

## Kinetics of pressure induced structural changes in super- or near-critical CO<sub>2</sub>-microemulsions

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### I. Materials

All materials except the surfactants were used without any further purification. The technical grade fluorinated surfactants are commercially available polyethylene glycol-perfluoroalkylether of the type F-(CF<sub>2</sub>)<sub>i</sub>-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>j</sub>-H (denoted as C<sub>i</sub>FE<sub>j</sub>) and were purchased from DuPont. Both the surfactants Zonyl FSN 100 (*i* = 6-8, degree of ethoxylation *j* = 8 to 12) and Zonyl FSO 100 (*i* = 6-8, degree of ethoxylation *j* = 6 to 10) were solved in ethanol, dried over NaSO<sub>4</sub>, filtered and ethanol was removed using a rotating evaporator prior to use. NaCl (purity > 99.5%) was purchased from Fluka (Neu Ulm, Germany). D<sub>2</sub>O was purchased from Eurisotop (quoted > 99.9%). Water (H<sub>2</sub>O) was deionized and distilled twice. CO<sub>2</sub> (technically pure) was obtained from Linde AG (Munich, Germany).

### II. The SHP-SANS cell and sample preparation

In order to investigate the structural changes which occur in a microemulsion containing super- or nearcritical CO<sub>2</sub> an innovative stroboscopic high pressure (SHP)-SANS cell was designed which allows performing fast pressure cycles with adjustable amplitude and duration. The sample volume (about 15-20 mL) is sealed by two sapphire discs that allow also for a visual inspection of the sample, i.e. the type and number of the coexisting phases. The starting pressure inside the cell can be adjusted using a tunable piston with an expandable metallic bellow at its end. Piston and bellow are filled with hydraulic oil and connected to a hydraulic pump that can provide two different pressures. Pressure cycles of adjustable amplitude, i.e.  $p_{\text{high}}$  and  $p_{\text{low}}$  and duration can be obtained using a combination of the hydraulic circuit and pneumatically actuated ball valves. The SHP-SANS cell was controlled using a specially designed electronic setup and the software *LABVIEW*®. The pressure inside the cell was recorded with a digital oscilloscope (*Picoscope*). The temperature of the sample can be adjusted in the range of 10°C to 50°C with an accuracy of ± 0.1°C. The maximum pressure which can be applied is 350 bar. The highest possible pressure cycle frequency is

10 Hz so far. A stirring bar is implemented into the bottom of the cell for homogenization. Also for this purpose it is possible to turn the cell upside-down.

The samples were prepared directly inside the HP-SANS cell. First, water and surfactant were added to the cell controlling the respective amounts by weight with an accuracy of  $\pm 0.001\text{g}$ . Using a custom made filling apparatus equipped with a membrane reservoir liquid  $\text{CO}_2$  was added to the cell at ambient temperature and 70 bar. The mass of  $\text{CO}_2$  was calculated from its volume and its density under the given conditions with an accuracy of  $\pm 0.05\text{g}$ . After filling the cell with  $\text{CO}_2$  the pressure was adjusted and the sample was heated/cooled to a desired temperature under magnetic stirring. Once the equilibrium temperature was reached the pressure was regulated, the magnetic stirring was stopped and the number and the type of the coexisting phases were determined. This was done by visual inspection of both the transmitted and the scattered light. After changing the temperature and readjusting the pressure, this procedure was repeated until the sample was in a phase state desired for the scattering experiments. The HP-SANS cell was directly placed into the neutron beam.

Phase behavior measurements were carried out in a high-pressure view cell with similar design but without the bellow. The filling procedure and the determination of the phase boundaries is basically the same and has been described by Klostermann *et al.* before (ref. 19).

### III. SANS-Measurements

All SANS-measurements were performed at the instrument D22 at the Institut Laue-Langevin in Grenoble, France adjusting a neutron wavelength of  $\lambda = 6 \text{ \AA}$ . The distances between sample and detector were set to 3 m, 11.2 m and 17.6 m. The collimation distance was chosen to be 11.2 m for the detector distances 3 m and 11.2 m. A collimation distance of 17.6 m was used for the long detector distance. Thus, the scattering vector  $q = 4\pi\sin(\theta/2)/\lambda$  ranged from 0.006 to  $0.3 \text{ \AA}^{-1}$ , where  $\theta$  is the scattering angle. The ILL specified a wavelength distribution of  $\Delta\lambda/\lambda = 0.1$  (full width at half maximum) for the D22 instrument. The kinetic measurements were performed at a detector distance of 11.2 m.

In order to calibrate the scattering data obtained to absolute scale the data normalization was performed with respect to the empty beam measurement. This leads to an expression for the scattering intensity in absolute units:

$$\frac{d\Sigma}{d\Omega}(\theta) = \frac{1}{V} \frac{I(\theta)}{\epsilon \Delta\Omega T J_0} = \frac{1}{\epsilon I_0} \frac{I(\theta)}{dT \Delta\Omega} \quad (1)$$

where  $V$  is the scattering volume,  $d$  is its neutron path length (2 mm),  $I(\theta)$  is the neutron intensity measured by a detector pixel at the scattering angle  $\theta$ ,  $\epsilon$  is the detection efficiency of the pixel,  $\Delta\Omega$  is the solid angle subtended by the pixel,  $T$  is the transmission of the sample,  $J_0$  is the incident neutron flux and  $I_0$  is the incident intensity.

#### IV. Scattering models

##### *Microemulsion Droplets*

In case of a semi-dilute system comprising  $N$  scattering particles in a homogeneous medium of volume  $V$  the scattering intensity can be factorized into inter- and intraparticle scattering contributions (decoupling approximation)

$$I(q) = n \cdot P(q) \cdot S(q) \quad (2)$$

with  $n$  being the particle number density  $N/V$ . In the case of spherical microemulsion droplets the particle number density  $n$  is defined as

$$n = \phi_{c,i} \frac{a_c}{4\pi v_c (R_0^2 + \sigma^2)}. \quad (3)$$

Here  $\phi_{c,i}$  denotes the volume fraction of the surfactant in the internal interface,  $v_c$  and  $a_c$  are the volume and area per surfactant molecule, respectively,  $R_0$  is the average radius and  $\sigma$  the polydispersity. The form factor  $P(q)$  describes the intraparticle scattering and is related to the shape of the particles. The structure factor  $S(q)$  accounts for scattering contributions arising from the interference of neutrons scattered from different particles.

The particle form factor is defined as the product of the squared particle volume  $V_{\text{part}}$  and the product of the normalized scattering amplitude  $A(q)$  and its complex conjugate  $A^*(q)$ . For spherical microemulsion droplets  $A(q)$  can be written as

$$A(q) = \frac{4\pi}{V_{\text{part}}} \int_0^{\infty} dr \Delta\rho(r) \cdot r^2 \frac{\sin(qr)}{qr}. \quad (4)$$

The radial scattering length density profile  $\Delta\rho(r)$  is related to the radial density distribution function  $f(r,R)$  by  $\Delta\rho(r) = \Delta\rho_{\text{film}} f(r,R)$ . Thereby the radial density distribution

$$f_{\text{droplet}}(r, R) = \frac{1}{\exp\left[\frac{r-R-d/2}{\chi}\right] + 1} - \frac{1 - \Delta\rho_{\text{core}}/\Delta\rho_{\text{film}}}{\exp\left[\frac{r-R+d/2}{\chi}\right] + 1}. \quad (5)$$

allows to account for scattering contributions of both core and film scattering (refs. 19, 38). Here,  $\Delta\rho_{\text{core}}$  is the scattering length density difference between the core and the solvent and  $\Delta\rho_{\text{film}}$  is the difference between the film and the solvent. The thickness of the amphiphilic film is described by the parameter  $d$  and the parameter  $\chi$  is a measure of the sharpness of the interface where  $\chi \rightarrow 0$  would lead to a step-like scattering profile. To account for polydispersity effects the particle form factor was convoluted with a Gaussian size distribution

$$W(R, R_0, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{-\frac{(R - R_0)^2}{2\sigma^2}\right\}. \quad (6)$$

### ***Cylindrical droplets***

In the limit of  $qR \ll 1$  the form factor of a cylinder  $P_{\text{cylinder}}(q)$  can be approximated by a factorization into an axial contribution of the rod scattering  $P_{\text{rod}}(q)$  and a cross sectional contribution  $P_{\text{cross}}(q)$  according to

$$P_{\text{cylinder}}(q) = L_0^2 \int_0^\infty dL P_{\text{rod}}(q) W_L(L, L_0, \sigma_L) \int_0^\infty dR P_{\text{cross}}(q) W_R(R, R_0, \sigma_R). \quad (7)$$

(refs. 39, 40). Thereby,  $L_0$  is the length of the cylinder. In order to account for a size distribution of the radius as well as of the cylinder length both scattering contributions are calculated with respect to a correspondent *Gaussian* distribution function. Here,  $W_R$  is given by (6) and  $W_L$  by

$$W(L, L_0, \sigma_L) = \frac{1}{\sqrt{2\pi\sigma_L^2}} \exp\left[-\frac{(L - L_0)^2}{2\sigma_L^2}\right], \quad (8)$$

with  $\sigma_L$  being the polydispersity of the cylinder length, which was fixed at  $\sigma_L = 0.25$  in this work. Assuming an infinitely thin rod and averaging over all possible orientations in space, the axial contribution is given by the form factor

$$P_{\text{rod}}(q) = \frac{2 \text{Si}(qL)}{qL} - \frac{4 \sin(0.5qL)}{q^2 L^2}, \quad (9)$$

where  $\text{Si}(qL)$  is the sine integral function of  $qL$ . By means of  $f_{\text{droplet}}(r,R)$  it is again possible to account for both core and film scattering. The form factor that describes cross sectional scattering contributions is given by

$$P_{\text{cross}}(q) = \left[ 2\pi \Delta\rho_{\text{film}} \int_0^\infty dr r f_{\text{droplet}}(r,R) J_0(qr) \right]^2. \quad (10)$$

Here,  $J_0(qr)$  is the zeroth order *Bessel* function of first kind. In the case of a cylindrical geometry of the droplets the particle number density  $n$  is defined as

$$n = \frac{\Phi_{\text{C,i}} a_c}{v_c 2\pi R_0 (L_0 + R_0)}. \quad (11)$$

The free fit parameters are the length of the cylinder  $L_0$ , the average cross section radius  $R_0$ , the corresponding polydispersities  $\sigma_L$  (set to  $\sigma_L = 0.25$ ) and  $\sigma_R$ , the thickness of the surfactant shell  $d$  as well as  $\chi$  that describe the shape of the density profile.

### ***Percus-Yevick structure factor***

For repulsive hard-sphere interactions of monodisperse and spherical particles, the structure factor can be analytically calculated using the *Percus-Yevick* approximation (ref. 41) Hence, the structure factor  $S(q)$  depends only on the interparticle interaction potential and can be related to the *Fourier* transform of the direct correlation function  $c(q)$  of the particles

$$S_{\text{PY}}(q) = \frac{1}{1 - nc(q)}. \quad (12)$$

Within the *Percus-Yevick* approximation  $c(q)$  is given by

$$nc(q) = \frac{36(1 + 2\phi_{\text{disp}})^2}{x^3(1 - \phi_{\text{disp}})^4} \phi_{\text{disp}}^2 [h_1 + h_2 + h_3] \quad (13)$$

With

$$\begin{aligned} h_1 &= -2 \left[ \frac{\sin(x) - x\cos(x)}{3\phi_{\text{disp}}} - \frac{4}{x^3} \right] \\ h_2 &= \frac{1}{3} \left[ \left(1 - \frac{6}{x^2}\right) 4\sin(x) - \left(1 - \frac{12}{x^2} + \frac{24}{x^4}\right) x\cos(x) \right] \\ h_3 &= 2 \left[ \left(\frac{2}{x^2} - 1\right) \frac{x\cos(x)}{2} + \sin(x) - \frac{1}{x} \right]. \end{aligned}$$

Here,  $x = 2R_{\text{HS}}q$  with  $R_{\text{HS}}$  being the hard sphere radius of the particles. In order to account for a size distribution of the non-ionic microemulsion droplets the averaged *Percus-Yevick* structure factor

$$\overline{S_{\text{PY}}(q)} = \int_0^{\infty} dR_{\text{HS}} S_{\text{PY}}(q) W(R_{\text{HS}}, R_{\text{HS},0}, \sigma_{\text{HS}}). \quad (14)$$

was used. Note, that Eq. (14) has to be solved numerically.

### ***Ornstein-Zernicke structure factor***

Because critical fluctuations, which typically occur in microemulsions, studied nearby the upper near critical boundary, have to be taken into consideration, the *Ornstein-Zernike* structure factor (refs. 36, 42)

$$S_{\text{OZ}}(q) = 1 + \frac{S_{\text{OZ}}(0)}{1 + q^2\xi^2}, \quad (15)$$

was convoluted with the Percus-Yevick structure factor. Here  $S_{\text{OZ}}(0) = nk_{\text{b}}T\chi_{\text{T}}$  with  $k_{\text{b}}$  being the *Boltzmann* constant and  $\chi_{\text{T}}$  the isothermal compressibility of the microemulsion. The parameter  $\xi$  describes the correlation length of the critical fluctuations. Accordingly, the scattering intensity is given by

$$I(q) = n \cdot \overline{P_{\text{CS}}(q)} \cdot \overline{S_{\text{PY}}(q)} \cdot S_{\text{OZ}}(q). \quad (16)$$

### **V. Scattering length densities and structural parameters**

The scattering length density differences  $\Delta\rho_{\text{core}}$  and  $\Delta\rho_{\text{film}}$  were calculated assuming the scattering lengths shown in Table 1. Within the calculations, different impurities and monomeric solubilities were accounted for. The scattering length density (SLD) of the

surfactants was taken from ref. 19. An impurity of 1 vol-% of H<sub>2</sub>O was assumed in D<sub>2</sub>O. The monomeric solubility of surfactant in CO<sub>2</sub> was also taken from ref. 19 and was fixed at 10 vol-%.

**Table 1:** Overview of the scattering length densities of the used components. All values are given in 10<sup>10</sup>cm<sup>-2</sup>.

surfactant mixture	D <sub>2</sub> O (brine)	CO <sub>2</sub> @ 150 bar	CO <sub>2</sub> @ 200 bar	CO <sub>2</sub> @ 250 bar	CO <sub>2</sub> @ 300 bar
1.76	6.05	2.05	2.15	2.21	2.27

Applying the above described scattering models for the analysis of the pressure dependent scattering curves of the system D<sub>2</sub>O/NaCl - CO<sub>2</sub> - Zonyl FSO 100/Zonyl FSN 100 ( $\gamma_a = 0.08$ ,  $\varepsilon = 0.01$ ,  $\delta_{\text{FSN}} = 0.75$ ) at  $w_{\text{B,SANS}} = 0.10$  and  $T_{\text{SANS}} = 30.0^\circ\text{C}$  the structural parameters summarized in Tab. 2 are obtained.

**Table 2:** Fit parameters resulting from the analysis of the pressure dependent SANS measurements of the system D<sub>2</sub>O/NaCl - CO<sub>2</sub> - Zonyl FSO 100/Zonyl FSN 100 ( $\gamma_a = 0.08$ ,  $\varepsilon = 0.01$ ,  $\delta_{\text{FSN}} = 0.75$ ) at  $w_{\text{B,SANS}} = 0.10$  and  $T_{\text{SANS}} = 30.0^\circ\text{C}$ . The parameter  $\Delta\rho_{\text{film}}$  was fixed at  $4.29 \cdot 10^{10} \text{ cm}^{-2}$ .

$p$ [bar]	$R_0$ [Å]	$\sigma/R_0$	$L$ [Å]	$\chi$ [Å]	$d$ [Å]	$\Delta\rho_{\text{core}}[\text{cm}^{-2}]$	$R_{\text{HS}}[\text{Å}]$	$\sigma_{\text{HS}}/R_{\text{HS}}$	$S_{\text{Oz}}(\mathbf{0})$	$\xi$ [Å]
150	66	0.30	---	5.6	17	$4.00 \cdot 10^{10}$	65	0.70	7	700
200	57	0.40	150	6.6	17	$3.90 \cdot 10^{10}$	62	0.70	50	800
250	57	0.40	190	6.6	17	$3.84 \cdot 10^{10}$	55	0.70	83	1000
300	57	0.50	220	7.1	17	$3.71 \cdot 10^{10}$	53	0.70	94	1300