionless Capillary number \( Ca \). This number relates the stresses, leading to drop deformation e.g. in laminar flow to the interfacial tension related stabilizing stress being the Laplace pressure. The Capillary number is used when the applied force originate from viscous interactions. Instead, when inertial stresses are compared to interfacial tension related stresses the equivalent Weber number is used. However very similar definitions of both numbers are used by different authors and readers have to carefully distinguish between the different forms. For a drop in laminar shear flow the following Capillary number can be used:

\[
Ca = \frac{\tau_{\text{shear}}}{\tau_{\text{int}}} = \frac{\dot{\gamma} \cdot \eta_{\text{cont}}}{\dot{\gamma} \cdot \eta_{\text{cont}} \cdot d_{\text{drop}}} = \frac{\dot{\gamma} \cdot \eta_{\text{cont}} \cdot d_{\text{drop}}}{\sigma},
\]  

with \( \tau_{\text{shear}} \) and \( \tau_{\text{int}} \) being the viscous and interfacial tension related stresses, \( \dot{\gamma} \) being the shear rate, \( \eta_{\text{cont}} \) the continuous liquid phase viscosity, \( d_{\text{drop}} \) the drop diameter as characteristic length and \( \sigma \) the interfacial tension.

**Emulsifiers**  Interfacial tension can be greatly reduced by the addition of emulsifiers, such as surfactants or proteins. Such molecules consist of different chemical groups which are soluble in one or the other phase, for example a lipophilic tail of a fatty acid and a polar (hydrophilic) head group. Because of their amphiphilic nature emulsifiers spontaneously occupy the interface. Diffusion and adsorption to the interface takes time. The kinetics describing the diffusion and adsorption procedure differ greatly among different types of emulsifiers. In an emulsification experiment the interfacial tension for a liquid-liquid material system containing surface active ingredients is, therefore, time and process dependent. This is because the process also influences convection of the emulsifier to and from the interface. Typically their kinetics can be measured on a time scale a magnitude larger than the drop formation events during emulsification processes. This complicates emulsification-modeling, because the interfacial tension at the time the interface is expanded and broken up is hard to measure or predict.

**Drop formation at a capillary or pore**

**Wetting of a solid by two competing fluids**  Interaction of a liquid with a solid surface becomes important when drops are formed by injection of the disperse liquid phase into a continuous liquid phase through a capillary or a membrane pore. For a drop to form, the continuous liquid phase (and not the disperse liquid phase) has
to wet the solid surface. But both liquid phases compete in wetting the surface. Depending on which interaction affinity is stronger, the disperse phase more or less spreads onto the solid surface. This competition is expressed by the Young’s-equation relating the interfacial tensions to the contact angle $\beta$ between the disperse phase and the solid surface and expresses this competition:

$$\cos \beta = \frac{\sigma_{\text{sol,cont}} - \sigma_{\text{sol,disp}}}{\sigma_{\text{cont,disp}}}$$

(8.9)

$\sigma$ are the interfacial energies between solid surface and disperse liquid (sol,disp), the solid surface and the continuous liquid (sol,cont) and between the two liquids (cont,disp). The contact angle can vary between 0 and 180°, where 0° indicates complete wetting of the disperse phase liquid onto the solid surface and 180° indicates non wetting. In practice it is not possible to reliably measure contact angles below 10°, therefore contact angles smaller than 10° are depicted as $<10°$. It is possible to predict the three-phase contact angle, when knowing the interfacial energies. In practice, interfacial energies between a surface and a liquid can only measured indirectly by contact angle measurement of a drop liquid with known interfacial tension between liquid and air (=surface tension) placed on the surface. The interfacial energies are influenced by impurities of the liquids and by other factors such as the surface roughness of the solid. For practical applications it is recommended to measure the wetting behavior with the materials of interest in the application. In many cases characterization of the surface and calculation of the interfacial energies from models based on the surface tension of the liquids, may lead to erroneous results.

As mentioned before, the contact angle between the three surfaces is determined by the interaction of all the three interfacial energies. Therefore, all three components have to be taken into account when assessing their wetting behavior. For example a drop of silicon oil completely wets a hydrophilic surface when placed on it (contact angle close to 0°). When the same experiment is performed under water, the silicon oil does not wet the surface and the contact angle is close to 180°. Informative publications on the wetting of a surface by one liquid in another are [14] and [51]. Marmur [51] discuss the role of different factors in modeling the interaction base on theoretical calculations. Clint and Wicks [14] focus more on experimental evaluations. This case will be discussed in the following paragraphs.

In the case that the membrane or capillary is not wetted by the disperse liquid phase, the interface pinnes on the pore perimeter and a drop is formed. For such a case, a force balance between forces leading to drop detachment and forces holding the drop at the pore can be set up.
8.2 Emulsion formation and drop breakup

![Diagram of cone-plate shear flow cell](image)

Figure 8.1: Scheme of the cone-plate shear flow cell adapted from [58]. Shear flow is induced by the rotor.

**Forces acting on a drop attached to a capillary** A force balance has been set up to better understand the factors leading to a drop detachment from a membrane pore or capillary [63, 74, 86]. Authors concluded that under cross flow condition the main forces relevant for drop detachment are the interfacial tension force $F_\sigma$ and the drag force $F_r$ coming from the continuous phase flow.

\[
F_\sigma = \sigma \cdot d_{\text{pore}} \cdot \pi 
\]

\[
F_r = k_x \frac{3}{2} \cdot \pi \cdot \tau_{\text{wall}} \cdot d_{\text{drop}}^2 
\]

$d_{\text{pore}}$ is the diameter of a circular pore, $\sigma$ the interfacial tension, $\tau_{\text{wall}}$ is the wall shear stress and $k_x = 1.7$ is a coefficient accounting for the shape of the drop at its detachment. The model is based on the assumption that interfacial tension is constant during the process and that the drops detach in the dripping regime having the shape of a sphere attached to a wall [63]. By assuming $F_\sigma = F_r$ and solving for the drop diameter $d_{\text{drop}}$, the size at which the drop detaches can be calculated as:

\[
d_{\text{drop}} = \sqrt{\frac{2 \cdot d_{\text{pore}} \cdot \sigma}{3 \cdot k_x \cdot \tau_{\text{wall}}}} 
\]

The wall shear stress $\tau_{\text{wall}}$ present at the membrane can be induced by different flow setups. In this work a pressure driven flow in a rectangular channel (Figure 8.2) and a shear flow in a cone-plate shear cell was used (Figure 8.1).
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Table 8.2: Table for selecting the channel constant $K_{chan}$ of a channel with rectangular cross shape according to the aspect ratio of the channel. Table cited from [65, chap. 6]

<table>
<thead>
<tr>
<th>$W_{chan}/H_{chan}$</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>10</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{chan}$</td>
<td>28.45</td>
<td>20.43</td>
<td>17.49</td>
<td>15.19</td>
<td>14.24</td>
<td>13.81</td>
<td>12.81</td>
<td>12</td>
</tr>
</tbody>
</table>

**Pressure driven flow in a rectangular channel** Pressure driven flow in a channel with rectangular cross section can be described similar to the flow in a pipe with a circular cross shape. The Hagen-Poiseuille equation describes the throughput $\dot{Q}$ in a pipe for a given pressure drop $\Delta p$, a given length and diameter of the channel $L_{chan}$ and $D_{chan}$, the viscosity $\eta$ and the density $\rho$ of the fluid inside the channel under laminar flow conditions.

$$\dot{Q} = \frac{\pi \cdot \Delta p \cdot D_{chan}^4}{128 \cdot \eta \cdot L_{chan}}$$  \hspace{1cm} (8.13)

When the cross shape is not circular, the diameter has to be replaced by a representative diameter. For laminar flow the equivalent diameter, for turbulent flow the hydraulic diameter is chosen. The equivalent diameter is not calculated equally for each channel shape. E.g. the equivalent diameter $D_E$ for a channel with a rectangular cross section is calculated as follows ([65, chap. 6] (cited from [62])1):

$$D_E = \left( \frac{128 \cdot W_{chan} \cdot H_{chan}^3}{\pi \cdot K_{chan}} \right)^{\frac{1}{4}},$$  \hspace{1cm} (8.14)

where $W_{chan}$ and $H_{chan}$ are the width and the height of the rectangular cross shape of the channel. $K_{chan}$ depends on the ratio $W_{chan}/H_{chan}$ according to Table 8.2.1.

The hydraulic diameter for every channel cross shape is defined as:

$$D_h = \frac{4A}{P},$$  \hspace{1cm} (8.15)

where $A$ is the cross section area of the channel and $P$ its perimeter.

The Reynolds number gives an indication of the flow state in the channel (laminar or turbulent).

$$Re = \frac{\rho \cdot \bar{v} \cdot d}{\eta},$$  \hspace{1cm} (8.16)

1 checking the original paper revealed that the reference in Perry and Green [65] is wrong. The correct paper was not found.
8.2 Emulsion formation and drop breakup

Figure 8.2: Laminar flow profile along the height of a rectangular channel.

with \( \rho \) the density of the fluid in the channel, \( \bar{v} \) its average velocity, \( d \) the characteristic length and \( \eta \) the viscosity of the fluid inside the gap. For a circular pipe the characteristic length is the inner diameter of the pipe. For a rectangular shape the hydraulic diameter is used for calculation of the Reynolds number. Flow in a channel with circular cross shape starts to change from laminar to turbulent at approximately \( Re \leq 2100 \) and is fully turbulent at \( Re \geq 5000 \). For other geometries these values may change.

The wall shear stress in such a channel is not the same at all locations at the wall, because in a rectangular channel the flow profile is not axisymmetric. In a pipe with circular cross shape the wall shear stress in laminar flow is given as

\[
\tau_{wall} = f \cdot \frac{\rho \cdot V^2}{2},
\]

with the friction factor for laminar flow being \( f = \frac{1}{Re} \) and \( V \) the velocity of the fluid. When substituting \( Re \) by its definition, the wall shear stress for a laminar flow in a channel with rectangular cross shape becomes:

\[
\tau_{wall} = \frac{8 \cdot \bar{v} \cdot \eta}{D_h},
\]

When using the hydrodynamic diameter, an average wall shear stress can be calculated. By applying only the height of the channel, the wall shear stress of the upper and lower wall is calculated. This can be shown when assuming a developed parabolic flow profile along the height of the channel, where \( v \) is the local velocity in main flow direction, \( H_{chan} \) is the height of the channel, \( y \) is the distance from the centre of the channel towards the upper and lower wall, \( \bar{v} \) is the average velocity in main flow direction (see 8.2).

\[
v(y) = 2\bar{v} \cdot \left(1 - \frac{y^2}{H_{chan}^2} \right)
\]
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The local shear rate at the wall \((y = H_{\text{chan}}/2 \text{ top or } y = -H_{\text{chan}}/2 \text{ bottom})\) can be calculated by differentiation of the velocity profile:

\[
\frac{\partial v}{\partial y} = -\frac{16 \cdot \bar{v}}{H_{\text{chan}}^2} \cdot y
\]

(8.20)

And substitution of \(y\) with the local position at the bottom wall \((y = -H_{\text{chan}}/2)\):

\[
\dot{\gamma}_{\text{wall}} = \frac{8 \cdot \bar{v}}{H_{\text{chan}}}
\]

(8.21)

The local shear stress at the wall then can be calculated from the viscosity of the liquid in the channel \(\eta\) and the local shear rate:

\[
\tau_{\text{wall}} = \dot{\gamma}_{\text{wall}} \cdot \eta = \frac{8 \cdot \bar{v} \cdot \eta}{H_{\text{chan}}}
\]

(8.22)

The difference between Equation 8.22 and Equation 8.18 is that the hydraulic diameter is changed in Equation 8.18 to the height of the channel in Equation 8.22.

The friction factor in turbulent flow for a Reynolds number \(4000<Re<10^5\) can be calculated with the Blasius equation:

\[
f = \frac{0.079}{Re^{0.25}}
\]

(8.23)

After the fluid enters the channel the flow profile has to develop. A Reynolds-criterion was defined by Dombrowski et al. (cited from [65]) for the entrance length \(L_{\text{ent}}\) of a channel with circular cross shape:

\[
L_{\text{ent}}/D_{\text{chan}} = 0.370 \exp(-0.148Re + 0.0550Re + 0.260)
\]

(8.24)

\(D_{\text{chan}}\) is the diameter of the channel. Formula 8.24 can serve for the design of a flow cell. Laminar developed flow is reached after a length larger then the entrance length. Thus, to achieve a developed laminar flow at the position of observation, which is desired in the case in this work, the channel before this position should be longer than the entrance length. When the flow is turbulent the entrance length should be about \(L_{\text{ent}}/D_{\text{chan}} = 40\).
8.2 Emulsion formation and drop breakup

Drop deformation and breakup in laminar shear flow. Pure shear flow can be established when a flat wall moves in parallel to another flat wall at rest. Assuming a Newtonian fluid in the gap without wall slip, a linear velocity profile develops from zero speed at the resting wall and maximum speed at the moving wall. Hence, the shear rate is constant along the gap height. When a drop is located somewhere in the gap (far enough from the wall to be able to neglect confinement effects), the drop deforms in the shear field. The degree of deformation is dependent on the Capillary number $Ca$ and the viscosity ratio $\lambda$ of the two liquid phases ($\lambda = \frac{\mu_{\text{disp}}}{\mu_{\text{cont}}}$). Taylor developed a formula for small deformations ($Ca \ll 1$) to describe the deformation of a drop in shear flow as a function of the Capillary number and the viscosity ratio [85]:

$$D = Ca^{19\lambda + 16} \frac{16(\lambda + 1)}{}$$

with

$$D = \frac{L - B}{L + B}$$

Here $D$ describes the deformation with $B$ being the width of the elliptical drop and $L$ its length:

When a critical Capillary number is exceeded, the drop will undergo strong deformation and finally break up into smaller drops. Grace [30] studied burst of drops in flow. He found a dependency of the critical Capillary number on the viscosity ratio (see Figure 8.3.) As a rule of thumb, the lowest critical capillary number is reached at $\lambda = 1$. For larger and smaller viscosity ratios the critical capillary number increases. For viscosity ratios $>4$ breakup in simple shear is not possible any more. The applied viscous stress leads to deformation and rotation of the drop without breaking it up.

8.2.2 Process designs for emulsification

Various setups for the production of emulsions have been established in the past. Cartoons of some typical configurations are depicted in Figure 8.4. Most applied emulsification systems in industry are still rotor-stator systems and high-pressure homogenizers, because they are robust, can be scaled well, and enable a high throughput. However, they disrupt drops mostly in turbulent flow following a brutal force approach. Large energy inputs are required, which leads to a large energy dissipation in the form of heat (rather than its use for dispersion).
Figure 8.3: Critical $E_B \approx C_{a_{crit}}$ as a function of viscosity ratio. When the value of $E_B$ is above the curve the drop bursts, if it is below it only deforms without bursting (Figure from [30] with kind permission from Taylor & Francis).

Figure 8.4: Cartoons showing various conventional techniques for emulsification from Urban et al. [91] with kind permission from John Wiley and Sons.
8.2 Emulsion formation and drop breakup

Figure 8.5: Cartoons and photographs from literature showing various microfluidic setups for emulsification from [17, 18, 34, 48, 83] with kind permission from Springer and John Wiley and Sons.
Figure 8.6: Dispersing characteristics for different emulsification methods (Sauter diameter versus volumetric energy input) taken from [50] with kind permission from Elsevier. GMC: grooved micro channels [82], STMC: straight-through micro channels [43, 45], Y-junctions [78], membrane emulsification, flat valve homogenizer, orifice valve and microfluidizer [49].
Nevertheless, there are alternative methods which need less energy input for dispersing: Microfluidic chips have been used for emulsification in various configurations (see Figure 8.4). These setups consist of channel geometries at similar length scales as the drops they create. They control flow conditions and interfacial effects precisely. As a result, emulsions with nearly mono-sized drops are produced. Energy dissipation is much lower compared to rotor-stator-setups or high pressure homogenizers. Despite the big advantages of microfluidic systems, they usually have very low throughputs (few milliliters per hour) and cannot compete with most other devices for emulsification (which produce at several liters per minute).

Membrane systems try to span the gap between the brutal force approach of conventional methods for emulsification and the high-controll approach of microfluidics. In Figure 8.6 some typical dispersing methods along with microfluidic techniques are compared in terms of volumetric energy input influencing drop size (shown as reported in [50]). High pressure techniques as a flat valve homogenizer or a Microfluidizer need a higher energy input compared to membrane emulsification or some microfluidic systems, but are capable to produce smaller drops. Some of the emulsification techniques are described in the following paragraphs.

**Rotor/Stator devices**

As the name suggests, rotor-stator system consist of an immobilized (static) part and a moving (rotor) part. Static and rotating teethed plates, mounted on a shaft, alternate and are separated only by a gap (< 1 mm). Between the teeth of the plates, shear and elongational flow is induced. Additionally vortices are created leading to dispersion under turbulent conditions. A pumping effect is induced by the rotating plates, which circulates the product through the device when mounted in a container or a pipe containing a liquid. Advantages of such systems are the high flexibility to be used in batch- or continuous mode. Dealing with high viscosity fluids is not an issue as long as convection for the whole liquid volume can be guaranteed.

**High pressure homogenizer**

High pressure homogenizers consist of a pressure pump, pushing a liquid through a small gap. Gap size and pressure depend on each other because the pressure is adjusted by adjusting the force on the spring regulating the gap size. Typical gap size is in the range of 10 – 100 µm. Front and back of the gap is filled with product. Through high pressures of 10 – 100 MPa a turbulent jet of liquid exits the gap at a high speed (e.g. 100 m/s). Drops in the jet are elongated and broken up into smaller drops through different mechanisms. In literature regimes of inertial and viscous turbulent breakup as well a contribution from cavitation due to the high pressure
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drop are discussed [31]. Depending on the material system, small median drop sizes of \( \approx 0.2 \mu m \) can be achieved.

**Microfluidic for emulsification**

In microfluidic chips, flow and geometry can be well controlled. Therefore it is ideal to produce drops on a one-by-one basis. Although drop production frequencies of approximately 3000 drops/(second and site) are possible, production rates are far away from the needs in pilot scale or industrial scale processes. Nevertheless, the methods based on microfluidic chips are introduced here, because they have many design approaches in common to the one chosen later in this work. For all methods mentioned it is possible to produce drops with extremely small deviations from one drop to the next.

**Cross-flow and co-flow micro channel setup** Drop formation was studied by various researchers with microfluidic co-flow [18] and cross flow designs [34, 35, 92]. A disperse liquid phase is pushed into a continuous fluid phase at a junction of two channels (formed as a T (cross flow) or as a capillary within a larger channel (co-flow)). In both cases drop size is influenced by the channel sizes, interfacial tension, the flow rates and the viscosities of the two liquid phases. For sufficiently small disperse phase flow rate drops are formed in a dripping mode for which the size of the drops at detachment is determined by the interfacial tension holding the drop at the pore and the drag on the drop induced by the flow of the continuous fluid phase.

**Silicon/glass micro channels and EDGE design** Emulsification setups have been introduced, where a disperse phase is pressed through one wide or various small slits into a step-shaped opening area, filled with continuous phase [48, 93]. Because the interface forms a slug-like shape on the narrow region and expands on the step to a spherical shape, the Laplace pressure is smaller in the spherical section. This pressure gradient helps to detach the drop. Very narrow drop size distributions can be achieved, because the pinch-off is mostly influenced by the interfacial tension and the size of the gap, without the need of strong cross-flow. For functioning of the device the plateau must not be wetted by the disperse phase. Large viscosity ratios \( \lambda = \frac{\eta_{\text{disp}}}{\eta_{\text{cont}}} \) from 0.1–10000 seem not to be an issue. For critically small viscosity ratios the relative drop size increases [17]. Drop size is dependent on the interfacial tension and the gap size. In experiments from Dijke et al. [17] for various oils in a watery solution with sodium dodecyle sulfate as emulsifier, drop size were around 4.5 times the gap height of 8 \( \mu m \). In experiments of [50] drop size for water in oil emulsions was around 6 times the gap height of 1 \( \mu m \).
8.2 Emulsion formation and drop breakup

When looking at the dispersing characteristics in Figure 8.6 a positive slope for the drop size as a function of the energy input can be seen. This is somewhat counterintuitive, because one would expect enhanced drop breakup (and thus smaller drops) when more energy is put to the system. However, the energy that has to be put to the system in order to emulsify with the EDGE devise is mainly the built-up of trans-gap pressure that induces the flow of the disperse phase through the narrow and the deformation of the fluid interface. Therefore it is directly linked to the disperse phase flow rate. When this flow rate is increased drops become bigger, because they are filled during the phase of detachment. In other words, when energy is put to the system over a certain threshold, these energy is not used for the drop breakup but has an counteracting effect on drop breakup.

Flow focusing  Different examples for flow focusing devices can be found in literature [83, 102]. The key element that distinguishes this technique from other microfluidic channel designs for emulsification, is the control of a jet breakup by an external flow. This external flow helps to form a jet of the disperse phase and helps to detach drops in a controlled way. With this technique the drop size can be adjusted to a smaller diameter as the capillary dimension. In Figure 8.4 one example is shown. Two capillaries form a tube in tube setup. From the inner capillary a jet is formed in co-flow conditions with the continuous phase in the outer capillary. Both phases are forced through an orifice which lead to acceleration. This leads to elongation of the jet and a reduction in diameter. Drops detach from the jet are much smaller than the inner capillary diameter.

Membrane emulsification

In membrane emulsification a disperse liquid phase is pressed through the pores of a membrane into a continuous cross flowing fluid phase. Drops form at the pore outlet and are detached by the hydrodynamic force induced by the flow of the continuous liquid phase. Main advantages of membrane emulsification from a processing perspective are (i) low energy input resulting in a gentle treatment of the components and (ii) good scalability, and concerning the material characteristics, the adjustability of (iii) the mean drop size and the (iv) narrow drop size distribution width.

Over the last 25 years several studies investigating different membranes, processing conditions and describing the flow dynamics during membrane emulsification where conducted and published. After Nakushima _et al._ [60], who introduced the process, pioneering works by Peng and Williams [63] and of Schröder [74] were carried out. Both used micro porous ceramic membranes to study emulsion formation in lab and pilot scale. Additionally they conducted model experiments with drops detaching from capillaries to better understand the mechanics of drop formation and detachment
under cross flow conditions. Both introduced force balance models taking interfacial force and drag force as the main interacting forces into account. In accordance to such analytical momentum conservation model and related experiments, drop size was controlled by the velocity of the continuous fluid phase. Consequently, drop size decreased with increasing the velocity of the continuous fluid phase. [73] showed experimentally that lowering the interfacial tension by using the emulsifier sodium dodecyl sulfate (SDS) instead of Tween 20 leads to smaller drops. In lab scale experiments carried out by Peng and Williams [63] drop size increased when the trans membrane pressure was increased. They claimed that the disperse phase exited the pore at a higher velocity and causes the drop to be filled more during the detachment phase compared to lower trans membrane pressures.

**Wetting of membranes** Geerken *et al.* [27] studied the influence of the surface properties of micro sieves on the contact angle at the drop formation sites, thereby demonstrating in lab scale experiments the importance of adapting the membrane surface chemistry to the emulsion formulation. In particular, they coated silicon nitride membranes with silanes to alter them hydrophobic and by then proved that a well-controlled formation of water drops in a lipophilic phase was possible. When leaving the membrane in its original hydrophilic state the disperse phase (water) wetted the membrane without forming drops at the pores. More recently, Wagdare *et al.* [96] published the results of their work on emulsification utilizing micro engineered membranes. For emulsifying sunflower oil in a watery solution, they treated the membranes by air plasma to alter them hydrophilic and tested different surfactant combinations in order to achieve the same drop detachment morphology over the whole membrane area. They empirically found a few combinations of surfactant and co-surfactant for production of emulsions on lab scale with a narrow drop size distribution.

**Pore shape in membrane emulsification** The influence of pore shape on the detachment of drops was investigated experimentally by Kobayashi *et al.* [44]. They found that the slot aspect ratio has an influence on the drop detachment mechanism and claimed that a length-to-width pore ratio of >3 is required to induce *spontaneous* drop formation independent of the applied cross flow velocity.

**Numerical simulations** Several authors investigated the detachment of drops from pores by computational fluid dynamics (CFD) or modeled certain aspects of drop detachment. Timgren *et al.* [87] compared the drop development and detachment from single capillaries visualized by particle imaging velocimetry (PIV) to CFD simulations at relatively low wall shear stresses of up to 1.2 Pa. The authors showed that the morphology of necking of the drop during detachment influences the final
8.2 Emulsion formation and drop breakup

size of the drop. E.g. they state that a drop that is strongly deformed detaches at a smaller size. The deformation is promoted by higher drag onto the drop and higher viscosities of the disperse phase. Abrahamse et al. [2] used a flow cell together with computational fluid dynamics (CFD) [29] to investigate the role of pore distance during drop detachment through micro sieves. The size and the uniformity of the detached drops was influenced by steric hindrance of the emerging drops and low continuous phase drag lead to bigger drops, which were more likely to interact at the membrane. Rayner et al. [67] developed a simulation using a Matlab algorithm based on the Surface Evolver package [8] and investigated the influence of the mass transfer of surfactants to the drop interface on drop detachment. They were able to improve the prediction of drop size of drops detaching under quiescent conditions including the dynamic effect coming from the expansion of the drop and depletion of surfactant at its interface. Feigl et al. [21] simulated drop detachment from a single pore in shear flow using the openFoam software. When increasing the gap-capillary number, which corresponds to increasing the shear rate or viscosity of the continuous phase, they observed a transition from a more dripping-like drop detachment to a drop detachment from an elongated jet.

Dynamically enhanced membrane emulsification

In conventional membrane emulsification the membrane remains static. A pressure driven flow of the continuous phase is directed along the membrane surface and its mean velocity directly correlates to the size of the resulting drops. The production of smaller drops requires higher continuous phase throughputs, which in general results in a lower disperse phase volume fraction, limiting the use of such conventional membrane emulsification. Introducing a shear flow over the membrane to decouple drag on the drops and the cross flow velocity, can overcome this limitation. In literature this was investigated by inducing a rotor moving on the top side of a static membrane [57, 70, 105], or a cylindrical membrane rotating within an outer static cylinder [32, 70]. The flow inside the gap determines the emulsification result.

Shear gap flow properties The flow state in the gap determines the drop detachment from membrane pores. Schadler and Windhab [70] showed in their Rotating membrane setup that drop diameters dropped abruptly to the pore diameter and below when a critical Taylor number was exceeded. 

The Taylor number is a measure for the flow state in the gap between two counter-rotating cylinders. It is defined as follows:

\[
Ta = Re_{gap} \cdot \sqrt{\frac{2 \cdot s}{R_o + R_i}} = \frac{D_i \cdot n \cdot s \cdot \rho}{\eta} \cdot \sqrt{\frac{2 \cdot s}{R_o + R_i}} \tag{8.27}
\]
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$Re_{\text{gap}}$ is the gap Reynolds number, $R_o$ and $R_i$ are the radius of the outer and inner cylinder, $s$ is the gap height $(R_o - R_i)$, $D_i$ is the diameter of the inner rotating cylinder, $n$ is the rotor speed, $\rho$ is the density and $\eta$ is the viscosity of the fluid inside the gap. Schadler and Windhab [70] refer to a critical Taylor number of $Ta_{\text{crit}} = 41$ where the flow regime changes from laminar Couette flow (at lower Taylor numbers) to laminar flow with Taylor vortices. They successfully correlated a drop in drop size when crossing the critical Taylor number.

Andereck et al. [4] studied secondary flows in such a gap, dependent on the rotational speed of outer and inner cylinder. A variety of different flow regimes were found such as pure laminar Couette flow, wavy vortex flow, turbulent Taylor vortices, featureless turbulence and others (see Figure 8.7). Interestingly, Couette flow is maintained when the outer cylinder rotates ($Re_o = [-4000, 1000]$) and the inner cylinder is at rest $Re_i = 0$. Hence, when laminar Couette flow is the goal, such a configuration would be the best choice.

**Laminar flow in cone-plate design** Ellenberger and Fortuin [20] studied the onset of secondary flows in a cone-plate and plate-plate rheometer setup. They defined a Reynolds number $Re^*$ describing the flow state in the gap:

$$Re^* = \frac{\omega_0 \cdot \rho \cdot \delta}{\eta}$$

(8.28)

$R$ is the outer radius of the cone, $\rho$ is the density and $\eta$ the dynamic viscosity of the liquid inside the gap. $\delta$ accounts for the gap size and is defined as $\delta_c = R \cdot \theta$ for a cone-plate geometry, where $R$ is the outer rotor radius and $\theta$ the cone angle. For a plate plate geometry $\delta = \delta_p$, where $\delta_p$ is the distances between plate and rotor. The flow is laminar without secondary flows when $Re^* \leq 1$. Secondary flows are expected when $Re^* > 1$. 

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Figure 8.7: Regimes observed in flow between independently rotating concentric cylinders. Dashed lines indicate the transition boundaries that are difficult to establish from visual observation alone since there is no abrupt change in the appearance. Dotted lines indicate the expected, but not yet observed, continuation of several boundaries. $Re_o$ and $Re_i$ are the the Reynolds numbers for outer and inner cylinder defined as $Re_i = R_i(R_o - R_i)\omega_i/\nu$; $Re_o = R_o(R_o - R_i)\omega_o/\nu$ with $R_i$ and $R_o$ the radii of the inner and outer cylinder, $\omega_o$ and $\omega_i$ the angular velocities of the two cylinders, and $\nu$ the kinematic viscosity of the fluid in the gap between the two cylinders. Graph from [4].
9 Experimental: Visualisation of drop detachment from porous membranes

9.1 Introduction

The pilot scale process (described in chapter 10) aimed to produce emulsions with a narrow drop size distribution. Therefore a parameter window has to be defined. Finding such a process window is equivalent to finding process conditions were drops detach from membrane pores in a very controlled manner. Because effects like coalescence at the membrane surface, sterical hindrance of drops or inhomogeneous detachment of drops for different pores was likely to happen, characterizing the process only via global parameters, such as the drop size would not lead to a deeper understanding nor to directed design of the process. To overcome this black-box-problem, a separate flow cell for visualization of drop detachment was designed. Aim was to observe drop formation from micro engineered membranes and from commercial available membranes, each with different pore sizes at conditions similar to the pilot scale setup. The stress on the drops was created with a pressure driven Poiseuille flow in the visualization setup and by a shear flow in the pilot scale setup. Hence, the comparison of both setups was carried out by the wall shear stress and aiming for laminar flow conditions in both setups. Thereby it was important to optimize the visualization setup to reach the range of wall shear stresses accessible in the pilot scale setup and still be able to visualize drop detachment.

Most drop visualization setups found in literature for observing drop detachment from membranes or capillaries would not fulfill these criteria as they are usually built to watch drop formation at low cross flow speeds. At such creeping flow conditions entrance length to fully develop laminar flow are short (see Equation 8.24). A fully developed laminar flow was assumed to be reached when having a distance longer than the entrance length from the channel entrance to the membrane mount.

In the flow cell study, process and membrane parameters were studied exemplarily on micro engineered membranes from silicon nitride. In detail, median drop size, drop
Experimental: Visualisation of drop detachment from porous membranes

Size distribution width, and drop detachment morphology was evaluated depending on:

- membrane surface chemistry
- wall shear stress applied
- pore size
- inter pore distance
- trans membrane pressure
- pore shape

Additionally commercially available membranes made from sinter metal, sinter ceramics, woven meshes, and nickel were evaluated for their capability to be used in membrane emulsification.

9.2 Materials and methods

9.2.1 Fluids

For the preparation of oil-in-water emulsions, Hydrioil SOD.24 (Cas 36078-10-1) (Hydrior AG, Wettingen, Switzerland) was used as the disperse phase. It consists of hydrated acylesters (C12, C14) of oleic acid. Hydrioil is Newtonian and has a viscosity of 17 mPa s and a density of 0.86 g/ml at 25°C. Prior to the emulsification the oil was filtrated through PTFE syringe filter with nominal pore size of 0.45 µm. If fluorescent microscopy was applied to visualize drops, the oil was stained prior filtration with < 0.1 mg/g nile red (9-(Diethylamino)benzo- [α]phenoxazin-5(5H)-one, Sigma-Aldrich, Steinheim, Germany). The continuous phase consisted of a mixture of water, polyethylene glycol (PEG – Cas 36078-10-1, Polyglykol 35000 S, Clariant, Frankfurt, Germany) and polysorbate 20 (Cas 9005-64-5, Sigma Aldrich, Steinheim, Germany). To avoid possible ionic interactions deionized water was used. With polyethylene glycol the viscosity of the continuous phase was adjusted with 0, 6, 9 and 13 % PEG to viscosities of 1, 12, 26 and 57 mPa · s at 20°C, respectively. The measured values for the density of the continuous liquid phases were in a range from 1.00 to 1.02 g/ml at 25°C. For every concentration viscosity was measured during a temperature sweep from 21 to 28 °C. Viscosities for 0 % PEG were taken from literature values for water [84]. Viscosities for calculation of the wall shear stress were obtained by measuring temperature of the continuous phase and reading the viscosity from the temperature sweep experiment. Polysorbate 20 was used, at a concentration of 2 %, as an emulsifier to guarantee a fast stabilization of drops after detachment from membrane pores. The value for the interfacial tension in between Hydrioil and
the 2% polysorbate solution was 4.8 mN/m. It was measured at pending drop of a
2% polysorbate solution in Hydrioil at 26°C, 2 s after drop formation using a ten-
siometer PAT-1 (Sinterface Technologies, Berlin, Germany). Polyethylenglycol was
scaled to give the desired concentration for a batch of 5 kg. Polysorbate 20 was scaled.
Water was added to the final amount and the mixture was stirred until it became
homogeneous and transparent without any lumps or bubbles. Typically the mixing
took 30 to 120 min.

9.2.2 Experimental setup

For the microscopic observation of drop detachment from membranes, the setup de-
picted in Figure 9.1 and Figure 9.2 was used. Core of the setup is the flow cell, where
the drops are created. The drops, emerging at the membrane surface are watched
through the microscope (Leica DM-IRB, Leica Microsystems AG, Heerbrugg, Switzer-
land) and recorded with high-speed imaging (MEMRECAM fx RX-6, NAC Image
Technology, Japan). The samples were illuminated through the objective of the mi-
croscope by a 100 W Hg-lamp. In bright field microscopy the light was directed with a
semi transparent mirror (50% reflection, 50% transmission) to the sample. Reflected
light from the sample passes the mirror and is directed to the ocular or the high speed
camera. In fluorescent microscopy a filter cube is applied to the optical path. These
assembly of filters and a mirror transmits wavelength λ of 500 to 560 nm (green light)
to the sample. Only the fluorescent signal emitted by the sample (λ>590) (orange
light) is transmitted to the ocular or the high-speed camera.

During the experiment the continuous phase is pumped from a container, through
the flow channel by a screw pump (MCP-Z STANDARD V4.00, Ismatec SA, Zurich,
Switzerland). The outlet of the flow channel is connected to a tube that can either be
used to recirculate the fluid or to collect it in another container. The disperse phase
is kept in a reservoir above the flow cell made from a piece of a transparent tube from
RAU-PVC 7806. The reservoir is connected via a T-junction to a pressure sensor (ED
510/354.241/065 0...6bar, Haenni, Switzerland) and a source of nitrogen gas pressure.
To adjust pressure from the gas bottle, a three-stage pressure controller and a one-
stage pressure controller where used in series. With the first one the pressure was
adjusted to a pressure of 6 bar. The second controller was used to adjust the disperse
phase pressure desired for each experiment.

Flow cells Two flow cell were used in the experiments which were constructed in-
house (Jan Corsano, ETH Zurich, Switzerland). Technical details of the flow cells are
summarized in Table 9.1. A photographic image of the second flow cell can be seen
in Figure 9.3.
Figure 9.1: Scheme of experimental setup used for observing droplet detachment from porous membranes under cross flow conditions.

Table 9.1: Key data of two flow cells

<table>
<thead>
<tr>
<th></th>
<th>Flow cell 1</th>
<th>Flow cell 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell material</td>
<td>Alumina</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Transparent cover of channel</td>
<td>Plexiglas 1 mm</td>
<td>Plexiglass 2 mm</td>
</tr>
<tr>
<td>Channel height</td>
<td>1 mm</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>Channel width</td>
<td>20 mm</td>
<td>10 mm</td>
</tr>
<tr>
<td>Channel length before membrane</td>
<td>56 mm</td>
<td>152 mm</td>
</tr>
<tr>
<td>Channel length after membrane</td>
<td>56 mm</td>
<td>72 mm</td>
</tr>
<tr>
<td>Hydraulic diameter</td>
<td>1.905 mm</td>
<td>0.952 mm</td>
</tr>
<tr>
<td>Equivalent diameter</td>
<td>2.871 mm</td>
<td>1.435 mm</td>
</tr>
<tr>
<td>Wall shear stress at 1900 ml/min, 10 mPa s</td>
<td>44 Pa</td>
<td>354 Pa</td>
</tr>
<tr>
<td>Entrance length at 1900 ml/min</td>
<td>48 mm</td>
<td>48 mm</td>
</tr>
<tr>
<td>Entrance length turbulent flow</td>
<td>114 mm</td>
<td>57 mm</td>
</tr>
</tbody>
</table>
Figure 9.2: Photo of experimental setup for droplet visualization experiments. Computer and body of high-speed camera for storing and converting pictures are not shown.
Membrane mount and glue  Membrane mounts were tailored to the need of each membrane type. For micro engineered membrane samples of defined size, a cavity was shaped on top of the membrane mount little bigger than the membrane sample itself. For irregular shaped samples of micro engineered membranes and for sintered mesh type membranes the mount was kept flat in spite of a hole of approximately 4 mm diameter to supply disperse phase. For circular membrane samples of sintered material (ceramic or stainless steel) a cavity of the exact size of the membrane was formed. Membranes were glued onto the mount using Hysol 9483 (Henkel, Duesseldorf, Germany). In some cases also Araldit Cristal (Tesa, Beiersdorf, Germany) was used. Both glues are two component epoxy resins.

9.2.3 Membranes

To study drop detachment from membrane pores several different membranes were tested. Basic phenomena in drop formation and detachment were studied with micro engineered membranes produced within this work. See part I for more information. For comparison some commercially available membranes of several types were used. Table 9.2 gives an overview of the membranes used and their relevant properties.
## 9.2 Materials and methods

Table 9.2: Membranes and their properties used for trials in the flow cell setup

<table>
<thead>
<tr>
<th>Material (Brandname)</th>
<th>Thickness</th>
<th>pores</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane/ Support</td>
<td>Membrane/</td>
<td>size</td>
<td>distance</td>
</tr>
<tr>
<td></td>
<td>Support</td>
<td>measured</td>
<td>(specified)</td>
</tr>
<tr>
<td></td>
<td>µm</td>
<td>µm</td>
<td>µm</td>
</tr>
<tr>
<td><strong>Micro engineered membranes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silicon</td>
<td>100/300</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td>silicon nitride</td>
<td>2/300</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>PECVD/ silicon</td>
<td>1x4</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5x20</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>silicon nitride</td>
<td>1/300</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>PECVD/ silicon</td>
<td>10</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1x4</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10x40</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1x100</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>nickel alloy</td>
<td>70</td>
<td>3</td>
<td>67</td>
</tr>
<tr>
<td><strong>Sintered woven mesh</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>stainless steel</td>
<td>50/200</td>
<td>2x15</td>
<td>(2)</td>
</tr>
<tr>
<td>stainless steel</td>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Absolta)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>stainless steel</td>
<td>100</td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>/-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sintered metal membranes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>stainless steel</td>
<td>R 1 AX (1.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Sika-R ... AX)</td>
<td>R 3 AX (3.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R 5 AX (6.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R 15 AX (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sintered ceramic membranes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO2/TiO2</td>
<td>10/2500</td>
<td>0.45</td>
<td>(0.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.8)</td>
<td>(1.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.4)</td>
<td>(3)</td>
</tr>
<tr>
<td>−/TiO2 (INSIDE DisRAM)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
9 Experimental: Visualisation of drop detachment from porous membranes

9.2.4 Methods

Hydrophilization of surfaces  Prior to usage, the membranes were rendered hydrophilic by coating their surface with a thin layer of silicon oxide. Silicon membranes were treated via plasma oxidation in a plasma cleaner (PlasmaEtch, PE50, Carson City, USA) twice 5 minutes at 40 Pa, 100 W, O₂. In the case of membranes of silicon nitride and of nickel, a thin layer of approximately 50 nm silicon oxide was deposited onto their surface utilizing a device for plasma enhanced chemical vapor deposition (System80+ PECVD, Oxford Instruments, Oxfordshire, United Kingdom). See in appendix Table A.2 for process parameters. Before deposition, wafers were treated for 5 min in a oxygen plasma (Technics Plasma 100-E, PVA TePla AG, Wettenberg, Germany) at a pressure of 700 mtorr and a forward power of 200 W. Additionally, all membranes were plasma oxidized right before emulsification with the same procedure as the silicon membranes. The deposition of silicon oxide and plasma oxidation changed the water contact angle to < 10°, which corresponds to complete wetting. Static water contact angle on surfaces before treatment were 66 ± 5° for silicon, 84 ± 6° for silicon nitride and 114 ± 2° for titanium. Contact angles were measured, at least at three different drops of water (5 µl) placed on the surface. Two different measuring devices were utilized: the PAT-1 measuring device from Sinterface Technologies (Berlin, Germany) for silicone and the A100 device from Krüss GmbH (Hamburg, Germany) for other membrane surface materials. Membranes of each type were used for comparison, to examine the influence of treating membrane hydrophilization on drop formation. Absolta sintered mesh membranes, stainless steel sintered membranes and sintered membranes from ceramics were used as received from the supplier. Simple mesh membranes from stainless steel where only capable in producing drops when they were coated with a thin layer of silicon oxide.

Drop visualization experiment  Prior to each experiment the membrane was glued onto the membrane mount. The mount was cleaned with water, acetone and isopropanol before gluing. The gluing procedure depended on the membrane type. In the simplest case of a micro engineered membrane with standardized size, the membrane piece was fixed with little glue in the rectangular cavity on the membrane holder. After short curing, remaining gaps between membrane and mount were carefully filled with additional glue. This procedure smoothened the connection between membrane piece and holder. If not stated otherwise the membrane was plasma cleaned.

The membrane mount was inserted into the flow cell and fixed by a sealing and tightened by two screws and closed with the lid. Tubings for disperse and continuous phase were connected. Prior to every experiment each membrane was tested with air to detect leaks. When air was successfully pushed through the pores of the membranes
and no leakage was detected, the disperse phase reservoir was filled with oil. The continuous phase flow pump was set to a low speed, to prevent oil exiting the pores to fill the channel and cause contamination of the membrane surface and the transparent wall. After remaining air was pushed out from underneath the membrane, the flow speed of the continuous phase was adjusted to the lowest speed in the test plan. Subsequently, the pressure of the disperse phase was adjusted to form drops in the dripping regime. After a time of equilibration of approximately 1 min a high-speed movie was recorded to capture the morphology of droplet detachment at the pores (frame rate 5000 fps). If a good contrast between drops and background was achieved, a second movie a bit further downstream was recorded, typically at a frame rate of 100 fps and a shutter speed as short as possible to avoid in-motion unsharpness. The second movie was used later to determine drop sizes.

For the next observation the flow rate of the continuous liquid phase was increased. The disperse phase pressure was increased to compensate for the pressure built up caused by the continuous phase flow. By this compensation the transmembrane pressure was kept constant throughout the experiment (see also following paragraph).

After covering a range of continuous liquid flow speeds, the continuous phase was exchanged. Therefore the channel and tubings where rinsed three times with the new solution.

**Pressure calibration for visualization experiment**  To maintain a constant transmembrane pressure, the pressure built up caused by the continuous phase flow was compensated. In the flow cell it was not possible to measure the transmembrane pressure online. Therefore, a pressure calibration procedure was set up: Pressure was measured as a function of pump speed and viscosity of the continuous liquid phase by the pressure transducer of the disperse phase. For these procedure the membrane mount was left empty (no membrane) and the pressure gas inlet was shut. The pressure was measured for each viscosity of continuous phase for five pump speeds. A linear fit to the data (pressure as a function of pump speed) was used during the flow experiment to adjust the disperse phase pressure. So, the difference between channel pressure and disperse phase pressure (= transmembrane pressure) was maintained constant.

The mass flow of the pump was measured by collecting and scaling continuous phase fluid during intervals of 30 s to 2 min. Measurements were carried out twice for at least four flow speeds for each viscosity. Data were fitted with a linear model to convert the pump speed in arbitrary units to mass flow. Volume flow was calculated by using the density measured for each fluid.
Calculation of flow characteristics

**Hydraulic diameter** of pores and flow channel were calculated by Equation 8.15.

**Equivalent diameter** of the flow channel was calculated according to Equation 8.14 with the shape factor $K_{\text{channel}}$ of 12:

$$D_E = \left( \frac{128 \cdot W_{\text{chan}} \cdot H_{\text{chan}}^3}{\pi \cdot 12} \right)^{\frac{1}{4}}, \quad (9.1)$$

where $W_{\text{chan}}$ and $H_{\text{chan}}$ are the width and the height of the rectangular cross shape of the channel.

**Fanning friction factor** The fanning friction factor was used to plot data in the Moody diagram ($f(\text{Re})$). It is defined as:

$$f = \frac{D_r \Delta P}{2 \rho V^2 L}, \quad (9.2)$$

where $\Delta P$ is the pressure drop measured in a channel over the length $L$. $D_r$ is the representative diameter of the channel, $\rho$ the density of the fluid in the channel and $V$ the average velocity of the fluid.

**Channel Reynolds number** has been calculated with the equation

$$Re_{\text{chan}} = \frac{D_h \rho \bar{v}}{\eta}, \quad (9.3)$$

where $D_h$ is the hydraulic diameter of the channel, $\bar{v}$ is the average velocity in the channel in the direction of flow, $\rho$ the density and $\eta$ the dynamic viscosity of the continuous liquid fluid phase.

**Wall shear stress** at the upper and bottom wall of the channel neglecting edge effects and assuming fully developed laminar flow have been calculated with the equation

$$\tau_{\text{chan}} = \frac{8 \bar{v} \eta}{H_{\text{chan}}}, \quad (9.4)$$

where $H_{\text{chan}}$ is the height of the channel.
9.2 Materials and methods

9.2.5 Analytics

**Viscosity measurement** Rheological measurement were carried out with a Rheometer (MRC 3000, Anton Paar, Graz, Austria). Viscosity of the fluids was measured as a function of the shear rate $\dot{\gamma}$ from 1 to 500 s$^{-1}$ (shear curve). Additionally the viscosity was measured as a function of temperature ($20 - 35^\circ C$) at a constant shear rate of 100 s$^{-1}$.

**Density measurement** Density of the fluids was measured with an oscillating U-tube density meter (DMA-38, Anton Paar, Graz, Austria).

**Interfacial tension measurement** Interfacial tension between the oil and a watery phase was measured with a pendant trop tensiometer (PAT-1, Sinterface Technologies, Berlin, Germany). The watery phase was used as the drop phase. A drop was formed at the capillary (2 mm, stainless steel) and the drop shape was recorded during 10 minutes. Interfacial tension was calculated with the device software by giving the densities of the two fluids and analyzing the drop shape.

**Bubble point determination of a membrane** The bubble point of a membrane is equal to the pressure difference $\Delta p$ at which air can be pushed through the membrane into a liquid. For circular pores it depends on the diameter of the pores $d_{\text{pore}}$, the interfacial tension between air and the continuous fluid $\sigma$, and on the contact angle of the continuous phase fluid with the membrane $\beta$. For simplification the contact angle can be neglected, if the continuous phase wets the membrane surface ($\cos \theta = 1$):

$$\Delta p = \frac{4 \cdot \sigma \cdot \cos \beta}{d_{\text{pore}}} \approx \frac{4 \cdot \sigma}{d_{\text{pore}}}$$

(9.5)

Prior to emulsifications experiments the bubble point was determined. The pressure is a good measure of thumb to confirm that the setup has no leaks and the membrane is without defects. The following procedure was used to determine the bubble point: The continuous phase channel was filled with liquid and the reservoir for the disperse phase was kept empty. The pressure of nitrogen was slowly increased. When the first pore of the membrane starts to bubble the pressure was documented as the bubble point.
Drop size determination  The droplet sizes in an emulsification experiment were determined by image analysis of the high-speed movies. Several frames of the movies showing drops after detachment were analyzed using ImageJ (Public domain software, NIH, USA, http://rsb.info.nih.gov/ij/). The high-speed movies were converted frame by frame to black and white images. Dimension of the image was converted from pixel to micrometer by length calibration with a known distance in the image (e.g. distance between pores). The threshold for that conversion was determined for each movie empirical by checking if drops were recognized without including to much of the shadow around the drop. After setting a threshold, the drops appeared as well-defined black spots. Their area was analyzed using the ImageJ software (macro script SH_IJ-drop-analysis.txt). The circularity for the particles to be analyzed had to be given. It was useful to set also a value for minimal and maximal expected drop size to reduce wrong positive recognition of other features in the images. Setting the circularity to a value of above 0.9 (1 would be a perfect sphere) ensures that overlapping drops are not analyzed. The diameter of each drop was calculated from this area, assuming that it reflects the cross shape through a spherical drop. For each data point typically over 400 drops were measured. Toward lower wall shear stresses fewer drops were captured, because of a longer drop formation time. Nevertheless, at least 25 drops were analyzed. From these diameters the drop size distribution tables for the cumulative and frequency distribution of the volume based distribution \((Q_3,q_3)\) were calculated. The drop size median value \((X_{50,3})\) of the cumulative distribution was used for plotting drop size data. The calculation was carried out according to the DIN/ISO standard [36] with a user defined Matlab\(^1\) script (semanalyzer_table_mac.m) or a user defined R-script\(^2\) (SHareasToPSD2.R). If an automatic analysis of the movies was not possible a few hundreds of drops were analyzed manually by marking droplets with a three points or a line and adding this to the ROI manager. The objects in the ROI manager than were finally analyzed and saved to a list of results.

### 9.3 Results

#### 9.3.1 Pressure calibration at emulsification site for different flow rates and viscosities

In Figure 9.4 A the pressure drop measured at the membrane site (without a membrane mounted) as a function of the pump speed is given. A linear function was fitted

\(^1\)MathWorks, Inc., USA, version R2010a

to each dataset and is also shown in the plot. It was attempted to apply models from literature to explain the pressure data. Several models were tested and plotted (not shown). The differential pressure from the two configurations (pressure drop over the long or short end) was overall explained well when applying the model commonly used for the pressure drop in a circular tube for laminar flow (Equation 8.13), and substituting $D_{chan}^4$ with $D_E^2 \cdot W_{chan} \cdot H_{chan}$ to account for the channel shape, where $D_E$ is the equivalent diameter, $W_{chan}$ and $H_{chan}$ are width and height of the channel cross shape (see Figure 9.5). For the two fluids with highest viscosities the data were well explained. For lower viscosities the model predicted a lower pressure drop than measured. For the individual pressures of one configuration no convincing model could be found. The deviation might have been caused by entrance and exit effects which were not modeled. To maintain a constant trans membrane pressure during emulsification, the pressure applied to the disperse phase was adapted. For this correction a linear fit of pressure drop as a function of pump speed was used (see Figure 9.4) (and not the model). For completeness the pump calibration data with the regressions used are depicted in Figure 9.4 B.

### 9.3.2 Variables influencing drop formation and detachment from membranes.

**Membrane surface properties**

In Figure 9.6 the influence of hydrophilization the membranes with silicon oxide is shown. Oil was pushed through the membrane into the cross flowing continuous phase. When the membranes were not coated by a thin layer of silicon oxide, the oil adhered to the membrane, thereby wetting the membrane surface and spread over it. It was not possible to achieve drop detachment in dripping regime by adapting disperse phase pressure or continuous liquid flow rate. When the surface was coated with a layer of silicon oxide of roughly 10 to 50 nm the oil was less affine to the surface and it formed drops. These drops detached at the pore rims. These trials were performed in *Flow cell 1*, without addition of PEG to the continuous phase. Therefore the channel Reynolds number were already in the range of the 1700-3000, which is above the laminar regime.

**Pore size**

Figure 9.7 shows drop size data corresponding to lab-scale experiments conducted in the flow cell using four different membranes with different pore sizes. Drop size increased with pore size for a given wall shear stress. For all pore sizes, the drop diameter decreased with increasing wall shear stress. The dependency of the drop
Figure 9.4: A: Pressure measured at the position membrane mount position as a function of the pump speed. Data are for four different viscosities. Channel length from position of measurement to the end of the flow channel was 72 mm. B: Calibration data of the pump used for the continuous phase. Points reflect the data taken by measuring the mass pumped in a certain time. The lines show the linear fit. Coefficients of the regressions for the fluids of different viscosities are given in the legend.
Figure 9.5: A: Differential pressure between two configurations of the flow channel as a function of volume flow rate (152 mm and 72 mm channel length from point of measurement to end of flow channel). The lines represent the model derived from the Hagen-Poiseuille equation substituting $D_{chan}^4$ with $D_E^2 \cdot W_{chan} \cdot H_{chan}$ to account for the channel shape, where $D_E$ is the equivalent diameter, $H_{chan}$ and $W_{chan}$ are height and width of the channel cross shape. The numbers next to the measurement points are the channel Reynolds numbers. B: same data plotted as Fanning friction factor versus Reynolds number. The equivalent diameter $D_E$ was used for the friction factor and the hydraulic diameter $D_h$ for the Reynolds number. The line goes along $f = \frac{16}{Re}$ showing the expected trend for purely laminar flow in a channel.
9 Experimental: Visualisation of drop detachment from porous membranes

Figure 9.6: Visual observation of wetting properties of three different membrane types. Oil is pushed through the membrane into the continuous phase which flows across the membrane (from right to left). The calculated wall shear stress was in the range of $10 \pm 3 \text{ Pa}$. The scale bar indicates a length of $100 \mu\text{m}$.
9.3 Results

Figure 9.7: Median drop size as a function of wall shear stress $\tau_{wall}$ for three pore sizes. The lines are fits of the equation $X_{50,3} = K \cdot \sqrt{\frac{1}{\tau_{wall}}}$

size on the wall shear stress was less pronounced towards smaller pores. The spans of the volume based drop size distribution for the same dataset are plotted in Figure 9.8. When considering the entire dataset, a tendency for increasing span with increasing wall shear was found. This became clearer when some large spans for measurements at wall shear stresses of $1 - 17 \text{ Pa}$ were neglected. Focusing on individual sets regarding the pore size, these tendency was still valid with one exception: the spans obtained from $12 \mu m$ silicon membranes showed a tendency for decreasing span with increasing wall shear stress. Overall the width of the distributions were narrow, which is indicated by the spans being (all but one) below unity.

In Figure 9.9 pictures of drops detaching from the three membrane types at different wall shear stresses are given. When comparing pore sizes, only little differences in the morphology of drop detachment were found. In all cases the drops detached in a dripping regime. The point of pinch off was at the pore rim. The drops deformed only slightly before detachment. The deformation was mostly pronounced for the bigger sized pores. There, the detachment morphology was already in transition to jetting (at a wall shear stress of $150 \text{ Pa}$). The high speed movies revealed interaction between emerging and detaching drops: it often happened that drops grew simultaneously at the membrane pores. When the first drop detached, it forced others to detach as well. This sometimes happened by one single drop bumping away the next when their trajectories coincided. It was also observed that drops in the vicinity of detaching drops detached, even when they did not touch each other. This presumably was
caused by induction of secondary flows by the moving drop. In none of the cases it was observed that drops coalesce. Coalescence did not even occur when neighboring drops touched while still attached to the pore rim.

**Dimensionless analysis** Dimensionless analysis was performed according to the Buckingham Pi Method (see Perry and Green [65]). The method reduces the number of variables relevant for drop creation in the membrane emulsification experiment from the four physical quantities: wall shear stress $\tau$, pore diameter $d_{\text{pore}}$, drop diameter $d_{\text{drop}}$, and interfacial tension $\sigma$, to two dimensionless quantities: dimensionless drop size, $d_{\text{dim}} = d_{\text{drop}} / d_{\text{pore}}$, and the Capillary number $Ca^* = \frac{\tau d_{\text{pore}}}{\sigma}$. The pore throughput and viscosity of the disperse phase liquid was not included, because all membranes were investigated in the dripping regime at a trans membrane pressure close to the minimum trans membrane pressure. Inertia effects coming from the pore flow were thus negligible. Plotting these two dimensionless variables versus each other in a log-log-plot for the dataset of circular pores, lead to a linear relationship (Figure 9.10).
9.3 Results

Figure 9.9: Droplet detachment from membranes viewed from top. Representative pictures are given. Continuous liquid flows from right to left. On each picture at least one drop pinches off at the moment of observation. The scale bar indicates 50 µm.

Figure 9.10: Dimensionless drop size as a function of Capillary number as obtained from dimensionless analyses. The dataset for micro engineered membranes having circular pores is plotted. The line represents a log-log-linear fit to the data.
**Inter pore distance**

A large porosity of the membrane was preferred for achieving a large membrane throughput. This is especially relevant for small sized pores (e.g. 1 µm diameter), because the pore flow rate decreases with pore size. However, reducing the inter pore distance lead to coalescence of the oil phase immediately after exiting the pore outlet. Thus the membrane was wetted by the disperse phase and no controlled drop formation was possible. The pore distance was optimized toward the closest pore distance possible, while maintaining good control over drop detachment. Therefore, experiments with varying distance between pores were carried out. Membranes with arrays of circular pores of 1 µm in diameter were produced with inter pore distances of 2, 6, 20 and 50 µm. Drop detachment experiments were carried out and the morphology of drop detachment was captured by means of high-speed imaging as a function of wall shear stress and trans membrane pressure. The continuous phase viscosity was adjusted by adding 6% PEG. The bubble point was measured to be 1.3 bar trans-membrane pressure at a continuous liquid flow rate of 400 ml/min ($\tau_{wall} = 220$ Pa).

For a low pore distance of 2 µm it was not possible to adjust drop formation to a dripping regime. Drops exiting from neighboring pores coalesced immediately. At all conditions tested, drops formed only from film rupture of the oil layer adhered to the membrane surface similar to to Figure 9.11. Also the mode of drop formation at low inter pore distance was not the same over several membrane squares indicating a state of drop formation which is unstable and may change due to small perturbations of processing conditions. With increased inter pore distance it became easier to adjust drop detachment to a dripping regime. For low trans membrane pressure ($\leq 0.23$ bar) and for pore distances 20 and 50 µm, dripping was found for a wide range of wall shear stresses from 100 to 600 Pa as shown in Figure 9.12. For pore distance of 6 µm, dripping was achievable at high wall shear stress. At low wall shear stress coalescence of drops emerging from neighboring pores was observed. However, the dripping state was hard to maintain stable. The increase of the trans membrane pressure over a threshold, which was close to the minimum pressure for disperse oil flow, induced coalescence on the membrane surface.

**Pore shape**

There is evidence in literature indicating an influence of pore shape on drop detachment from membrane pores. In particular it is stated that aspect ratios of slit pores of above three lead to spontaneous drop detachment at a small drop size without the need of applying a drag force [44]. In this work, drop detachment from slit shaped pores was compared to drop detachment from circular pores of same width, to investigate this effect. Slit pores of aspect ratio 4 (1x4, 5x20, 10 x40 µm) and 100 (1x 100 µm)
Figure 9.11: Example for membrane wetting when pores distance is too small. Oil exiting a silicon nitride membrane with pore diameters of 1 µm and inter pore distance of 2 µm.

Figure 9.12: Drop detachment from silicon nitride membranes for different pores distances of pores of 0.9 µm diameter and two different wall shear stresses. Viscosity of the continuous phase was adjusted with 6% PEG. Flow of the continuous liquid from right to the left.
Table 9.3: Silicon nitride membrane parameters.

<table>
<thead>
<tr>
<th>Pore size</th>
<th>pore distance</th>
<th>membrane thickness</th>
<th>pores per square</th>
<th>flow direction</th>
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<tr>
<td></td>
<td>[µm]</td>
<td>[µm]</td>
<td></td>
<td>comp. to long pore side</td>
</tr>
<tr>
<td>1x4</td>
<td>50</td>
<td>1</td>
<td>4x4</td>
<td>perpendicular</td>
</tr>
<tr>
<td>1x100</td>
<td>single pore</td>
<td>1</td>
<td>1</td>
<td>perpendicular</td>
</tr>
<tr>
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<td>single pore</td>
<td>2</td>
<td>1</td>
<td>perpendicular</td>
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<td>perpendicular</td>
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<td>single pore</td>
<td>1</td>
<td>1</td>
<td>parallel</td>
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<td>1</td>
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<td>3x3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>single pore</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

were chosen (see also Table 9.3). In Figure 9.13 the dimensionless drop size is plotted as a function of the applied wall shear stress. When comparing drop size obtained from pores with same pore width, the dimensionless drop diameters were similar for slit pores compared to circular pores of width 5 and 10 µm. In case of pores of 1 µm width the dimensionless drop diameter for a given wall shear stress is smallest for the pores with aspect ratio 4. The dimensionless drop size obtained from circular pores of 1 µm diameter compared to drop diameter obtained from 1 times 100 µm were very similar at a given wall shear stress with a tendency of bigger dimensionless drop size for the slit pore. For all cases studied with slit pores in this work, a strong dependency was found between the drop size and the wall shear stress. In case of 1x4 µm slit pores minimum drop size was already reached at low wall shear stresses of approximately 50 Pa. For even higher wall shear stress the decrease in drop size was small.

As seen in Figure 9.14 the drop interface attached to the entire pore rim and the point of droplet pinch-off is outside the pore, leveled above the membrane surface. It was not possible to detect the exact morphology of the interface at the pore for smaller pores, because the optical resolution of the setup was not high enough to resolve detail in this size range.

In Figure 9.15 the span for the same dataset as in Figure 9.13 is plotted as a function of the wall shear stress. A general tendency was found of increasing span with increasing wall shear stress. This trend is only infringed by the data for a slit pore of dimension 1x100 µm. There spans were overall higher at a given wall shear stress compared to the rest of the data and the span had a tendency to decrease with increasing wall shear stress.

Pictures taken from high-speed imaging of drops detaching from a pore of 1x100 µm...
9.3 Results

Figure 9.13: Dimensionless drop size as a function of the wall shear stress. Comparison of circular and slit shaped pores. One plot for each pore width. Data from 0% PEG in the continuous phase were excluded. The legend depicts the dimension of the pores in micrometer.

Figure 9.14: Drop detachment from a 10x40 µm pore. The drop interface attaches to the wall at all stages of drop growth and detachment.
9 Experimental: Visualisation of drop detachment from porous membranes

Figure 9.15: Span values based of the volume based drop size distribution for various pore sizes as a function of the applied wall shear stress for circular- and slit-shaped pores. One graph for each pore width. The legend indicates the pore dimensions in micrometer. The lowest viscosity of 0% PEG has been excluded. All channel Reynolds numbers were below 400.

Figure 9.16: Pictures from high-speed imaging of drops detaching from a slit pore of dimension 1x100 µm for different wall shear stresses. Pictures where taken directly before pinch-off of the drops. Black arrows indicate drops at the pore where not clearly visible.
at different wall shear stresses are depicted in Figure 9.16. At low wall shear stress of 10 Pa drops grew large and neighbor drops touch. With increasing wall shear stress this interaction was reduced because the number of drop detachment sites remained nearly constant and the drops detached at a small size. The trans membrane pressure (calculated from the difference between continuous phase pressure from calibration measurement and disperse phase pressure) was adjusted to 0.3 ± 0.1 bar. The number of drop creation sites at one pore varied between 3 and 9 but showed no systematic trend as a function of the trans membrane pressure or the wall shear stress.

Drop detachment from slit shape pores oriented perpendicular or parallel to the continuous flow direction  In the initial phase of drop growing from slit shaped pores the shape of the interface was not spherical (as it would be for drops growing at circular pores) but had more an elliptic shape. This was caused by the interface attaching to the perimeter of the high aspect ratio pore. When the pore is oriented perpendicular or parallel to the continuous flow direction for the same volume of fluid attaching at the pore (above the membrane surface level) a different cross shape of the drop is exposed. Thus it was expected that the mechanism of drop detachment may differ for different orientation also resulting in a different dependence between the drop size and the wall shear stress. In Figure 9.17 the drop size as a function of the wall shear stress is compared for pores arranged parallel and perpendicular to the continuous flow direction. For large pores of 10 x 40 µm the orientation had no significant influence on the drop size for a given wall shear stress. When crossing a critical wall shear stress from low to high, for pores of 5 x 20, 1 x 4 and 1 x 100 µm, smaller drops were detected for pores oriented perpendicular to the flow compared to parallel orientation.

In Figure 9.18 the span of the volume based drop size distributions is depicted for the same data set. For 1 x 100 µm pores oriented parallel to the flow, mechanical supersession of drops at the back of the pores by drops emerging at the front of the pore, and moving towards the back, was observed. This lead to early detachment of the latter drop or to coalescence. Coalescence was seen more regularly when increasing the wall shear stress. Such events of supersession and coalescence are depicted in Figure 9.19.

Membrane type – commercial membranes

Customized micro engineered membranes were studied in comparison with commercially available ones. As previously described, the parameters (i) membrane surface properties, (ii) pore size, (iii) inter pore distance, (iv) pore shape have been studied independently. For typical commercial membranes these parameters are dependent on each other. The focus was set to some typical examples for commercially available
Figure 9.17: Dimensionless drop size as a function of applied wall shear stress for slit shaped pores oriented perpendicular and parallel to the continuous flow direction. Pore size is depicted in the legend as micrometer. E.g. 10x40 is a pore of 10 x 40 µm with the long side perpendicular to the flow, whereas 40x10 is the same pore oriented the long side parallel to the flow direction.
Figure 9.18: Span of the volume based drop size distribution as a function of the applied wall shear stress. In each graph the orientation of one pore size is compared with respect to its orientation to the continuous liquid flow direction. E.g. 10x40 is a pore of 10 x 40 µm with the long side perpendicular to the flow, whereas 40x10 is the same pore oriented the long side parallel to the flow direction.
Figure 9.19: Pictures from high-speed imaging of drops detaching from a slit pore of dimension $1 \times 100 \, \mu m$ oriented parallel to the continuous flow direction. Occasionally drops emerging at the front of the pores are pushed against neighbor drops emerging at the back of the pore. This leads to an early detachment of the latter (left) drop or to coalescence of drops (right). Arrows indicate the corresponding event.
membranes. These were sintered membranes of ceramics and metal. Additionally, sintered metal mesh membranes were studies. For further information see Table 9.2.

Drop detachment was studied with the same procedure as micro engineered membranes by visualization of drop detachment from the membrane surface by high-speed imaging of flow cell experiments. It was necessary to increase the contrast between membrane and drops to visualize them. This was carried out by switching to fluorescent microscopy and staining the disperse liquid phase with the fluorescent dye nile red. Size measurement where carried out by manual evaluation of high-speed movies taken with bright-field microscopy at a spot downstream (after the membrane mount). This compromise was made, because fluorescent microscopy did not provide sharp images of drops flowing over the membrane or channel wall. In addition the contrast with bright-field imaging was good enough to detect drops when flowing over the channel wall but not good enough to detect them automatically as otherwise done in this work.

**Control of drop detachment regime by adjusting disperse phase pressure.** As already mentioned the trans membrane pressure is an important parameter to control transition from a dripping regime to a jetting regime. In the dripping regime drops detach at the pore rim, in the jetting regime drops detach from a jet originating from the pore. Increasing the trans membrane pressure above a certain threshold, that mainly depends on the membrane used, lead to a flooding of the membrane surface by the disperse phase fluid. If drops still detached from the wetted area, their size varied strongly and there was no control over drop size by the pore size. For large pores and high porosity membranes the different regimes of drop detachment depended strongly on variation of the trans membrane pressure. For some of the membranes tested in this section it was therefore difficult to adjust drop detachment regime. Even different regimes where observed depending on the location on the membrane. The results on drop sizes presented in this section are based on adjusting a dripping mode at the lower end of transmembrane pressure possible for creating drops.

**Drop size distribution obtained from drop detachment experiments from commercial membranes** In Figure 9.20 and Figure 9.21 the median diameter and the span of drop size distributions are plotted for drops detached from different types of commercial membranes. For comparison, the fitted lines from experiment completed with micro engineered membranes with circular pores from this work are plotted.

The expected trend of decreasing drop size was found for most of the membranes tested. However, for sintered membranes with nominal pore size of 1 µm (metal type)
Figure 9.20: Median drop diameter plotted as a function of wall shear stress applied in the flow cell, obtained for different kinds of commercially available membranes with different nominal pore sizes. A: Sintered metal membranes SIKA-R-Ax, B: Sintered Ceramic membranes TAMI, C: Ceramic membrane from titanium oxide, D: unsupported metal mesh. Fits from data obtained from micro engineered membranes with circular pores are plotted for comparison. The numbers in the legend relate to nominal pore size in micrometer.
Figure 9.21: Span values of drop size distribution plotted as a function of the wall shear stress applied in the flow cell, obtained for different kinds of commercially available membranes with different nominal pore sizes. A: Sintered metal membranes SIKA-R-Ax, B: Sintered Ceramic membranes TAMI, C: Ceramic membrane from Titanium oxide, D: unsupported metal mesh.
and 0.45 µm (ceramic type) and wall shear stresses between 3 and 44 Pa this trend was inverted. When comparing drop size to nominal pore size especially for the series of ceramic type membranes the smallest pore size produced the largest drops at a given wall shear stress and the membrane with largest pores produced the smallest drops (see Figure 9.20 B). An unusual relationship between drop size and wall shear stress was observed for a ceramic membrane of titanium oxide. The drop size was almost independent from the wall shear stress (see Figure 9.20 C).

For sintered metal membranes the drop size obtained is roughly in the same size range as for micro engineered membranes with circular pores between 10 an 12 µm. Smallest drop size for sintered ceramic membranes are in the size range produced by micro engineered membranes with pore diameters in the range of between 1 to 5 µm. The drop size from the woven mesh type membrane fits best to the data from micro engineered membranes with pore diameter of 10 µm.

The width of drop size distributions measured for sintered membranes made of metal or ceramics had a trend to decrease with increasing wall shear stress, which is an opposite trend compared the results obtained in most of the cases from micro engineered membranes in this work. For the ceramic titanium oxide membrane the span was low and close to constant over the wall shear stress range tested. For the metal mesh type membrane spans are scattered versus wall shear stress and show no obvious trend.

**Morphology of drop detachment from commercial membranes** Membrane surfaces were observed by microscopy during emulsification of disperse liquid phase pressed through the membrane into cross flowing continuous phase. Figure 9.22 gives an overview over the different morphologies of drop formation observed for membranes tested which are commercially available. The trans membrane pressure was empirically adjusted to achieve the best uniformity of drop formation over the membrane area in a dripping regime at a low wall shear stress. Increasing the trans membrane pressure over a certain threshold, which depended on the pore size and the membrane type, usually lead to flooding the membrane surface with disperse liquid phase and no controlled drop formation was observed.

**Drops from sintered woven stainless steel membranes** (Figure 9.22 A) The critical trans membrane pressure between drops forming in dripping state and complete flooding of the membrane with disperse phase was in the range of a few millibar, which is lower than the pressure possible to adjust in a reliable manner with the setup used. When matching a pressure that enabled flow not causing flooding, drops formed individually from the pores between the wires of the mesh. Part of the drops coalesce with neighbor drops. The coarse protective mesh, sintered to the top surface
Figure 9.22: Visualization of drop detachment from different types of commercial membranes at different wall shear stresses applied. Pictures are taken from the top drops coming out of the paper plane. Images were taken in bright light microscopy or fluorescent microscopy. Continuous flow direction is from left to right in all images. In some cases (C, D, F,) the disperse phase is marked for clarity.
of the membrane, acted as a flow barrier for the continuous phase and prevented direct access to the pore outlets. Detaching droplets were observed to move in a circular motion, first moving against the average flow direction and then accelerating in main flow direction, which indicated the formation of vortices in the cavities between the wires of the coarse topside mesh. The regime of drop formation was inhomogeneous over the membrane area. At 10 Pa wall shear stress drops detached in a dripping regime from the pores or in a more jet-like manner where drops were ruptured from larger drops trapped in the cavities of the coarse mesh. For a wall shear stress of 90 Pa the jet-like drop detachment regime was dominant. It was not clear if drops detached far downstream away from the pores from a stable jet or more close to the pore, because time resolution during fluorescent microscopy was not sufficient. It was assumed that drops detached relatively close to the pore, because light intensity of the streamlines was oscillating with time.

**Drop formation from stainless steel mesh** Drop formation at stainless steel mesh membranes was only possible with the liquids chosen, when coating the membrane with a silicon oxide layer before emulsification. The maximum trans membrane pressure to maintain drop detachment in the dripping regime was low, similar to the sintered woven mesh membranes. Drop formation was feasible without coalescence of neighboring drops, if the right pressure for the dripping regime was matched.

**Drop formation from stainless steel sintered membranes** (Figure 9.22 B) The mechanism of drop formation was similar for the different nominal pore sizes tested. Therefore various representations of the drop formation are shown in Figure 9.22 C/D to illustrate the morphologies observed. At low wall shear stresses (as illustrated on the left pictures of SIKA-R 15 and Sika-R 1) drops formed at the irregular shaped cavities between the sintered particles and detached in dripping regime. The disperse phase was forced to fill more of the cavities and drops detach from these larger reservoirs of disperse phase, when the wall shear stress was increased. In D such a drop detachment is illustrated. There seemed to be a transition to a jetting regime for the highest wall shear stresses tested. Because of the poor time resolution of the imaging the exact point of detachment could not be determined at large continuous flow rates.

**Drop formation from sintered ceramic membranes** It was observed that part of the drops stucked to the membrane after formation. This was observed for all pore sizes of these membrane type. At high wall shear stresses (e.g. at 280 Pa) this was less pronounced and drops were carried away by the continuous liquid flow immediately after being formed. The detachment morphology changed with the nominal pore size. The most homogenous drop detachment in dripping regime was observed for
a nominal pore size of 1.4 µm. At a large fraction of the membrane area, drops formed and detached from the membrane. For nominal pore sizes of 0.8 and 0.45 µm (strongest for the latter) coalescence of neighbor drops was observed. This lead to areas of the membrane completely wetted with disperse phase. From these islands of disperse liquid phase sticking to the membrane surface, drops detached in a jet-like manner.

**Drop formation from ceramic membrane from titanium oxide**  Drops formed in a dripping regime at site with a large distance from each other. The smallest distance between two sites found from the high speed movies was about 60 µm. The drop detachment morphology did not change significantly over the wall shear stress range tested (10 – 360 Pa), however, the frequency of drop formation was faster for high wall shear stresses applied.

**Drops detaching from commercial micro engineered membranes made from nickel**  Drop formation was mostly uniform over the membrane area observed, and drops detached in dripping regime for all wall shear stresses tested. When the trial was continued on the next day the disperse phase tended to stick to the membrane surface and the interface sticked to the circular structures surrounding the pores.

### 9.3.3 Transition from dripping to jetting

Exiting the dripping regime by crossing a threshold of the trans membrane pressure was observed in most of the membrane emulsification experiments in this work. Additionally, a high wall shear stress promoted jetting. For small pores of 1 µm diameter the jetting mode was only reached at high transmembrane pressure and high wall shear stresses. In Figure 9.23 an example of the transition from dripping to jetting for pores of 1 µm diameter and 20 µm distance is shown. For low wall shear stresses the drops grew to a size leading to touching of neighboring drops without coalescence. Increasing the wall shear stress lead to a drop detachment in dripping mode with less drop-drop interactions at the membrane surface. For a wall shear stress of 600 Pa some pores already showed drop formation in the transition to jetting, indicated by a deformation of the drops before detachment and a drop pinch-off slightly downstream. When starting from this state and increasing the trans membrane pressure (from 0.2 to 2.0 bar), the drop detachment mode changed from dripping to jetting.

In Figure 9.24 the modes of drop detachment are summarized for the experiments carried out with circular pores of 1 µm diameter. The mode of drop detachment was
Figure 9.23: Pictures from high speed imaging showing drop detachment from silicon nitride membranes with circular pores of 1 µm in diameter and a pore distance of 20 µm. Increase of the applied wall shear stress and of the trans membrane pressure leads to a transition from dripping to jetting mode.

classified by visual evaluation of the high-speed movies. Three modes were distinguished: dripping, transition, and jetting. To decide whether still dripping or already a transition mode was entered was not clear in every case. Low trans membrane pressure and low wall shear stress lead to dripping. High wall shear stress and/or high transmembrane pressure lead to transition mode or already jetting mode.

9.3.4 Detachment morphology versus wall shear stress for silicon membranes with 12 µm pore diameter

The wall shear stress showed a stronger influence on drop detachment morphology for 12 µm pores in silicon membranes compared to smaller pore sizes. Figure 9.25 compares pictures extracted from high-speed movies taken at different wall shear stresses. The development of the drop morphology during detachment corresponded to distinct dynamic regimes. At low wall shear stresses drops detached in a dripping mode at the pore rim exhibiting a nearly spherical shape when detaching. In addition, drops were formed at every pore over the whole membrane area. At low flow rates of the continuous fluid phase drops grew to large volume. Despite the relatively large distance between pores the drops came in contact with each other but without coalescing. When increasing the wall shear stress by increasing the continuous phase velocity and/or its viscosity, the morphology of drop detachment changed. Drops deformed to a larger extent before they detached. Since the drops also detach at
a smaller size, they did not touch. At some pores, the transition from dripping to jetting was already observed: the drop pinch-off moved away from the pore rim to a position further downstream. The disperse phase formed a jet at almost all pores at a wall shear stress of 490 Pa. The jets seemed to adhered to the membrane surface. Drops with a diameter in the range of the pore and smaller detached from the ends of the jets. In some cases, jets from consecutive pores coalesced to one single jet.

9.4 Discussion

9.4.1 Experimental setup

Trans membrane pressure determination and flow state. Trans membrane pressure was calculated by subtracting the built up of pressure at the membrane site (measured in the calibration experiment) from the disperse phase pressure measured during emulsification. Thus the calculated trans membrane pressure was dependent on the accuracy of pressure measurement and the accuracy of the calibration. The average standard error of the residuals of the linear fit of pressure versus pump speed was 0.045 bar. From this, the accuracy of the pressure built up by the continuous

Figure 9.24: Plot showing the different detachment regimes as a function of trans membrane pressure and wall shear stress. Increasing one or both parameters over a threshold leads to jetting. Plot data from experiments with pores of 1 µm.
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Figure 9.25: Microscopic pictures of drop detachment at a silicon type membrane with pore diameters of 12 µm at different wall shear stresses indicated by the numbers. Continuous flow goes from right to the left. The arrow on (b) indicates the transition to the jetting regime at one pore. The arrow on (c) indicates coalescence of jets.

Phase is estimated to be around ±0.05 bar. Additionally an error caused by inaccuracy of the pressure measurement or reading the pressure while not complete pressure equilibrium was reached had to be taken into account. It was estimated that these errors may sum up to an inaccuracy of the calculated transmembrane pressure of approximately ±0.1 bar.

It was shown that it was necessary to calibrate the pressure drop by measurements, because the tested models failed to match the pressure measured. Pressure drop over 80 mm channel was indirectly measured by the pressure drop in two configurations: (i) long side – 152 mm – downstream and (ii) short length – 72 mm – downstream. The pressure drop over 80 mm was then calculated from the difference between the two values. The best prediction of pressure drop over the 80 mm channel length was achieved by using the Poiseuille equation and inserting the equivalent diameter and the width and height of the channel as characteristic lengths. The matching of the data was significantly better for low Reynolds numbers (as a result of high liquid viscosity of 23 and 51 mPa · s), reflecting the validity of the model for laminar flow and the presence of a fully developed laminar flow. The poorest agreement with the model is found for the continuous liquid phase with viscosity of 23 Pas and channel Reynolds number ranging from 0 to 500, where laminar flow should still be present. Peng et al. [64] showed for various aspect ratios of micro channels, ranging from hydraulic diameters of 0.1–0.3 and heights of 0.1 to 0.3 mm, that the onset of the transition from laminar to turbulent flows occurred already far below the Reynolds number usually expected to be 2100 for a channel flow. The presence of secondary flows might therefore explain the discrepancy between model and measurements. Contrary, when plotting Fanning friction factor versus Reynolds number, the data follow closely the expected trend for purely laminar flow, significant deviations are only seen for the lowest continuous viscosity and highest Reynolds numbers (see plot B of Figure 9.5).
Because calculation of the wall shear stress was based on the assumption of developed laminar flow, it is concluded that it was reasonable to exclude datasets not fulfilling these criteria which was mostly the case for the solution with 0% PEG in the continuous liquid phase.

9.4.2 Parameters influencing drop formation and detachment

Membrane surface properties  Depositing a thin layer of silicon oxide onto the membranes proved to be an effective method to alter membrane material, and render it hydrophilic. Wetting of the untreated membranes by the disperse phase did not allow controlled drop formation, and emphasized the necessity to adjust the surface properties to the liquid-liquid-system selected for emulsification. Already previous studies pointed out the influence of surface wetting in membrane emulsification [26, 27, 59]. However, liquid-surface interactions seem to be often underestimated and surprisingly considered with insufficient priority compared to other physical membrane parameters such as pore size distribution and pore distance. The latter parameters become irrelevant when the surface chemistry is not adequately adjusted.

Inter pore distance  Coalescence of disperse liquid phase exiting from neighbor pores was observed for micro engineered membranes with close inter pore distance (e.g. 2 and 6µm for circular pores of 1µm diameter) and for ceramic membranes having small nominal pore sizes of 0.45 and 0.8µm. Coalescence was never observed in this work, when drops pinned at the pore rim and touched neighboring drops. What might be the reasons for the coalescence of drops emerging close to each other and the non-coalescence of droplets emerging farther apart in spite of touching of drops in both cases? In Figure 9.26 a cartoon for two membranes with same pore diameter but different inter pore distances is shown. The second stage of drop formation where drops grow to a size where they touch is indicated in the bottom for both membrane types. For close inter pore distance the drops grow to a smaller radius compared to large inter pore distances. The Laplace pressure inside the drops is larger for smaller drops (see Equation 8.7). It therefore needs a stronger force to deform a small than a big drop. The drops attached to the membrane pores have no room to escape, because they are surrounded by neighboring drops. Consequently they have to deform when they grow which causes a force acting from one droplet on the other. This force increases when the inter pore distance decreases. It is well known that coalescence of drops is promoted when the contact between them is supported by mechanical force. This leads to a faster drainage of the liquid film of continuous phase between them. A review worthwhile reading comes from Chan et al. [11], who discuss theory and experimental results of coalescence of drops and bubbles. Coalescence may be
Experimental: Visualisation of drop detachment from porous membranes

Inter pores distance = 2 x pore diameter

Inter pores distance = 4 x pore diameter

Figure 9.26: Cartoon of drops growing and detaching from membrane pores for two inter pore distances.

Prevented by stabilization of the interface by surfactant. At pores with large inter pore distance the growing phase before drops of neighbor pores touch takes longer and the average surface increase rate is smaller, because drops have to be larger to touch neighbor drops. As a result the interface occupation density of surfactant at the drop interface is likely to be larger which leads to a stronger stability of the drops against coalescence. The ability to tailor the inter pore distance, as it was carried out in this work is important to inhibit coalescence at the membrane and improve the control over the drop size in membrane emulsification.

**Pore shape** The opening aspect ratio of pores may have a significant influence on drop detachment. This mechanism would offer controlling drop detachment. Kobayashi et al. [43] compared drop detachment from silicon membranes with slit shaped pores and circular pores. Slit shaped pores produced nearly monosized drops independent of the continuous cross flow velocity applied. The same authors in a later study [44] showed a dependency of drop detachment from the pore opening aspect ratio of slit shaped pores. Pore aspect ratios of above 3 lead to spontaneous drop detachment producing drops with narrow drop size distribution without the need of applying hydrodynamic force induced by the continuous cross flow. Also Rayner [68] found by numerical simulations that the largest stable volume attached to a pore is significantly smaller for pore aspect ratios larger than 3. It was proposed that necking of the filament between remaining disperse phase and detaching drop occurred inside the pore (below the membrane surface). This would causes a smaller impact of the hydrodynamic drag force on drop detachment, because it mostly acts above
the membrane surface.

In this work few differences in the drop size as a function of wall shear stress was found when comparing slit shape pores of opening aspect ratio 4 to circular pores. Only in the case of pores of width of 1 µm, differences in the dependency were detected. These differences were a weaker drop size dependency for slit-shaped pores compared to circular pores. If spontaneous drop detachment originated from the pore shape played a significant role, absence, or weak dependency, of drop size from the wall shear stress was expected.

The explanations of Kobayashi et al. [44] and Rayner [68] about the physical reason for spontaneous drop detachment from slit-shaped pores remains unclear. The most convincing explanation can be found when comparing slit shaped pores to the designs of so called microfluidic EDGE devices. Such devices were initially introduced by Dijke et al. [17] and are somewhat similar to devices introduced by Kawakatsu et al. [41]. A cartoon of drop detachment is such a device is depicted in Figure 9.27. The key structuring element in the setups is a flat plateau where the disperse liquid phase is forced to enter. This plateau is followed by a zone of expansion which is filled with the continuous liquid phase. The disperse phase which forms a slug-like shape, squeezes into the continuous liquid phase. As soon as the interface enters the expansion zone, a spherical surface is formed. In terms of Gibbs free energy any other shape is unfavorable. The radius of curvature is necessarily larger where the channel expands. Consequently, the Laplace pressure inside the slug at the narrow region of the channel, which causes a pressure gradient inside the liquid slug. The pressure gradient is a driving force to accelerate flow from inside the slug into the forming drop in the expansion region and hence promotes rupture of the drop filament and detachment of the forming drop. In a slit-shaped pore a similar mechanism can be expected when the disperse liquid phase expands into the continuous liquid phase. If the pore height (membrane thickness) is large compared to the diameter of the forming drop and the continuous phase is wetting the inner surface of the pore, then the best conditions are met to form a slug like interface inside the pore. However, when the inner pore perimeter is entirely filled with disperse liquid phase it is expected that the drop initially follows she shape of the pore. This leads to an elliptical drop interface when exiting the pore. This shape also deviates from the ideal spherical shape. The relaxation due to surface forces of this nonideal shape to the ideal spherical shape should promote rupture of the filament connecting the formed drop to the pore.

In experiments performed in this work the aspect ratio of pore height to smallest opening dimension was in the range of (0.1 to 1). The membrane thickness was probably too low to take advantage of the elongated pore shape. In the EDGE device used in [17, 93] and slit shaped membrane pores in [44] these ratio were 6, 166 and 19. For the largest ratio of 1 tested in this work (1x4 µm pores) an effect of the pore
opening aspect ratio was measured, which would support that a large ratio (height to width) promotes interfacial tension driven drop detachment.

Pores with a large opening aspect ratio (1x100 µm) in this work produced drops in a similar size range as circular pores of 1 µm. Therefore, slit shaped pores could still be an alternative to circular pores. Trenches can usually easier produced in micro fabrication as circular structures of same characteristic size. Etching to larger depths, and hence increasing membrane thickness, would be better feasible with trench-shaped structures.

**Membrane type – micro engineered versus commercially available membranes**

Micro engineered membranes as produced for this study, were not wetted by the disperse phase during emulsification and were designed with sufficient large inter pore distance. This makes them superior over most commercial available membranes in producing drops with narrow drop size distribution. Most commercial membranes tested in this work produce drops with larger size variation compared to micro engineered membranes, because pore sizes were not uniform. Additionally, different states of drop formation were found over the membrane area. This also resulted in less control over drop size by the wall shear stress applied. One might argue that for all membranes tested drop size span were low, and only a slight improvement in control over drop detachment was achieved by using micro engineered membranes. It should be kept in mind, that the measurement method of the drop size has a limit at a drop size smaller than about 5 µm. Thus drops close to that value are underrepresented in the evaluation for the drop sizes. Satellite drops, which may form during rupture of drop filaments are expected to be completely excluded from the analysis. Such drops, when included in the measurement (e.g. by measuring drop size distributions of emulsions by laser diffraction) would significant increase the overall span of the obtained drop size distributions and probably also lead to a more pronounced differences for micro engineered and commercial membranes. Nevertheless, when focusing on larger drops the comparison of different membrane types was still applicable.

One advantage of commercial membranes tested in this work, were their greater stability against mechanical stresses applied during handling of membranes during mounting procedure and emulsification. This is also true for the regeneration of the membranes by cleaning steps, although not specifically tested in this work.

**Sticking of drops to the surface of ceramic membranes**

Vladisavljevic et al. [95] observed adherence of drops at the membrane surface during their study of drop from soybean oil detaching in a watery continuous liquid from SPG membranes. Drops adhered strongly to the membrane surface when Tween 80 was used as an emulsifier.
Contrary, drops detached well when sodium dodecyl sulfate (SDS) was used as emulsifier. The authors argue, that the polar emulsifier (SDS) on the drop surface leads to electrostatic repulsion of the drop from the negatively charged membrane surface. The used glass membranes have silanol groups on their surface which makes them hydrophilic in a wide range of pH. In this work only neutral (not charged) emulsifier polysorbate (=Tween 20) was used. It is expected that a change of the emulsifier to a polar surfactant like SDS would improve the drop detachment from sintered ceramic membranes from this work. This is likely, because the surface chemistry of glass membranes as they were used in the work of Vladisavljevic et al. [95] is similar to the ceramic membranes discussed here.

**Transition from dripping to jetting** Increasing wall shear stress or the trans membrane pressure over a certain threshold lead to transition of drop detachment from dripping to jetting. The threshold depends on the membrane pore size. For large pore size, jetting starts at lower wall shear stresses and lower trans membrane pressures compared to smaller pore sizes. Cramer et al. [16] and also Duxenneuner [18] observed a similar behavior when they studied drop detachment from capillaries in co-flow. Drop detachment was changing from dripping to jetting when crossing a threshold of the disperse phase throughput or the velocity of the continuous phase.

Controlling the state of drop detachment in this work was more difficult in the flow cell setup when using large size pores with thin membranes (e.g. circular or rectangular pores of 10 µm width and membrane thickness of 1 µm). When assuming validity of the results in co-flow from Cramer et al. [16] for the cross flow drop formation in this work, the pore throughput has a large influence on the state of drop formation (dripping or jetting). Pore throughput is directly proportional to the trans membrane pressure, when considering the pore as straight circular channel. According to Hagen-Poiseuille equation, applied for such a case, for a given trans membrane pressure pressure $\Delta p$, the throughput $\dot{Q}$ depends on the diameter of the pore $d_{pore}$, the thickness $t_{mem}$ of the membrane and the viscosity of the disperse phase $\eta_{disp}$:

$$\dot{Q} = \frac{\pi \cdot d_{pore}^4 \cdot \Delta p}{128 \cdot \eta_{disp} \cdot t_{mem}} \quad (9.6)$$

The trans membrane pressure relevant for this throughput is the actual trans membrane pressure minus the pressure drop induced by the interfacial tension, which has to be overcome to create drops at the pores:

$$\Delta p = \Delta p_{total} - \Delta p_{int} = \Delta p_{total} - \frac{4 \cdot \sigma}{d_{pore}} \quad (9.7)$$
9 Experimental: Visualisation of drop detachment from porous membranes

Based on these equations, the area specific throughput of a pore can be plotted as a function of transmembrane pressure and different pore sizes (Figure 9.28). It becomes obvious that the change in throughput is much more susceptible for large compared to small pores. These relationships explain the difficulty in adjusting a dripping regime for thin membranes with large pore sizes. An increase in transmembrane pressure leads to a much stronger increase in specific pore flow rate for a 12 µm pore compared to a 1 µm pore. Consequently, in the first case, small pressure changes might already cause the drop formation state to change from dripping to jetting. When thicker membranes were used (as for silicon membranes), the dripping regime was much easier to adjust compared to thin membranes. This is expected since a large pressure increase is necessary to increase the specific flow rate, because of increasing flow resistance with the length of the pore (see also Figure 9.28).

9.4.3 Imaging of drops

Imaging of detaching drops at commercial membranes turned out to be less straightforward compared to studies carried out with microengineered membranes in this work. The rough membrane surface of commercial membranes lead to scattering of light. This resulted in less bright images compared to images from microengineered membranes. The contrast between drops and membrane was extremely weak in bright-field microscopy, which literally rendered drops invisible when they were growing at pore outlets or when flowing over the membrane surface. The visibility of drops was greatly enhanced by staining the disperse fluid phase with the fluorescent dye Nile Red and applying fluorescent microscopy. In fluorescent microscopy, the light reflected by the camera is filtered out. The light emitted from the disperse phase liquid was detected with the high-speed camera. The intensity of light emitted in fluorescence is generally orders of magnitude lower compared to bright-field microscopy. The shutter time therefore had to be increased, to detect enough light for imaging. This prevented the imaging of drops as sharp entities, when they followed the flow above a certain velocity threshold. Measurement of drop size after detachment was therefore not possible when the drops were flowing over the membrane. However, imaging by bright-field microscopy was possible when drops had already detached and reached the area located downstream from the membrane. There the contrast between drop and channel wall was better compared to drops flowing over the membrane. In most of these cases, drop size was measured manually from the pictures, because contrast was still poor compared to imaging drops over microengineered membranes of silicon or silicon nitride. Vladisavljevic et al. [95] faced also problems when observing drop formation at surfaces of SPG membranes. They reduced the scattering of light and improved image quality by polishing the membrane surface with diamond paste, which reduces the roughness of the surface. However, for this work, this method was not suitable, because such a treatment changes the surface
roughness of the membrane. This could cause a different drop detachment behavior. Additionally, the finest pore structure on the top side of sintered ceramic membranes would suffer from degradation by such a treatment. Finally, it is expected that image quality cannot be improved sufficiently by polishing for studies as they were performed in this work. This is proposed because the cross flow velocity at which Vladisavljevic et al. [95] imaged drops were much smaller compared to this work.
Figure 9.27: Cartoon of drop detachment mechanism in EDGE device.

Figure 9.28: Area specific pore flow rate calculated from Hagen-Poiseuille equation assuming circular pores, considering pressure loss due to interfacial tension.
9.5 Conclusion

Drop detachment (oil in water) was successfully visualized from different types of membranes in a flow cell by high-speed imaging. By using in-house produced microengineered membranes important membrane properties like the surface wetting of the membrane, the inter-pore distance, the trans membrane pressure, the size and shape of the pores were separately investigated. Drop detachment was studied dependent on these parameters and the cross flow conditions in the channel. Thereby the cross flow was adjusted in the laminar regime (Reynolds number <600) by choosing a narrow channel and adapting the continuous liquid phase viscosity. The wall shear stress was calculated and used to correlate drop size after detachment and spans of the drop size distribution measured.

It was found that drops could only be formed in a controlled manner when the membranes were sufficiently hydrophilic and the inter-pore distance sufficiently large. Then drop formation was adjustable in the dripping regime and at given wall shear stress, drop size correlated with the pore size.

Increase of wall shear stress and/or the trans membrane pressure over a threshold (depending on the membrane used) lead to a transition from dripping to jetting. It was assumed that dripping leads to narrow drop size distributions. A general trend could be seen for increasing drop size span for with increasing wall shear stress, however not in all cases.

A minor influence of the pore opening aspect ratio was found in contradiction to literature result. However, this discrepancy could be explained by the thin membranes used in this work, which might not sufficiently support the interfacial tension driven drop detachment in literature. However, it was possible to produce drops from very long and narrow slits, where the width of the drop size distribution decreased for higher wall shear stresses. The drop size formed with slit-membranes was in the range of drop sizes obtained from circular pores of same with. Therefore these type of pores could be an alternative in micro engineered membranes, because the fabrication of slits is easier (regarding the pore etching process) compared to the fabrication of circular pores. However, the cross flow should be kept perpendicular to the pore, because a parallel orientation to the flow caused inhomogeneous detachment of drops and lead to coalescence.

Visualizing drop detachment from commercial available membranes was only possible by switching to fluorescent microscopy. Therefore image quality was worse, compared to the visualization of drops from micro engineered membranes and less accurate results regarding drop size and drop detachment morphology were obtained.

Drop formation was unstable at sintered woven mesh membranes because the little increase in trans membrane pressure already lead from a dripping regime to flooding
of the membrane surface with oil. A protective mesh on these membranes was a baffle for the cross flow stream and caused turbulence of the flow. Membranes of this type without a protective mesh could be an alternative to micro engineered membranes if the trans-membrane pressure is precisely controlled.

Sintered metal membranes showed drops detaching with different sizes and in different regimes over the membrane area. The nominal pore size influenced median drop size less compared to micro engineered membranes. Nevertheless, these types of membranes could be used for emulsification if drop size distribution width is not important.

Oil exiting different pores from sintered ceramic membranes coalesced and the membrane was partly wetted by disperse phase when the nominal pore size was too small. Otherwise sintered ceramic membranes showed stable drop formation, which also explains why these types of membranes were frequently used for membrane emulsification in the past.

The results suggest that the production of emulsions with narrow drop size distributions is possible by dynamically enhanced membrane emulsification when the membrane properties and flow properties above the membrane are well controlled.
10 Experimental: Dynamically enhanced membrane emulsification - determine boundaries for taylor made emulsions

10.1 Introduction

Scaling up a dispersing process from lab scale experiments is a challenge in process engineering. Achieving the same dispersing characteristics when moving from the lab- to pilot scale requires the knowledge of scaling laws, which relate physical parameters that can be controlled in the process to the dispersing result.

A pilot scale apparatus is introduced in this chapter, designed for continuous production of emulsions with narrow drop size distribution. Scaling from lab to pilot scale was approached by using similar characteristic dimensions of the shear gap and the same membranes in both setups. The major difference between the setups was how the cross flow was initiated. A cone-plate shear flow cell was applied in the pilot scale, to decouple shear and continuous liquid phase throughput. In lab scale, all investigations were carried out in Poiseuille flow enabling to visualize drop detachment. Results of both methods were compared using the wall shear stress induced by the cross-flow over the membrane surface.

Lab scale experiments, as presented in chapter 9, determined the process window, which leads to a controlled drop formation and detachment. As a quantitative measure for the quality of the emulsification process, the drop size and the drop size distribution width was used. Qualitatively the drop detachment morphology was accessed and categorized in dripping-, jetting- and wetting regimes and combinations thereof. Studies on micro engineered membranes clearly showed, that drop size correlated inversely with the wall shear stress applied and the pore size of the membrane.
Experimental: Dynamically enhanced membrane emulsification

had a direct influence on the drop size, if drops detached in a well controlled dripping regime. Additionally, it was found that drop formation in the dripping regime (without wetting of the membrane by disperse fluid phase) was only possible when the membrane surface was adapted to the fluid material system and pores were sufficiently far apart. Furthermore, some commercial membranes were identified that enabled for controlled production of drops in a dripping regime. Widths of drop size distributions were narrow for almost all the membranes tested during visualization; a trend towards increasing size variations for increasing wall shear stresses was found. An influence of the pore shape was hardly seen. This chapter deals with the following research questions:

- Can the same trends regarding drop size as a function of process parameters found compared to the lab scale study?
- Is there a link between drop detachment morphology observed in the pilot scale experiments and the dispersing result?
- Is it possible to produce emulsions with narrow drop size distribution on a pilot scale, focusing on membrane and flow properties?
- Are micro engineered membranes applicable in a pilot scale process?

To answer these questions, three membrane types were tested in the pilot scale process, i.e. a silicon, a silicon nitride and a sintered metal membrane. Thereof silicon membranes with circular pores and pore diameter of 12 µm were studied most extensively. As a measure for the dispersing process the drop size and the width of the distribution was assessed as a function of membrane type, wall shear stress and flow state in the gap. Wall shear stress and flow state in the gap were derived assuming laminar shear flow in the gap and using a model from Ellenberger and Fortuin [20] to distinguish between laminar flow and onset of secondary flows.

In literature, membrane emulsification has been studied on lab and pilot scale [63, 72, 73, 99]. Also based on lab scale experiments the advantages that could arise from using micro engineered membranes in membrane emulsification were shown [28, 96]. However, a direct link between lab scale experiments and pilot scale emulsification with micro engineered membranes is missing. The experimental work presented here tries to close this gap.

10.2 Material and methods

**Fluids** For the preparation of oil-in-water emulsions, Hydrioil SOD.24 (Cas 36078-10-1) (Hydrior AG, Wettingen, Switzerland) was used as the disperse phase. It consists of hydrated alcylesters (C12, C14) of oleic acid. Prior to the emulsification
the oil was filtrated through cellulose nitrate filter with nominal pore size of 1.2 µm (Whatman, Maidson, UK). The continuous phase consisted of a mixture of water, polyethylene glycol (Cas 36078-10-1, Polyglykol 35000 S, Clariant, Frankfurt, Germany) and polysorbate 20 (Cas 9005-64-5, Sigma Aldrich, Steinheim, Germany). Tap water was used for pilot scale emulsification. The addition of polysorbate to tap water led to slight turbidity, which was not the case for deionised water. Although the possible formation of aggregates in a low concentration was not likely to distort drop size measurements, for emulsification using a silicon nitride membrane where only very low disperse phase volumes could be reached, deionized water was used for the preparation of the continuous liquid phase. With polyethylene glycol the viscosity of the continuous phase was adjusted to 1, 2, 3, 5, 8, 10 and 22 mPa s at 20°C by applying concentrations of 0, 0.5, 2, 3, 4.6, 6 and 9%, respectively. For every concentration viscosity was measured during a temperature sweep from 21 to 28°C. Viscosities for calculation of the wall shear stress were obtained by measuring the inlet temperature of the continuous phase and reading the viscosity from the temperature sweep experiment. Polysorbate 20 was used as an emulsifier to guarantee a fast stabilization of drops after detachment from membrane pores.

10.2.1 Experimental setup

Rotating Membrane Extruder - ROMER II

The experimental setup was developed in collaboration with the Bühler AG (Switzerland, Uzwil). A photograph and a scheme of the device is depicted in Figure 10.1. The device consists of a chamber for emulsification, two containers and pumps for the fluid phases, a vessel to collect the product and units for controlling, measuring and logging process parameters. A detailed drawing of the core of the device is shown in Figure 10.2. Technical data are summarized in Table 10.2.1.

Emulsification chamber The emulsification chamber consists of a stator with membrane mount and the rotor (see Figure 10.2). The stator is screwed into the housing with a fine thread (diameter: 100 mm, slope: 2 mm/round). The thread serves for adjusting the distance between rotor and stator. The fluid inlet for the continuous phase is located radial above the rotor. The inlet for the disperse phase is located at the bottom of the stator. The disperse phase was separated from the continuous phase by the membrane glued onto the membrane mount. The product outlet is located in the middle of the ring-shaped membrane. A hollow shaft connects this opening to the product outlet at the bottom of the stator.
Table 10.1: Technical data of experimental setup ROMER II

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>typically used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle of cone</td>
<td>0.126°</td>
<td></td>
</tr>
<tr>
<td>Diameter of cone</td>
<td>90 mm</td>
<td></td>
</tr>
<tr>
<td>Throughput disperse phase</td>
<td>0 – 50 g/min</td>
<td></td>
</tr>
<tr>
<td>Throughput continuous phase</td>
<td>20 to 2900 g/min</td>
<td>250 g/min</td>
</tr>
<tr>
<td>Maximum internal pressure</td>
<td>15 bar</td>
<td>1 – 6 bar</td>
</tr>
<tr>
<td>Transmembrane pressure</td>
<td>0 – 6 bar 2)</td>
<td>0.2 – 2 bar</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>30 – 12 000 rpm</td>
<td>30 – 4 000 rpm</td>
</tr>
<tr>
<td>Gap distance inner diameter</td>
<td>0 – 3 000 µm</td>
<td>50 µm</td>
</tr>
<tr>
<td>Resulting shear rate</td>
<td>0 – 5 × 10^5 1/s</td>
<td>0 – 2.5 × 10^5 1/s</td>
</tr>
<tr>
<td>Temperature adjustment of fluids</td>
<td>RT–90°C</td>
<td>RT 3)</td>
</tr>
<tr>
<td>Wall shear stress</td>
<td>1 0 – 1 500 Pa</td>
<td></td>
</tr>
</tbody>
</table>

1 lowest throughput measurable 15 g/min, 2) depends on membrane stability, 3) room temperature

The rotor is cone-shaped with a flattened tip (see also Figure 8.1). The outer radius of this flatted section is 20 mm. Before production, the distance between the rotor and the flat membrane is adjusted so that the virtual tip of the cone sits on the surface of the membrane. During production the disperse phase is pumped through the membrane into the emulsification chamber. Simultaneously the continuous phase is pumped into the chamber and the rotor spins. This spinning induces shear flow above the membrane surface. The drops are created at the membrane pores and are detached by the viscous drag induced by the flow.

**Adjusting and sensing of flow, temperature, pressure and density** The mass flow of the two liquids was controlled by two gear pumps (Type E/FLM 210, Linn Pumpen GmbH, Schalksmühlen, Germany) and measured by two mass flow meters (Proline Promass 83, Endress+Hauser Metso AG, Reinbach, Switzerland). These meters measure the mass flow through the Coriolis principle. The sensors were additionally equipped to measure the density and the temperature. Additionally pressure and temperature for the two liquids were measured by two temperature sensors (PT100 Class 1/3 DIN B, Jumo, Stäfa, Switzerland) and two pressure sensors (Type 680 G, 0...25 bar, Huba Control, Würenlos, Switzerland).

**Measuring the distance between rotor and membrane** The distance between membrane and rotor was measured indirectly with three distance sensors (GT2-H12K,
Keyence, Mechelen, Belgium) mounted on the housing of the membrane holder. The sondes of the distance sensors were mounted perpendicular to a flat surface of the upper housing (see Figure 10.2). At the beginning of the adjustment procedure, distance of membrane and rotor was adjusted to zero distance, by screwing the membrane holder into the housing of the emulsification chamber until the membrane touches the rotor, which was detected by a sudden increase of the torque. The outer ring, used for screwing the holder, indicated this increase in torque by releasing the connection between ring and holder. At zero-distance all three sensor readings were calibrated to zero. The working distance between membrane and rotor was then adjusted by unscrewing the holder and measuring the distance. The adjustment was carried out by matching the mean of the three readings of the distance sensors. Distance of rotor and membrane was adjusted, to place the virtual tip of the rotor on the membrane top surface. The rotor used in the experiments had an angle of $0.13^\circ$ and the rotor cone was flattened at a radius of 20 mm. Thus the distance was adjusted to $50 \pm 5 \mu m$ (see also Figure 8.1).
Figure 10.1: Photograph and scheme of pilot scale apparatus for shear enhanced membrane emulsification
Figure 10.2: Drawing of emulsification chamber of ROMER II device. Modified from drawings provided by Bühler AG, Uzwil, Switzerland.
10.2.2 Membranes

Three membrane types were used for emulsification experiments.

**Silicon membrane**  Silicon membranes were produced in-house by the procedure described in Section 4.1. Flat membranes were produced with circular pores of 12 µm in diameter and an inter pore distance of 100 µm (distance between the centers of the pores). The thickness of the active membrane area was 100 µm, the overall thickness of the membrane sample was 300 µm. The membrane support structure design is depicted in Figure 4.8. Silicon membranes were hydrophilized prior to the emulsification experiment. This was done by treating the membranes in a plasma cleaner (PlasmaEtch, PE50, Carson City, USA) after glueing on the holder. The treatment was carried out twice 5 minutes at 40 Pa, 100 W, O₂. For trials with 'untreated' membranes these hydrophilization step was left out.

**Silicon nitride membrane**  Membranes made of silicon nitride supported by a flat silicon substrate were fabricated according to the procedure described in Section 4.2. The active membrane area consisted of about 1000 transparent silicon nitride squares of each 140 µm wide. A rectangular array of 3x6 circular pores of 0.8 µm in diameter were etched into each square. Pores had inter pores distances of 20 µm. After membrane fabrication the upper membrane surface was coated with 50 nm of silicon oxide by means of plasma enhanced chemical vapor deposition (PECVD) to alter the membrane surface hydrophilic. See also Section 9.2.4 for this procedure.

**Stainless steel sintered membrane**  Sintered membranes of type SIKA R AX3 were purchased from GKN Sinter Metals Filters GmbH (Radevormwald, Germany). The membranes as delivered, were flat, circular in shape with a diameter of 90 mm and a thickness of 3 mm. For use in the ROMER II setup membranes were shaped by means of a lathe to a ring shape having an outer diameter of 68 mm and an inner diameter of 40 mm. As a result of this procedure the samples were slightly distorted. Because of the sintered structure of the membrane the surface and the edges of the membrane had pores interconnected with the area where disperse liquid phase was supplied. Therefore the outer and inner edges, where no controlled shear between rotor and membrane can be applied, were sealed with ring-shaped spacers of stainless steel, glued to the membrane with epoxy resin. Prior to emulsification the sintered membranes were plasma treated with the same procedure as the silicon membranes.

Photos of the membrane holder and a silicon nitride and a sintered membrane glued to the membrane holder are depicted in Figure 10.3.
10.2 Material and methods

10.2.3 Methods

Mounting of membranes  Epoxy resin (Hysol 9483, Henkel, Düesseldorf, Germany) bonded membrane and membrane holder. The resin was spincoated onto a flat surface (a silicon wafer or a plastic petri dish) at a rotational speed of 1000 rpm for one minute. The membrane mount was then dipped into the homogeneous layer of epoxy resin and then placed on a flat, transparent surface, equipped with backside illumination. The membrane was positioned by holding the membrane approximately a millimeter above the holder and checking the correct position with the help of the illumination (support areas appear black, membrane areas appear illuminated through the membrane). Illumination was not possible with sintered metal membranes, which was not an issue because the membrane is homogeneous over the whole area and has no support structure which has to be matched during the bonding procedure. Then the membrane was deposited onto the holder and secured against slip. This was achieved by fixation of three (about 5mm wide and 1 mm thick plastic barriers to the sides of the holder with scotch tape. Bonding was only supported by gravity, because additional force or covering lead to contamination with resin of the membrane and the holder or lead to displacement of the membrane. Finally, the holder was placed into an oven on a leveled surface at 60°C for 3 h to harden the epoxy resin and to establish a permanent bond between holder and membrane.

Pre-filtration of disperse phase  The disperse liquid phase was filtered prior to emulsification. For this procedure the disperse phase (Hydrioil) was pumped through a cylindrical dead-end filter unit (BHS, Sonthofen, Germany), equipped with a cellulose nitrate filter with nominal pore size of 1.2 μm (Whatman, Maidson, UK). The membrane filter was covered with a standard pre-filter of fiber glass and supported
by a sintered metal membrane of nominal pore diameter of 5 \( \mu \)m (Bopp AG, Zurich, Switzerland). The disperse phase pump of the ROMER II setup was used for pumping the oil through the filter at a throughput of 100 – 300 g/min and a pressure of < 4 bar.

### 10.2.4 Analytics

**Determination of drop sizes** The drop size of emulsions was analyzed by laser diffraction (LS13 320, Beckman Coulter, Nyon, USA). A sample was diluted in the measurement cell of the device to an obscuration of 8 – 12 %. The stirrer speed of the unit was limited to 40 % when a sample was in the measurement chamber to avoid shear induced breakup of drops during measurement. Drop size was measured at least once for each sample. The Frauenhofer model (method Fraunhofer.rf780d) was used to calculate the drop size distribution. A diffraction index of 1.332 was used for the watery continuous phase. The theoretical range of drop sizes detectable by the method is between 0.04 and 2000 \( \mu \)m.

**Rotor angle** The rotor of the ROMER II setup was specified having a cone angle of 0.14 \( \degree \). To determine the actual angle the rotor plate was placed downside up on a computer controlled x-y-table of a microscope. The height of the rotor was measured along two lines in x- and y-direction by focusing the rotor at various points and noting the z-displacement (height) of the microscope. With this procedure the surface profile along two lines were obtained. The height profile obtained was plotted and the slope of both sides was evaluated by two lines fitted to the data for each side of the rotor. The average of both line angles obtained was used as rotor angle, which was 0.127 \( \degree \).

**Bubble point determination** The bubble point is equal to trans membrane pressure that has to be applied to induce air bubbling from the membrane pores. According to Equation 9.5 it depends on the pore size and the liquid uses to cover the membrane. The bubble point is therefore a good measure for the integrity of the membrane and the absence of leaks. When the bubble point is far below the expected one, larger pores (or defects) are present. Therefore the bubble point was measured before emulsification. This was done by mounting the stator of the ROMER II with the integrated membrane on a stand. A ring-shaped barrier was mounted on the stator to enabling covering of the membrane surface with liquid. If not otherwise mentioned, deionized water was poured onto the membrane. The air pressure below the membrane was slowly increased. When the first bubbles showed up, this pressure was noted as the bubble point.
10.2 Material and methods

10.2.5 Calculation of process index values

Shear rate in gap  The shear rate in the gap of a rotor above a flat surface can be calculated by dividing the rotor speed at the radius $r$ by the distance of the rotor to the plate $d_{gap}$:

\[ \dot{\gamma} = \frac{v_{rotor}(r)}{d_{gap}(r)}. \]  

When calculating the shear rate for a cone-plate geometry, the shear rate becomes independent of the radius, if the tip of the cone-shaped rotor sits on the membrane surface. When using small opening angles of $\theta < 5^\circ$ the $\tan \theta$ can be replaced by the angle in rad with differences in less than 0.25% for the shear rate:

\[ \dot{\gamma} = \frac{v_{rotor}(r)}{d_{gap}(r)} = \frac{r \cdot \omega_0}{r \cdot \tan \theta} = \frac{\omega_0}{\tan \theta} \approx \frac{\omega_0}{\theta}. \]

$\omega_0$ is the angular velocity of the rotor.

If the rotor is not exactly positioned (to place the virtual cone tip on the top of the membrane surface), the shear rate depends on the radius. When the rotor is displaced by a distance $d_{add}$ towards a larger gap the shear rate calculates as follows:

\[ \dot{\gamma} = \frac{v_{rotor}(r)}{d_{gap}(r) + d_{add}} = \frac{r \cdot \omega_0}{r \cdot \tan \theta + d_{add}} \approx \frac{r \cdot \omega_0}{r \cdot \theta + d_{add}} \]

Wall shear stress  The wall shear stress $\tau_{shear}$ under laminar Couette flow conditions was calculated as:

\[ \tau_{shear} = \dot{\gamma} \cdot \eta \]

$\dot{\gamma}$ is the shear rate and $\eta$ the viscosity of the fluid between the plates.
Throughout this work the general assumption was made that better control of drop detachment is achieved while maintaining laminar flow conditions within the gap. For the particular case of a cone-plate geometry, Ellenberger and Fortuin [20] developed a Reynolds criterion for the flow type in such a gap:

\[ Re^* = \frac{\omega_0 \cdot \rho \cdot R \cdot \theta}{\eta} \]  

(10.5)

\( R \) is the outer radius of the cone, \( \rho \) is the density and \( \eta \) the dynamic viscosity of the liquid inside the gap (in this work the material properties of the continuous fluid phase were used). The flow is laminar, without secondary flows for \( Re^* \leq 1 \). Secondary flows are expected for \( Re^* > 1 \).

10.3 Results

10.3.1 Emulsification for silicon membranes with different surface treatments

To show the influence of the surface properties of the membrane, treated (hydrophilized) and untreated silicon membranes were used to produce emulsions with the ROMER II setup. The setup using untreated membranes produced poorly defined emulsions with a pronounced creaming layer, indicating the flotation-demixing of large drops, coalescing at the sample surface. For these samples no representative drop size distribution could be measured. In contrast, well defined emulsions were formed using treated membranes. The narrowest size distribution obtained for such an emulsion is shown in Figure 10.4, using a membrane with pore diameter of 12 µm.

10.3.2 Drop size distribution influenced by wall shear stress – emulsification with silicon membranes

Hydrophilized silicon membranes with a pore diameter of 12 µm were used for emulsification in the ROMER II setup. The gap Reynolds number was maintained \( \leq 1 \), by adjusting the rotational speed and the viscosity of the continuous liquid phase accordingly. The variation of the median drop size and the corresponding span as a function of the wall shear stress are shown in Figure 10.5. The median size decreases exponentially with the wall shear stress, while the size distribution becomes wider.
10.3 Results

Figure 10.4: Result of drop size distribution obtained with the ROMER II setup for a silicon membrane with pore diameter of 12 µm, which was hydrophilized by plasma oxidation prior to emulsification. Wall shear stress was adjusted to 20 Pa, by using continuous liquid phase without PEG and setting the rotational speed to 400 rpm.

with increasing wall shear stress, up to about 50 Pa. At 20 Pa, the drop size distribution is the narrowest, with a span of 0.6. For higher wall shear stress values, within a range of 50 to 600 Pa, the span is close to constant. At higher wall shear stresses, the span decreases again. The spans were all smaller or equal to 1.7.

10.3.3 Emulsification with membranes of silicon nitride type

Emulsification was carried out with the ROMER II setup equipped with hydrophilized micro engineered membranes made of silicon nitride. Prior to emulsification the membrane was glued onto the membrane holder and checked by means of light microscopy for defects, originated from the fabrication process. Thereby five defects were detected which were each sealed with a drop of epoxy resin.

The bubble point of the membrane covered with water was determined to be 0.8 bar. Before the membrane was built into the ROMER II emulsification chamber, the membrane was tested outside the device by pumping oil through the membrane pores into continuous phase liquid. Uniform droplet creation over the whole membrane area was observed from the membrane squares. The disperse phase did not wet the membrane surface.
Figure 10.5: Drop median diameter and span as a function of wall shear stress in pilot scale apparatus using a membrane with pore diameter of 12 µm. For three points the measured drop size distributions are shown in the insets A, B, C.

As continuous liquid phase, a solution of 2% polysorbate was used with and without addition of 6% PEG to adjust viscosity to 1 and 10 mPa·s. Trans membrane pressure was adjusted to 0.9 bar which is within the limit of < 2 bar as learned from drop visualization experiments to guarantee for drop detachment in dripping regime. Due to the low porosity of the membrane, the disperse liquid phase throughput and the continuous liquid phase throughout were smaller than the limits of measurements which were 5 g/min and 50 g/min, respectively. Therefore the phase volume of the disperse phase was not exactly known. The speed of the continuous phase pump was adjusted as low as possible to still have some flow. The speed of the disperse phase pump was adjusted not to exceed a certain pressure.

Emulsification was carried out at two speeds (400, 430 rpm). Samples were collected and drop size was measured with laser diffraction. Results of these measurements are depicted in Figure 10.6 in comparison with results obtained from flow cell experiments with similar pore size. The drop size distributions obtained from the three measurements were not narrow (spans from 1.4 to 3.1). However the drop size distribution obtained at a wall shear stress of 110 Pa shows two distinct peaks. The larger peak is located at the expected drop diameter of 10 µm. The second peak is at about 1 µm which about the same diameter as the pore. It is assumed that the main peak originates from well controlled drop formation in a dripping regime. The smaller peak might originate from satellite drops formation. The drop size obtained
in the dripping regime is very close to the drop sized obtained for the satellite drops. Therefore the satellite drops have a large influence on the span. Assuming that the size and number of satellite drops (per formed drop from dripping) does not change when the drop size (and pore size) is larger (than in this experiment). Then the volume occupied by the drops of the main peak would be much larger, but the volume of the satellite drops would stay constant. Therefore the peak in the distribution plot would be much smaller. Hence the span would be much smaller compared to the case investigated in this experiment.

![Graph showing drop median diameters and wall shear stress relationship](image)

Figure 10.6: Drop median diameters for three wall shear stresses, obtained in ROMER II device with micro engineered silicon nitride membranes. Data points are plotted together with the data obtained from visualization experiments in a flow cell (see chapter 9). The line corresponds to the fit of these data points with \( X_{50,3} = K \cdot \sqrt{\frac{T}{\tau}} \). Additionally the drop size distributions are plotted.

### 10.3.4 Emulsification with sintered metal membrane

To compare the performance of micro engineered membranes in the ROMER II setup with commercial membranes, emulsification was carried out with a sintered metal
membrane (SIKA-R AX3). A solution of 2% polysorbate was used with and without addition of 6% PEG, as continuous liquid phase. Trans membrane pressure was adjusted to 0.3 to 0.4 bar, which was derived from flow cell experiments maintaining drop detachment in dripping mode for a wide range of wall shear stresses. The distance between rotor and membrane was adjusted to 100 instead of 50 µm. This additional distance became necessary, because the rotor started to scratch at the membrane surface for lower distances. This was probably caused by a splinter originated from the membrane material. The additional distance was taken into account in the calculation of the wall shear stress by adding 50 µm to the gap distance used for the shear rate calculation according to Equation 10.3. The average shear rate of outer and inner radius of the cone was used for the calculation of the wall shear stress. Theoretically the shear rate at the outer radius compared to the inner radius of the membrane was 21% larger.

The resulting emulsions partly creamed, but did not show strong coalescence. Especially for the case of continuous phase without PEG some millimeter sizes oil drops were detected at the top of the emulsions.

Results from drop size analysis using laser diffraction are plotted in comparison with drop size results obtained with micro engineered silicon membranes in Figure 10.7. The data are plotted with different symbols for gap Reynolds numbers $\leq 1$ and $>1$. The trans membrane pressure was $\leq 0.4$ bar for all the data points from the sintered membrane.

The drop size decreased with increasing wall shear stress. Compared to the micro engineered membrane the drop size at a given wall shear stress was much larger (often more than two times) for emulsification with the sintered membrane, in spite of the nominal pores size of 3 µm (compared to 10 µm for the micro engineered membrane).

The span of the drop size distribution obtained with the sintered membrane showed a steep increase from a wall shear stress of 150 Pa for gap Reynolds number $\leq 1$. Also the drop size dropped rapidly with increasing wall shear stress. This unsteady change both in drop size and drop size span indicated a change in drop formation regime. E.g. the flow state in the gap may have changed from laminar to turbulent and the drop detachment might have changed from dripping to jetting or a mixture of both. When including data for gap Reynolds number $> 1$ the steep change occurred at lower wall shear stress compared to gap Reynolds number $\leq 1$ (Figure 10.7). This supports the hypothesis of a change in drop formation regime caused by the flow state in the gap.
10.3 Results

Figure 10.7: Drop median diameter and span of volume based drop size distribution from emulsification experiment in ROMER II. Datasets obtained from a sintered stainless steel membrane and a micro engineered silicon membrane are compared. The dataset of the sintered membrane are marked with different symbols according to the gap Reynolds number. All data points from the micro engineered membrane were obtained at $Re^* \leq 1$. The vertical lines indicate the sudden change in the drop formation characteristic at a wall shear stress of 150 Pa.

10.3.5 Comparison of drop size and drop size distributions from pilot scale experiments to flow cell experiments

Emulsification was carried out in the ROMER II setup with three membrane types. The same membranes were used to visualize drop detachment in the flow cell (see chapter 9). Here these results are compared to the data obtained from the ROMER II experiments in terms of drop size (Figure 10.8) and span of drop size distributions acquired (Figure 10.9). Median drop size measured from both techniques agree best for micro engineered membranes made of silicon nitride. Drop sizes from silicon membranes were smaller compared to the flow cell. The agreement of the drop size between both experiments is improved, when comparing the $X_{50,3}$ from the flow cell to the $X_{90,3}$ with the ROMER II setup. This comparison is reasonable, if small drop sizes were under represented in the drop size measurements carried out in the visualization flow cell. For the sintered metal membrane the drop sizes obtained for Reynolds numbers $Re^* \leq 1$ are larger compared to the flow cell. The drop size data from the ROMER II including points for $Re^* > 1$ clearly agree better to the drop
Figure 10.8: Drop median diameter of volume based drop size distribution as a function of the wall shear stress. Results from emulsification experiment in ROMER II are compared to drop size measured in flow cell experiments from chapter 9. The three plots show results from three different membrane types.
10.3 Results

Figure 10.9: Span of volume based drop size distribution as a function of the wall shear stress. Results from emulsification experiment in ROMER II are compared to drop size measured in flow cell experiments from chapter 9. The three plots show results from three different membrane types. 9 for different membranes.
sizes measured in the flow cell.

As shown from flow cell experiments in this work (Section 9.3.2), the span of the drop size distribution typically increased when increasing the wall shear stress. This overall trend was found also in the data for the silicon membrane and the sintered metal membrane in the ROMER II setup. However, for the silicon membrane in the flow cell experiments, the span was decreasing with increasing wall shear stress. For the silicon nitride membrane in the ROMER II setup the spans decreased with increasing wall shear stress, however only a few data points are available.

10.3.6 Membrane stability

Silicon membranes were quite stable during production experiments in the ROMER II. Failure was observed, when the pressure rose larger than the measured burst pressure. Also pressure shocks by a sudden increase in disperse flow rate could lead to failure. When the oil used for emulsification was not filtrated, the membranes blocked over time, until no further emulsification was possible.

Silicon nitride membranes After about 20 min of emulsification at 400 rpm in the pilot scale apparatus a few membrane squares broke near the center of the membrane. The same behavior was observed with a second membrane. Therefore now further experiments were carried out on the pilot scale apparatus with silicon nitride membranes. Breakage of membrane squares was never observed in the visualization flow cell experiments.

10.4 Discussion

10.4.1 Emulsification for different surface properties of membranes

As shown in the previous chapter (see Paragraph 9.3.2) detaching drops in a dripping regime required a hydrophilic membrane surface. If the membrane surface was not treated to alter it hydrophilic, no controlled drop detachment was possible and the membrane was wetted by the disperse phase. Here, a significant influence of membrane wetting was found also on the pilot scale emulsification. Well defined emulsion were produced with hydrophilic membranes. For membranes with a more hydrophobic surface the same processing conditions lead to insufficient emulsification. This was causing a large layer of oil, separated on top of the produced samples. This
10.4 Discussion

Figure 10.10: Drop median diameter as a function of gap Reynolds number $Re^*$ in pilot scale experiment using a membrane with pore diameter of 12 $\mu$m. Lines represent an exponential fit ($X_{50.3} = ae^{-bRe^*}$) with $a$ and $b$ the fitting parameters to the data of 1, 3–4, and 6–7 mPa s continuous phase viscosity.

result again emphasizes, that the surface-liquid interaction between membrane and both liquid phases is extremely important, and should be studied for the material system of interest when a membrane emulsification process is developed.

10.4.2 Drop size as a function of wall shear stress

The drop size decreased with increasing rotational speed, shear rate or shear gap Reynolds number. Plotting median drop size as a function of these parameters leads to a separate curve for each continuous phase viscosity as shown in Figure 10.10 for the gap Reynolds number, $Re^*$. As seen in Figure 10.5 all data points fall onto one master curve, when plotting the drop size for different continuous fluid phase viscosities as a function of the wall shear stress. Accordingly, modeling the drop size data by applying a model dependent on the wall shear stress seems to be most
appropriate. A common approach is to apply the force-balance model which predicts the size of the drop when the interfacial tension force $F_\sigma$, holding the drop at the pore rim, is equal to the force acting from the continuous liquid cross flow on the drop $F_\tau$:

$$F_\sigma = \sigma \cdot d_{pore} \cdot \pi$$  \hfill (10.6)$$

$$F_\tau = k_x \frac{3}{2} \cdot \pi \cdot \tau_{wall} \cdot d_{drop}^2$$ \hfill (10.7)$$

Where $d_{pore}$ is the diameter of a circular pore, $\sigma$ the interfacial tension. The factor $k_x = 1.7$ accounts for the drop attached to the membrane being not spherical but having the shape of a sphere attached to a wall [63]. The model is based on the assumption that interfacial tension is constant during the process and that the drops detach in the dripping mode. By assuming $F_\sigma = F_\tau$ and solving for the drop diameter $d_{drop}$, the size at which the drop detaches can be calculated as:

$$d_{drop} = \sqrt{\frac{2 \cdot d_{pore} \cdot \sigma}{3 \cdot k_x \cdot \tau}}$$ \hfill (10.8)$$

Although the model fits well for some datasets, as described in the literature [63], the drop size predicted may deviate significantly from experimental data. A possible reason for this is that this model does not take into account the impact of dynamic phenomena such as convection and diffusion of surfactant at the interface. Other dynamic effects which are not considered are the inflation of the drop during growth and detachment, shielding effects of drops at the membrane by the neighbor drops, indefinite pinning of the drop interface at the pore rim and deviation of the drop shape from an ideal sphere. Rayner et al. [67] addressed some of these aspects using numerical simulation. They developed a model taking into account the dynamics of the interfacial tension variation during drop expansion. The model allowed for a significantly improved prediction of drop size data obtained from drops detaching under quiescence conditions. Since no appropriate model under highly dynamic conditions was available, a simplified equation based on the force balance model was fitted to the data of this work:

$$X_{50,3} = K \cdot \sqrt{\frac{1}{\tau_{wall}}}$$ \hfill (10.9)$$

Where $K$ is the fitting parameter and $\tau$ the wall shear stress.
10.4 Discussion

Drop size related to drop detachment morphology  In Section 9.3.4 the drop detachment morphology was investigated for silicon membranes in the visualization flow cell. The development of the drop morphology during detachment corresponded to distinct dynamic regimes. In particular, a transition from dripping to jetting occurred when increasing the wall shear stress. In the dripping mode drops formed in a more controlled and reproducible manner, leading to a narrower drop size distribution. With increasing wall shear stress, drop detachment became less homogeneous and varied in detachment shape over the membrane area. Additionally, jets started to form at some of the pores. As a consequence, the size distribution is expected to widen, which was observed in the ROMER II experiment using the same type of membrane as used for the visualization experiment. Further increasing the wall shear stress lead to a pure jetting mode, in which jets of disperse phase exit the membrane pores and get stretched until they break into drops. The jet formation is in qualitative agreement with Feigl et al. [21]. They simulated drop detachment from a single pore in shear flow using the openFOAM software. When increasing the gap-Capillary number, which corresponded to increasing the shear rate or viscosity of the continuous fluid phase, they observed the transition from dripping-like drop detachment to a filament forming and its breakup into drops.

10.4.3 Viscosity ratio of continuous and disperse liquid fluid phase

In the ROMER II experiment, at wall shear stresses higher than 600 Pa the span of the resulting size distribution decreased. This behavior can be explained when considering the influence of the continuous phase viscosity and the morphology of drop breakup. Wall shear stresses above 600 Pa were only achieved at laminar flow conditions with a high continuous phase viscosity. As observed in the visualization experiments at these conditions jets form from the pore, which are stable over several centimeters. Hence the jets were stretched before they finally broke up into drops. Cramer et al. [15] and Duxenneuner [18] found, that under laminar flow conditions in co-flow, viscosity ratios between the dispers- and the continuous fluid phase far from unity increases jet stability. E.g. Cramer et al. [15] showed that the jets showed similar stability at viscosity ratios of 0.1 and 10. Jets were less stable when the viscosity ratio was close to unity. In the ROMER II experiment the viscosity ratio ranged from 2.5 to 17. This ratios are far from unity. To conclude, the viscosity ratio and the laminar flow conditions while applying high wall shear stresses lead to stable jets, which are stretched to a large extent. A correlation between the stretching of the jet and the homogeneity of the breakup could explain the reduction in drop size span towards higher wall shear stresses observed in the pilot scale process. However, so far, such a relation has not been shown.
In pure laminar shear flow breakup of freely swimming drops without been attached to the wall is only possible at viscosity ratios below 4 [30, 90]. Higher viscosity ratios lead to rotation of the drop rather than to elongation and breakup. In membrane emulsification large viscosity differences between drop- and continuous liquid phase are not problematic regarding the ability to break up drops from the pores or the liquid jets exiting the pores. This is because the attachment of the drops at the pores suppresses energy dissipation by rotation of the drop.

At high shear rates and viscosity ratios close to unity also secondary breakup of larger drops may occur in the gap of the ROMER II setup. This could explain median drop size measured which were smaller than the pore size. From the visualization experiments however, it is concluded that drops detached in a jetting regime, with the jet still attached to the pore outlet.

10.4.4 Disperse phase throughput as a function of pore size

Mostly the disperse phase throughput determines the efficiency of the process. When high production rates are important a large disperse phase throughput is necessary. The disperse phase throughput achievable while maintaining a sufficiently low transmembrane pressure to maintain the dripping regime is limited by the pore size and the porosity of the membrane. The throughput was extremely small for silicon nitride membranes with pore diameters of 0.8 µm compared to silicon membranes with pore diameters of 12 µm. For the smaller pores it was below 1 g/min, for the bigger one about 20 g/min. This difference was linked to the different porosities of the two membranes which were 0.0001 % for the small pores and 0.25 % for the large pores. This porosity was calculated by relating pore area to the whole are of the 25 membrane sections which could theoretically be used as active membrane area. If the active membrane area can be increased, small pores of 1 µm might be nevertheless applicable in terms of disperse phase throughput. This is suggested by calculation derived from visualization experiments (see Table 10.2). Two throughputs were calculated from drop formation observed in the visualization flow cell at conditions found favorable for good control over drop formation. When comparing the membrane with small pores to the one with bigger pores, the throughput is only reduced by a factor of 2 in spite of porosity decrease by a factor of 5. Such a decrease in throughput from large pores to smaller ones might be still acceptable for specific applications, when this compromise enables well controlled emulsification with narrow drop size distribution in the drop size range relevant for the application.
Table 10.2: Calculation of disperse phase throughput based on drop visualization experiments.

<table>
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<tr>
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<th>12</th>
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<tbody>
<tr>
<td>Pore diameter [µm]</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Inter pore distance [µm]</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Membrane porosity [%]</td>
<td>1.1</td>
<td>0.2</td>
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<tr>
<td>Wall shear stress [Pa]</td>
<td>50</td>
<td>200</td>
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<tr>
<td>Drop frequency observed at a pore [Hz]</td>
<td>8</td>
<td>19</td>
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<tr>
<td>Drop diameter measures [µm]</td>
<td>53</td>
<td>11</td>
</tr>
<tr>
<td>Entire drop volume throughput [l/(h m²)]</td>
<td>225</td>
<td>120</td>
</tr>
<tr>
<td>Entire drop volume [%]</td>
<td>100</td>
<td>53</td>
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10.4.5 Membrane stability

As reported in Section 10.3.6, the stability of silicon membranes was sufficient in the ROMER II process to be used in many emulsification runs. Membranes from silicon nitride had a much shorter lifetime. As tested during the development of the membranes (see Section 4.6), the trans membrane pressure should not be an issue. The pressure applied was a magnitude lower compared to the burst pressure measured for the membrane square size used. Three reasons were taken into account for the occurrence of defect membrane squares during production: (i) The larger free standing support area might cause bending of the membrane sample and thus induce bending stresses on the little membrane squares. Those bending stresses would occur to a smaller extent during lab scale emulsification and pressure testing, because the unsupported sample area was smaller in these tests. This would explain why membranes did not break during these tests at similar conditions compared to the ROMER II emulsification. (ii) Scratching of particles between rotor and membrane could lead to failure of membrane squares. In pilot scale emulsification membrane squares broke near the center of the membrane. If particles contaminate the product stream, the probability to interact with the membrane would be largest at this membrane location. There the entire product stream passes. Additionally the gap at this position is smallest. (iii) Vibrations coming from the rotor might shatter the membranes. Membrane squares broke during fabrication procedures when they were exposed to ultrasound of a cleaning bath at maximum power, which indicated that the membrane might break when exposed to pressure fluctuations inside a liquid. Such fluctuations are not present in lab scale or pressure testing, but might be induced by the rotation if the rotor in the ROMER II setup.
10.5 Conclusion

Process windows for membrane emulsification in a dripping regime, identified in drop visualization experiments, were successfully transferred to a pilot scale emulsification process. For these transfer from lab to pilot scale, the membrane type, its surface modification, the maximum trans membrane pressure and the wall shear stress was maintained.

The drop size measured in lab scale visualization experiments and in the pilot scale experiments were not identical. However, the accordance could be improved when assuming an underrepresentation of small drops in the visualization experiment, which may appear as satellite drops during breakup of a drop from the pore. Even when an exact quantitative comparison was questionable, it was possible to link the drop detachment regime found in the visualization flow cell qualitatively to the drop size distributions measured in the pilot scale experiment. A transition from dripping to jetting was observed in the visualization experiments, which corresponded well to the span increase in pilot scale experiment for increasing wall shear stress. Stable jets were observed in the visualization experiments which corresponded well to a decrease of the size distribution width in the pilot experiments for the corresponding parameterset. Also the wetting (or non-wetting) of the disperse liquid phase on the membrane depending on the hydrophilicity of the membrane surface, was directly correlated to the failed (or successful) emulsification on pilot scale. This result corresponded well to the wetting behavior observed in the visualization experiment. The somewhat chaotic drop formation from sintered metal membranes observed in the visualization experiment correlated well to the strong increase of the drop size distribution span, when increasing the wall shear stress in the pilot scale apparatus.

Micro engineered silicon membranes showed good performance in the pilot scale apparatus in spite their anticipated fragility. Although they worked without failure in flow cell experiments, a few membrane squares on membranes from silicon nitride broke after some production time in the pilot scale setup. When emulsification was successful, micro engineered membranes were capable in producing emulsions with narrow drop size distributions, when the wetting properties were controlled and the wall shear stress was kept low. Hence it is concluded that the control over membrane properties and the applied cross flow are the key factors to control the emulsification result. Additionally the trans membrane pressure has to be low enough to maintain the dripping regime.

For a practical application silicon membranes as developed in this work might be used to achieve emulsions with narrow drop size distributions with median drop diameters of about 20 – 50 µm. Because silicon nitride membranes with smaller pore sizes compared to the silicon membranes failed in the pilot scale process, other membranes had to be used in future to achieve smaller drop. However, experiments with silicon
nitride membranes in the pilot scale and in the visualization cell proved that small drops can be produced in a controlled manner, when the membrane pores are sufficiently small. In these pore size range membranes with a larger mechanical stability are needed for emulsification in the ROMER II setup. Further optimization of the fabrication process for silicon membranes could reduce the minimal pore size to be reached for this membrane type. If the size distribution span is not important, drop sizes smaller than the pore diameter can be easily reached with silicon membranes by increasing the wall shear stress and entering the jetting regime of drop detachment. Although the disperse phase throughput is expected to be lower for decreasing pore diameter, it is still expected that emulsion with about 5% disperse phase volume can be reached with pore diameters of about 1 μm, when the membranes with a porosity of about 0.2% would be available.
11 General conclusion

In this work it was shown, that drop formation and detachment from membranes can be well controlled in a lab and pilot scale process. Contrary to breakup of drops in simple shear, drop breakup from membrane pores is possible in a wide range of viscosity ratios (0.3 to 17 tested). Best control and narrowest drop size distributions is found, when drop detachment is in the dripping regime (in contrast to jetting or drop rupture from a liquid film on the membrane). To achieve the dripping regime, flow through and across the membrane as well as the membrane properties have to be correctly chosen. Concerning the flow parameters, the flow through the membrane has to be sufficiently low. The cross flow should be in a laminar state thereby inducing a wall shear stress large enough to detach drops at a sufficiently small size and small enough to prevent entering a jetting regime. Concerning the membrane properties, the pores should be sufficiently apart from each other to prevent interaction of the drops. Interaction of drops may lead to coalescence or steric hindrance during the growing phase of the drops. Further, a flat membrane is better for controlling drop detachment, because rough membrane structures and additional supports on the membrane surface induce turbulence and prevent the cross flow from attacking the drops equally at each pore. Further, control by the flow through and above the membrane is only possible, when the membrane surface is not wetted by the disperse liquid phase during emulsification.

Micro engineered membranes offer free adjustment of pore size and distance. This makes them superior over commercially available membranes regarding the control of drop detachment in cross flow conditions. Additionally, visual investigations on drop detachment from micro engineered membranes is beneficial. This is because membrane parameters can be independently adjusted through the membrane fabrication process. Further, the drop detachment can be observed well in light microscopy, because the optical contrast between drops and membrane is much larger for flat micro engineered membranes compared to rougher commercially available membranes.

Among commercial available membranes, micro engineered membranes from nickel performed best and have also the potential to be used in the pilot scale process. Sintered membranes from ceramics with sufficiently large pore size showed good performance in lab scale trials and can be tested in pilot scale emulsification. However the adaptation of the membrane shape to the membrane holder will be a challenge because of the brittleness and hardness of the material.
12 Outlook

Modeling In this work, the dimensionless drop size obtained in the dripping regime correlated well as a function of the Capillary number. However, the interfacial tension, and the viscosity of the disperse phase were the same for the entire dataset. For future applications of the process, a deeper understanding about the influence of fluid material properties on the resulting drop size would be helpful. This would require experiments with fluid systems of different interfacial tensions and disperse phase viscosities.

Larger throughputs of the disperse liquid phase can be achieved in the jetting regime compared to the dripping regime. When a somewhat wider drop size distribution is acceptable, this regime is of interest for applications. Therefore more experimental studies focusing on this regime are of interest. The results of this work an others suggest that a parameter window can be found where the width of the distribution is narrow also in the jetting case.

Visualization experiments The visualization cell used in this work allowed for the microscopic observation of drop detachment from membrane pores. However, for small pore sizes the optical resolution was not sufficient to observe the neck formation during the drop formation or the pore itself. In principle light microscopy would allow larger resolutions. The distance between objective and site of observations has to be smaller for larger magnifications. The setup allowed the use of an objective of magnification 40x. For larger magnifications the thickness of the transparent wall has to be decreased and the flow cell and its mount has to be constructed such, that the transparent wall can be positioned closer to the lens. Additionally it is expected that high-speed imaging will require a stronger light source at large magnifications.

An additional pressure measurement within the continuous phase near the position of the membrane would lead to more accurate results. Such a measurement would make the pressure calibration as a function of the continuous liquid phase throughput and the viscosity obsolete and hence would reduce the influence of the error of such a calibration.
Product applications The presented work showed the feasibility of dynamically enhanced membrane emulsification in the pilot scale for model fluids. Consequently, the process should be tested for possible applications. Such an application is the encapsulation of active ingredients, like micronutrients or drugs in drops (or particles made from the drops). Release studies of such materials should be conducted with a focus on the influence of the drop size and the size distribution to evaluate the benefit of a narrow drop size distribution. Production of formations based on double emulsions could be also produced with the process. The drop size range which was achieved with the apparatus until now suggests the formation of the primary (outer) drops by the method.

Another, not yet tested application of dynamically enhanced membrane emulsification would be the in-place preparation of personalized foods or cosmetics. Especially, when membranes with pores of 1 µm width were uses, only a small wall shear stress has to be applied to detach the drops at relatively small size, and the drop size above these minimum wall shear stress changes little as a function of the wall shear stress. This low wall shear stress could be applied by a small continuous phase pump or a stirrer within a modular assembly of devices built into a vending machine. Small quantities of oil carrying aroma compounds or other active ingredients could be emulsified shortly prior consumption. This procedure would protect susceptible ingredients from degradation when in contact with the watery environment or oxygen.

For all possible applications, drop detachment should be studies in the visualization flow cell, because well defined emulsions can only be produced, when the disperse liquid phase does not wet the membrane surface and the trans membrane pressure is chosen correctly. This parameters are hard to evaluate from the dispersing result alone. If the continuous liquid phase is not transparent, visualization experiments should still carried out with the disperse phase fluid and the membrane of interest, by choosing a model fluid for the continuous liquid phase. The properties of the model continuous phase liquid should match the continuous liquid phase used in the process as close as possible. This approximation should be done by adapting the rheology and the surfactants present in the continuous liquid model phase. Additional it is required that the disperse phase does not block the membrane pores. Therefore the disperse phase should be free of particles or molecules that adhere to the membrane surface and form a fouling layer. This can be tested by an emulsification pretrial, where the throughput of the disperse phase should be constant for a given trans membrane pressure over the operating time required for emulsification.

Productivity aspects A broad application of the presented emulsification process require detailed studies on the operating efficiency. The efficiency can be measured in terms of emulsion throughput and the disperse phase concentration. Such an evaluation includes also an evaluation of the cycle time of the membrane for a given
liquid material system and the development of cleaning and regeneration procedures for the membrane. The cycle time will depend on blocking of the membrane by contaminants in the disperse phase liquid. Additionally the wetting properties of the membrane have to be studied over (a longer) time.

**Membranes** Contrary to lab scale experiments, only one of the two types of microengineered membranes tested showed good performance in the pilot scale process. This was mainly caused by a good mechanical stability of one membrane design (silicon) and a failure of part of the membranes for the other (silicon nitride). Microengineered membranes for the pilot scale device therefore are available with circular pore of 12\(\mu\)m diameter. Studies aiming to a similar pore size and bigger can be carried out with the same membranes. Adaptation such as a wider or closer interpore distance or a change in the pore opening aspect ratio can be made by changing the photolithographic mask used for the fabrication of membranes. The use of pores smaller than 10\(\mu\)m is interesting for the application, because at a given wall shear stress the drop size at detachment scales with the pore diameter. Smaller drops are more stable against creaming and mechanical stresses. To use microengineered membranes with pore sizes in the range of e.g. 0.4 to 10\(\mu\)m the membrane fabrication process has to be refined or another fabrication approach has to be chosen. Optimization of the fabrication process for silicon based membranes has the potential to fabricate membranes with pore sizes down to a few micrometers. It is likely that therefore the etching procedure has to be adapted. If etching can not be sufficiently optimized, thinner membranes compared to the ones used in this work have to be chosen. Another approach to produce smaller drop sizes with narrow drop size distributions can be the adaptation of the pore opening aspect ratio. In this work this effect was not significant for 1\(\mu\)m thick silicon nitride membranes. However, literature results and a few of the results gained in this work indicate that interfacial tension driven drop formation at smaller drop diameters compared to a circular pore of same width happens from slit shaped pores, when the aspect ratios of the pore – length to width and height to width – are big enough. Slit shape pores, smaller than the round pores of 12\(\mu\)m could be fabricated with the present process, because etching rates are faster for slits compared to circular structures.
Bibliography


[18] Duxenneuner, Manuela R: Visualization, design, and scaling of drop generation in co-flow processes. Laboratory of Food Process Engineering, Swiss Federal Institute of Technology (ETH) Zürich, November 2009.


[34] Hürlimann, Laurenz: Microfluidics as a model system for membrane emulsification - Design of the membrane surface to control droplet detachment. MSc Thesis, ETH Zurich, pp. 1–72, July 2009.


Bibliography


Appendix
A Appendix

A.1 PECVD process recipes

A.1.1 Deposition of low stress silicon nitride

In Table A.1 the deposition recipe as used with the control software of the device is shown.

Table A.1: Steps of silicon nitride deposition recipe *Holzapfel 1SiNx 2011*

<table>
<thead>
<tr>
<th>Step name</th>
<th>duration</th>
<th>pressure</th>
<th>gas flow</th>
<th>power</th>
<th>temp.</th>
<th>pulse</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[s]</td>
<td>[mTorr]</td>
<td>[sccm]</td>
<td>[sccm]</td>
<td>[sccm]</td>
<td>[W]</td>
<td>[W] [°C] [s] [s]</td>
</tr>
<tr>
<td>SiH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1200</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>300</td>
<td>0 0</td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiNx Deposition</td>
<td>5451</td>
<td>900</td>
<td>400</td>
<td>30</td>
<td>30</td>
<td>300</td>
<td>10 17 RF always on</td>
</tr>
<tr>
<td>N2 purge</td>
<td>300</td>
<td>500</td>
<td>0</td>
<td>500</td>
<td>0</td>
<td>300</td>
<td>0 0</td>
</tr>
</tbody>
</table>

A.1.2 Deposition of silicon oxide to alter membranes hydrophilic

A.2 RIE process recipes

A.2.1 Pattern transfert to titanum hard mask and silicon pore etching into silicon nitride

In Table A.3 the process steps of the etching recipe as used with the control software of the dry etching setup are shown. The steps between *repeat* and *loop* were repeated as many times as indicated. In Table A.4 the steps for the recipe used after mask renewal (deposition of titanium on tilted sample) are listed.
### Table A.2: Steps of PECVD recipe *Holzapfel First Petra SiOx* for deposition of Silicon oxide

<table>
<thead>
<tr>
<th>Step name</th>
<th>duration</th>
<th>pressure</th>
<th>gas flow</th>
<th>power</th>
<th>temp.</th>
<th>pulse-time</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>Flush</td>
<td>150</td>
<td>900</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>Deposition SiOx</td>
<td>60</td>
<td>900</td>
<td>500</td>
<td>710</td>
<td>0</td>
<td>30 30</td>
<td>300 10 10</td>
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<tr>
<td>Purge N2</td>
<td>180</td>
<td>900</td>
<td>0</td>
<td>0</td>
<td>500</td>
<td>0</td>
<td>300</td>
</tr>
</tbody>
</table>

### Table A.3: Steps of etching recipe *Holzapfel etch PK110517 (26072012)* for hard mask etching and silicon nitride etching of structures into silicon nitride

<table>
<thead>
<tr>
<th>Step name</th>
<th>duration</th>
<th>pressure</th>
<th>gas flow</th>
<th>power</th>
<th>DC bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeat 4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purge N2</td>
<td>120</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pump</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Loop</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pump</td>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Flush gas lines</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>Pump 20 sec</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>*Ar sputtering</td>
<td>30</td>
<td>40</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>Pump 5sec</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>*Ti etch SF6/N2</td>
<td>345</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Purge N2</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>Pump</td>
<td>60</td>
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<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>Repeat 70</td>
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<td></td>
</tr>
<tr>
<td>Flush CHF3</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pump 5 sec</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>* SiNx etch</td>
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<td>190</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Flush O2</td>
<td>30</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>*Ox</td>
<td>15</td>
<td>200</td>
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<td>0</td>
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<tr>
<td>Loop</td>
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<td></td>
<td></td>
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<td>0</td>
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</tr>
</tbody>
</table>

1 Power was adjusted by control software to match DC bias.
Table A.4: Steps of etching recipe for hard mask etching and silicon nitride, second step after mask renewal

<table>
<thead>
<tr>
<th>Step name</th>
<th>duration</th>
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<th>gas flow</th>
<th>power</th>
</tr>
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<td>[s]</td>
<td>[mTorr]</td>
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<tr>
<td>Repeat 4</td>
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<td>0</td>
</tr>
<tr>
<td>Pump</td>
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<td>0</td>
</tr>
<tr>
<td>Loop</td>
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<td>0</td>
</tr>
<tr>
<td>Repeat 45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pump</td>
<td>60</td>
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<td></td>
<td></td>
</tr>
<tr>
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</tr>
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<td>Pump 5 sec</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>* SiNx etch</td>
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<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**A.2.2 Large area etching of silicon nitride**

In Table A.5 the process steps of the etching recipe as used with the control software of the dry etching setup are shown.

Table A.5: Steps of etching recipe *Holzapfel SiNx* for large area etching of silicon nitride

<table>
<thead>
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<th>Step name</th>
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<th>pressure</th>
<th>gas flow</th>
<th>power</th>
</tr>
</thead>
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<tr>
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<td>[s]</td>
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<td>[sccm]</td>
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<td>[sccm]</td>
<td>[sccm]</td>
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<tr>
<td>Pump</td>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2 flush</td>
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<td>100</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>SiNx etch</td>
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<td>100</td>
<td>80</td>
<td>20</td>
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<tr>
<td>Purge</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>
Curriculum Vitae

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- **citizen of**: Germany

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