

## 1 Introduction

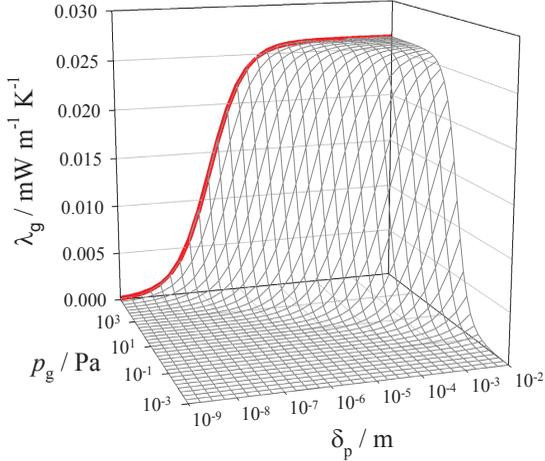
Liquid and solid foams have a wide area of applications in everyday life. While liquid foams are for example used as fire-fighting foams, the latter are used as building material, foam rubber, for packaging or thermal insulation [1]. For thermal insulation materials, typically expanded or extruded polystyrene (PS) or polyurethane (PU) foams are used [2]. In general, PU foams are obtained by polyaddition of polyol and polyisocyanate, each exhibiting at least two functionalities, in the presence of a chemical and/or physical blowing agent [3]. In recent years, nanoporous materials with pore sizes in the nanometer range have gained increasing interest. Compared to non-porous materials and foams with pore sizes in the micrometer range, these nanoporous materials exhibit improved and new properties, e.g. optical transparency, mechanical stability and low thermal conductivity [4–7]. With respect to the envisaged production of high performance insulation materials, PU is particularly suitable, as it exhibits a large potential for improvements.

The insulating capacity of porous materials is quantified by the inverse of the thermal conductivity  $\lambda_{\text{therm}}$ , which comprises contributions of the entrapped gas  $\lambda_g$ , the solid material  $\lambda_m$  and the thermal radiation  $\lambda_{\text{IR}}$  [8]. State of the art polyurethane foams exhibit pore size of around 100  $\mu\text{m}$  and a thermal conductivity of  $\lambda_{\text{therm}} \approx 0.030 \text{ W/mK}$  [3, 9]. As the gaseous thermal conductivity makes the major contribution [9], the most promising approach to lower the thermal conductivity is a reduction of  $\lambda_g$ .

One possibility to reduce  $\lambda_g$  is the use of gases with a low gas phase thermal conductivity  $\lambda_{g,0}$ . In the case of PU foams, ozone-depleting chlorofluorocarbons (CFCs) with  $\lambda_{g,0} \approx 0.008 \text{ W/mK}$  were used as blowing agent from the late 1950s until the mid-1980s [10, 11]. With respect to the environmental protection, nowadays PU is mainly foamed using  $\text{CO}_2$  ( $\lambda_{g,0} \approx 0.016 \text{ W/mK}$ ) or pentane ( $\lambda_{g,0} \approx 0.011\text{--}0.016 \text{ W/mK}$ ) [2, 10].

Another method to reduce  $\lambda_g$  is the *Knudsen* effect (see Figure 1.1) [12–14]. If the pore size  $\delta_p$  is comparable with or smaller than the mean free path length of an enclosed gas ( $\sim 100 \text{ nm}$  at atmospheric pressure), the probability for a gas molecule to collide with another gas molecule is lower than for a collision with the pore walls. This means, that the gaseous thermal conductivity approaches zero. Beside a reduction of the pore size, the *Knudsen* effect can also be achieved by reducing the mean free path length via a reduction of the gas pressure  $p_g$  (e.g. down to 1 mbar)

[15]. Figure 1.1 shows the gaseous thermal conductivity  $\lambda_g$  as a function of the gas pressure  $p_g$  and characteristic size of pores  $\delta_p$ .



**Figure 1.1:** Calculated values for the gaseous thermal conductivity  $\lambda_g$  as a function of the gas pressure  $p_g$  and characteristic size of pores  $\delta_p$ .  $\lambda_g$  was calculated via the *Knudsen* number with:  $\lambda_{g,0} = 0.0179$  W/mK, the constant  $\beta_{Kn} = 1.5$ , the diameter of the gas molecules  $d_g = 3.76 \cdot 10^{-10}$  m and  $T = 293.15$  K (compare [12]).

In case of vacuum insulation panels (VIP), an open-cellular porous materials combined with a low gas pressure and surrounded by a gas-tight envelope (often made of aluminium) used to prevent air from entering the panel [12]. For instance the thermal conductivity of fumed silica  $\lambda_{\text{therm}} \approx 0.020$  W/mK can be lowered to  $\lambda_{\text{therm}} \approx 0.003$  W/mK by applying a vacuum of  $p_g \approx 5 \cdot 10^3$  Pa. However, VIPs are expensive, very fragile, sensitive towards puncture and difficult to process. Furthermore, permeation with time cannot be entirely excluded, which results in an increasing thermal conductivity. Thus, in order to achieve a highly efficient thermal insulation material, a reduction of the pore size is the most promising method.

The best-known example for nanoporous bulk materials are aerogels. Organic, inorganic as well as organic-inorganic hybrid materials are already described in literature [4, 16–18]. The preparation of aerogels via the sol-gel-process was first described in 1931 by *Kistler* [4, 5]. The first step is the formation of sol particles with a diameter of 1–3 nm from dissolved molecular precursors [19]. Condensation of these sol particles forms a spongelike, three-dimensional gel network. By definition, in the case of aerogels, the solvent is replaced by air. Though,

conventional drying by evaporating the solvent results in shrinkage of the material due to capillary forces. To avoid altering of the gel network, a supercritical (sc) drying step using e.g. CO<sub>2</sub> is necessary. However, in the case that water is used as solvent, firstly water has to be replaced by e.g. acetone or ethanol. Subsequently the liquid can be exchanged by scCO<sub>2</sub>, whereby the required time is connected to the diffusion of scCO<sub>2</sub> and thus the dimensions of the gel. E.g. in case of rods with a diameter of 1.5 cm, the replacement takes 3 hours [20]. In sum, the production of aerogels requires an autoclave and is not readily possible in a continuous way. Furthermore, a solvent-replacement is required, which is time-consuming as well as cost-intensive.

Another approach for the production of nanoporous bulk materials is the “Nanofoms by Continuity-Inversion of Dispersion” (NF-CID) procedure developed by *Strey* and *Müller* [21, 22]. Here, in a first step a dispersion of monodisperse, thermoplastic polymeric nanoparticles, e.g. PS or polymethylmethacrylate (PMMA) is prepared via emulsion polymerization. Drying yields a close-packed colloidal crystal, whose nanodisperse voids in the next step are filled with a supercritical fluid, e.g. scCO<sub>2</sub>. Thereby the supercritical fluid reduces the glass transition temperature  $T_g$  of the polymer [23]. Increasing the temperature above the lowered  $T_g$  results in the continuity-inversion, i.e. the colloidal crystal is converted into a polymer matrix with nanometer sized spherical pools of the supercritical fluid. Expansion results in a foaming and a simultaneous fixation of the polymer, since the glass transition is increased again due to the decreasing amount of sc-fluid soluble in the polymer matrix. It is found that the foam pore size is directly proportional to the particle size [22]. In addition, the use of a colloidal crystal template made of polymeric nanoparticles allows a rapid saturation of the thermoplastic polymer with the supercritical blowing agent and thus a rapid decrease of  $T_g$ . Moreover, the colloidal crystal template provides the high number density of blowing agent pools. Applying the NF-CID procedure, PS and PMMA foams with pore diameters in the range of 0.1 to 10  $\mu\text{m}$  were realized [22, 24].

Very recently, *Grassberger et al.* described a blowing-agent free process to produce a nanostructured polymer material [24–26]. A polymeric network is swollen by a homogeneous mixture of two solvents. While the first solvent decreases  $T_g$  and swells the polymer, the second solvent does not swell the polymer but must have a lower vapor pressure than the first one. PMMA for instance can be swollen with a mixture of acetone and cyclohexane acting as swelling and non-swelling agent, respectively. A slight volume decrease occurs upon evaporation of the

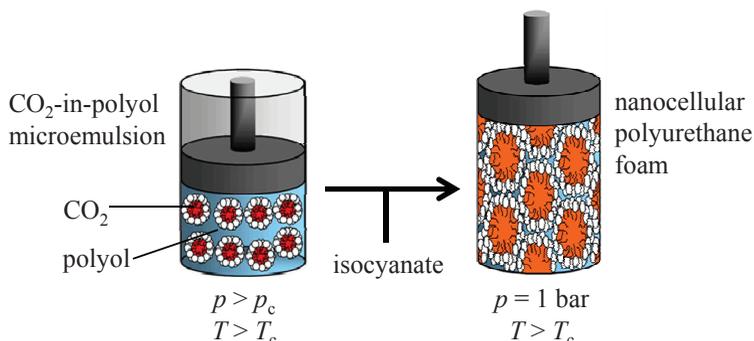
swelling-agent, while the network cannot collapse due to the embedded second solvent. Furthermore,  $T_g$  of the polymer is increased and the fixation is achieved. At the end the non-swelling agent can then be evaporated to obtain the nanostructured polymer material. Thus, PMMA materials with a pore diameter between 80 and 800 nm were realized [25]. Furthermore, *Grassberger et al.* showed that the gaseous thermal conductivity of these PMMA materials can be described by the *Knudsen*-effect. By decreasing the characteristic pore size, the gaseous thermal conductivity at ambient pressure was reduced from  $\lambda_g = 0.026$  W/mK for 300  $\mu\text{m}$  down to  $\lambda_g = 0.009$  W/mK for 80 nm [25].

However, the procedures for the production of nanoporous materials presented so far imply several elaborate steps, e.g. require the synthesis of a dispersion of monodisperse, thermoplastic polymeric nanoparticles or polymer networks in the first step. In addition often different solvents are required. In contrast the POSME principle described below, requires only one blowing agent and should generally facilitate a continuous production of polymeric nanofoams.

The “Principle Of Supercritical Microemulsion Expansion” (POSME) was proposed by *Strey, Sottmann* and *Schwan* in 2003 [27, 28]. This approach uses thermodynamically stable and nanostructured microemulsions as the templates for the production of highly porous nanostructured foams. Microemulsions are mixtures of at least three components, whereby an amphiphilic film facilitates the mixing of two otherwise immiscible components, i.e. a hydrophilic and a hydrophobic component. In case of the POSME approach, the replacement of the hydrophobic component with a near or supercritical fluid, e.g.  $\text{scCO}_2$ , allows for the formulation of a foamable nanostructured template consisting of supercritical fluid-swollen domains in an hydrophilic matrix with number densities up to  $10^{19} \text{ cm}^{-3}$  [28]. Thereby  $\text{CO}_2$  is the supercritical fluid of choice, because it is abundant, inflammable, non-toxic and inexpensive. Furthermore  $\text{CO}_2$ , exhibits a relatively high critical density of  $\rho_c = 0.468 \text{ g}\cdot\text{cm}^{-3}$  at technically feasible critical pressure  $p_c = 73.77 \text{ bar}$  and temperature  $T_c = 30.98 \text{ }^\circ\text{C}$  [29]. Adjusting a temperature above  $T_c$ , the density of the supercritical fluid reduces steadily and without a nucleation step upon expansion of the template microemulsion. Thus, ideally each  $\text{CO}_2$ -swollen micelle will be transferred into a foam bubble. However, a precise knowledge of the phase behavior and microstructure of these template microemulsions is essential to apply the POSME procedure. First experiments showed that both the expansion step and the solidification of the liquid foam is challenging. *Klostermann* showed that sugar foams with a pore diameter of 1–30  $\mu\text{m}$  and a nano-sized substructure can be produced by foaming microemulsions consisting of

highly concentrated sugar solutions and propane [30, 31]. The coarsening of the structure was explained by *Ostwald* ripening [32–34] and coagulation followed by coalescence [34–36].

In 2005 the Bayer MaterialScience AG (BMS) started the cooperation with the *Strey* group (Institute of Physical Chemistry, University of Cologne), which aimed at the production of nanocellular polyurethane foams as a highly efficient thermal insulation material utilizing the POSME procedure (Figure 1.2).



**Figure 1.2:** Schematic representation of the most relevant steps of the “Principle Of Supercritical Microemulsion Expansion” (POSME) process for the production of a nanocellular polyurethane (PU) foam. First a microemulsion of CO<sub>2</sub>-swollen micelles in a polyol matrix is formulated at supercritical conditions ( $p > p_c$ ,  $T > T_c$ ). After addition of polyisocyanate, which starts the polyaddition reaction, the expansion to ambient pressure induces the foaming of the solidifying foam. Modified from [28].

Within the project polyol-CO<sub>2</sub>-microemulsions were formulated at the University of Cologne and afterwards foamed at BMS. As has been found for the sugar-foams, the PU foams produced by the POSME principle show coarsening phenomena, which are partly related to the high monomeric solubility of CO<sub>2</sub> in polyol. In order to reduce these coarsening phenomena, the Anti-Aging-Agent-concept was proposed [37–39]. In this approach a low-molecular, hydrophobic co-ol is added as an Anti-Aging-Agent (AAA) to decrease the unfavorable interfacial tension between CO<sub>2</sub> and polyol during the expansion step. In mid-2015 a cooperation between BMS and the *Sottmann* group (Institute of Physical Chemistry, University of Stuttgart) was established, which was followed by the project “Polyurethane nano-cellular foams made from blowing agent based microemulsions for high performance thermal insulation” (PuNaMi) funded by the German Federal Ministry for Economic Affairs and Energy (BMWi). Note that BMS has become a separate legal entity in 09/2016, operating under the name Covestro Deutschland AG. Affiliated

partners are the Covestro Deutschland AG, Evonik Industries AG, CAM-D, the Fraunhofer LBF, as well as groups from the Johannes Gutenberg University Mainz and Friedrich Alexander University Erlangen-Nürnberg. Thus, the effort and focus to use the POSME procedure for the production of nano-cellular PU foams were increased.

As pointed out, the detailed knowledge of the phase behavior and microstructure of these polyol-containing CO<sub>2</sub>-microemulsions, as well as the influence of the expansion step on the microemulsion properties is crucial to put the POSME procedure into practice. Thus, the formulation and characterization of well-structured polyol-rich CO<sub>2</sub>-microemulsions exhibiting a high number density of CO<sub>2</sub>-swollen micelles was the major task of the subproject of the University of Stuttgart.

In order to accomplish this task, the detailed knowledge of the properties of closely related microemulsion systems of the type water – CO<sub>2</sub> – non-ionic surfactant might be of great benefit. In recent years these systems have also attracted increasing attention due to their potential as a possible replacement for organic solvents and as reaction media [40]. Furthermore, they are also highly interesting from a fundamental point of view, since their properties such as bending elasticity constants can strongly be influenced by varying the pressure without changing the composition [41]. Unfortunately, environmentally unfriendly fluorinated surfactants are the amphiphiles of choice to solubilize CO<sub>2</sub> in water efficiently [42–44]. In recent years a number of aqueous CO<sub>2</sub>-microemulsion systems have been systematically studied with respect to their phase behavior, microstructure and the properties of the amphiphilic film [41, 45–51]. Nevertheless, so far the entire phase inversion and the respective structural inversion starting from CO<sub>2</sub>-in-water over bicontinuously structured to water-in-CO<sub>2</sub> microemulsions induced by temperature wasn't shown.

Similar to the corresponding state description of real gases by *van der Waals* in 1881 [52], *Strey* and *Sottmann* have shown that for microemulsion systems of the type water – *n*-alkane – C<sub>i</sub>E<sub>j</sub> the temperature dependence of the phase behavior, the oil/water-interfacial tension  $\sigma_{ab}$  and the characteristic length scale  $\xi$  can be scaled onto each other [53–56]. However, until now it was not proven, whether a corresponding state description also exists for water – CO<sub>2</sub> – non-ionic surfactant microemulsion systems.

Recently, for the microemulsion system of the type water – CO<sub>2</sub>/cyclohexane – fluorinated surfactant *Pütz et al.* observed that the efficiency follows a pressure-specific parabolic trajectory as a function of the mass fraction of the co-oil cyclohexane [47, 57]. Thereby, the efficiency is

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maximal at a certain cyclohexane mass fraction and a reduction of the amount of surfactant needed to formulate a one-phase microemulsion by a factor of 2 to 5 was found. From SANS-measurements an accumulation of cyclohexane in the center of the CO<sub>2</sub>-swollen micelles due to repulsive interactions between the cyclohexane and the fluorinated hydrophobic surfactant part was found [47]. Moreover, it was proposed that the increase of the efficiency is connected to an increase of the bending rigidity of the amphiphilic film, however, a probe is so far missing [58, 59].

## Objectives

The first goal of this work was a fundamental study of model-type aqueous CO<sub>2</sub>-microemulsions stabilized by the new fluorinated, environmental friendly surfactant Capstone® FS-3100. A second task was to use the results obtained for the model-type aqueous CO<sub>2</sub>-microemulsions to formulate and characterize well-structured polyol-rich CO<sub>2</sub>-microemulsions as templates for the production of nano-cellular polyurethane-foams via the POSME principle.

Thus, the main aim of the first part was to show, that model type aqueous CO<sub>2</sub>-microemulsions stabilized by the nonionic Capstone® FS-3100 resemble the main features of classical water/oil-microemulsions stabilized by *n*-alkyl polyglycol ether surfactants [53, 54, 56]. Consequently, the phase behavior of the water-rich, balanced as well as CO<sub>2</sub>-rich microemulsions had to be characterized firstly by recording the respective sections through the phase prism at different pressures between 150 and 300 bar. With the knowledge of the phase diagrams, a systematic study of the microstructural evolution by SANS was conducted in order to prove whether a temperature dependent scaling of the characteristic length scale is possible. Furthermore, additional NSE measurements should provide the pressure dependence of the bending rigidity of the amphiphilic film. Having in mind the use of co-oils as so-called Anti-Aging-Agents (AAAs), the influence of the co-oil cyclohexane on the phase behavior, microstructure and dynamics of balanced aqueous CO<sub>2</sub>-microemulsions had to be studied. Main focus was, to prove whether the partial replacement of CO<sub>2</sub> by cyclohexane leads to an increase of the bending rigidity, as predicted in studies of aqueous CO<sub>2</sub>-microemulsions stabilized by Zonyl® surfactants [47].

As the production of nano-cellular polyurethane-foams via the POSME principle was the main driving force of this thesis, the goal of the second part was the formulation and characterization of well-structured polyol-rich CO<sub>2</sub>-microemulsions using the results obtained for the model-type aqueous CO<sub>2</sub>-microemulsion. In order to clarify, whether nonionic trisiloxane surfactants are able to form micelles in polyol, measurements of the Gibbs adsorption isotherm as well as SANS studies were planned. Subsequently, in order to formulate foamable polyol-rich microemulsions, the influence of the amount of CO<sub>2</sub> and pressure on the phase behavior had to be studied. Whether the added CO<sub>2</sub> leads to the swelling of the micelles should be proven by SANS increasing the scattering contrast via the use of a partly-deuterated polyol. Additionally, time-resolved SANS measurements were foreseen to study the structural changes due to periodic pressure jumps. Finally 1,2 and 1,10-decanediol were planned to be added as AAAs in order to study their influence on the phase behavior, microstructure and demixing kinetics.

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## 2 Fundamentals

### 2.1 Microemulsions

Microemulsions are defined as thermodynamically stable, macroscopically isotropic, but nanostructured mixtures of at least three components, stabilized by an amphiphilic film [54, 56, 60, 61]. The first microemulsion system water–oil–alkali-metal soap was already described in 1943 by *Hoar* and *Schulman* [62]. The term microemulsion, however, was first used by *Schulman* in 1959 [63]. The first two components, typically a polar (A, e.g. water) and a non-polar component (B, e.g. an oil), are mutually immiscible. The third component is an amphiphile (C, surfactant). It allows for the formulation of a microemulsion by solubilizing both A and B completely within each other, whereas one-phase results. The surfactant, which consists of a polar (lipophobic) as well as a non-polar (hydrophobic) molecular part, adsorb due to this amphiphilicity at the interface between water and oil. Thereby these phases are separated by the formed amphiphilic film. This process decreases the interfacial tension  $\sigma_{AB}$  between A and B effectively to almost zero, while at the same time the interfacial area strongly increases. As result of the low interfacial tension the surface energy  $E_S$  is raised by the thermal energy  $k_B T$ , which is why these systems are thermodynamically stable. Even though the systems are macroscopically homogeneous, the two immiscible components are still separated from each other via the amphiphilic film. Depending on the composition of the system, temperature  $T$  and pressure  $p$ , different structures like layers (e.g. lamellar  $L_\alpha$ -phase) or droplets are formed. The influence of temperature on the phase behavior of ternary systems was intensively studied by *Kunieda*, *Shinoda* and *Friberg* [64, 65]. In 1987 *Gale et al.* were the first to study pressure-dependent microemulsions containing a supercritical fluid as the hydrophobic component [66].

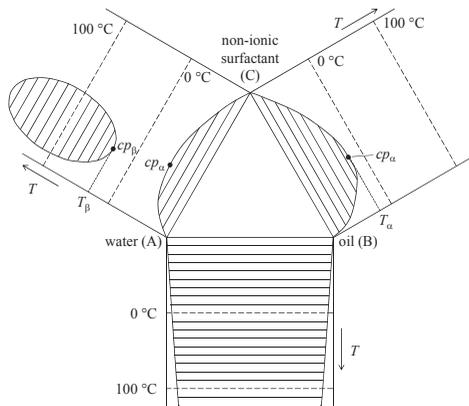
#### 2.1.1 Phase behavior

As pointed out above, microemulsions consist of at least three components, while being stabilized by a surfactant. In general cationic, anionic, zwitterionic and non-ionic surfactants can be used for the formulation of microemulsion systems. Since only non-ionic surfactants were used in this work, the following section is limited to microemulsions stabilized by non-ionic surfactants. As shown by *Kahlweit et al.*, at a constant pressure, the phase behavior of ternary systems of the type water (A)–oil (B)–non-ionic surfactant (C) can be best shown in a temperature dependent *Gibbs* phase triangle, since the phase behavior is rather complex [67]. For

a better understanding of the complex phase behavior of ternary systems, looking at the three temperature-dependent binary side systems of the type water – oil (A – B), oil – non-ionic surfactant (B – C) and water – non-ionic surfactant (A – C) can be helpful.

### Binary side systems

As shown in Figure 2.1, the binary side system of the type water – oil (A – B) represents the simplest one. Water and oil are mutually immiscible with each other over the entire temperature range. Consequently a pronounced lower miscibility gap with an upper critical point, normally above  $100\text{ }^{\circ}\text{C}$ , is found. In contrast, the binary side system of the type oil – non-ionic surfactant (B – C) exhibits a lower miscibility with an upper critical point  $cp_{\alpha}$ . The critical temperature  $T_{\alpha}$  is in the range of the melting point of the mixture, whereas it is strongly dependent on the nature of both oil and non-ionic surfactant [60].



**Figure 2.1:** Schematic drawing of the three binary side systems of water (A), oil (B) and non-ionic surfactant (C), whose superposition describes the ternary system. The components A and B are mutually immiscible, while the lower miscibility gap of the binary system B – C is often located below  $0\text{ }^{\circ}\text{C}$ . The binary system A – C shows a lower miscibility gap at low temperatures and an upper miscibility gap, which is relevant for the description of microemulsions. Redrawn from [60].

The more complex binary side system water – non-ionic surfactant (A – C) shows a lower as well as an upper miscibility gap. The lower miscibility gap with the upper critical point  $cp_{\alpha}$  lies in most cases far below the melting point of the mixture and can therefore be neglected. The upper miscibility gap with the lower critical point  $cp_{\beta}$ , on the other hand, is located in the range of  $T=0\text{--}100\text{ }^{\circ}\text{C}$  and is highly relevant for the microemulsion system. Again, the corresponding