# Supplementary Information: Surfactant Induced Autophobing

B. Bera, M.H.G. Duits, M.A. Cohen-Stuart, D. van den Ende, F. Mugele January 14, 2016

# 1 Variation Experimental Parameters

## 1.1 Surfactant Concentration



Figure S1: Equilibrium contact angles on (a) mica and (b) silica; in ambient decane with stearic acid vs. pH for various concentrations of CaCl<sub>2</sub>: 1 mM (cyan downward triangles), 10 mM (red circles), 100 mM (blue upward triangles), 1 M (black squares). Stearic acid concentration: 1 mM. The arrow with the letter 'c' denotes the direction of increasing salt concentration.

#### 1.2 Influence of Fatty Acid-Chain Length

In order to investigate the influence of the aliphatic chain length on adsorption, we have performed the autophobing experiments with various fatty acids. As we gradually decrease the aliphatic chain length, a decrease in the final contact angle is observed compared to that for SA. Aqueous drops of CaCl<sub>2</sub> in ambient decane containing decanoic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>COOH) autophobes at pH 9 (the autophobing is negligible at pH 6), and the maximum equilibrium contact angle is ~ 30°, which is significantly lower than in the case of SA (~60°). If we change the fatty acid from decanoic acid to hexanoic acid (C<sub>5</sub>H<sub>11</sub>COOH) in the ambient decane, then the behaviour of the aqueous drops of CaCl<sub>2</sub> are similar to those for decanoic acid, but the equilibrium contact angles are slightly higher.

Hence, as expected, the aliphatic chain length plays a role in the adsorption. It is plausible, that the adsorption of these fatty acid molecules at the O/W interface is proportional to the chain length, and hence SA adsorption is strongest, followed by decanoic acid and hexanoic acid. However, the equilibrium contact angle does not follow this order, since the post-autophobing contact angle for hexanoic acid lies in between that of decanoic acid and SA. While trying to explain this trend, we have to take into consideration the solubility of these fatty acids. SA and decanoic acid are not soluble in water, while hexanoic acid dissolves in water. This implies, that in the case of hexanoic acid adsorption at O/W interface, a fraction of the acid molecules are subsequently transported across the aqueous drop to get directly adsorbed onto the solid substrate. Hence, the substrate is already more hydrophobic (compared to the scenarios of decanoic acid and SA), when the autophobing starts. The contact angle trends for various fatty acids at different CaCl<sub>2</sub> concentrations are represented in Figure S2.

#### 1.3 Influence of Alkane-Chain Length

The influence of the aliphatic chain-length of the solvent upon fatty acid adsorption is found out to be relatively small. We have performed experiments switching the solvent of SA from decane to heptane ( $C_7H_{16}$ ) and hexadecane ( $C_{16}H_{34}$ ). As represented in Figure S3, the autophobing trends as well as the equilibrium contact angles are comparable to the case of SA in decane.



Figure S2: Equilibrium contact angles on mica in ambient decane with (a) hexanoic acid and (b) decanoic acid vs. pH for various concentrations of CaCl<sub>2</sub>: 1 mM (cyan downward triangles), 10 mM (red circles), 100 mM (blue upward triangles), 1 M (black squares). Hexanoic and decanoic acid concentration: 100  $\mu$ M. The arrow with the letter 'c' denotes the direction of increasing salt concentration.



Figure S3: Equilibrium contact angles on mica in ambient (a) heptane and (b) hexadecane with stearic acid vs. pH for various concentrations of CaCl<sub>2</sub>: 1 mM (cyan downward triangles), 10 mM (red circles), 100 mM (blue upward triangles), 1 M (black squares). Stearic acid concentration: 1 mM. The arrow with the letter 'c' denotes the direction of increasing salt concentration.

### 2 Calculation for Autophobing Modeling

In the article, we have introduced a model to address the salient features of adsorption kinetics and evolution of contact angle during autophobing. However, the mechanism of autophobing contains several concurrent processes and we have used a number of assumptions in the described model to simplify the analysis. In the following section, we will provide the general approach of this modeling, which is valid under all conditions.

The aquous drop is considered to be of spherical cap geometry during the entire process of autophobing, hence the radius of the drop as well as the radius of the contact line is a function of contact angle  $\theta$  through the following relations:

$$R = R_0 \left(\frac{4}{2 - 3\cos\theta + \cos^3\theta}\right)^{1/3} \tag{1}$$

$$r = R\sin\theta \tag{2}$$

$$A = 2\pi R^2 \left(1 - \cos\theta\right) \tag{3}$$

$$L = 2\pi R \sin \theta \tag{4}$$

where R is the radius of the spherical cap and  $R_0 = (3V/(4\pi))^{1/3}$ .

The contact angle of the autophobing drop at a specific time-instant t is assumed to be the result of an instantaneous equilibrium, where both the O/Wand the S/O interfacial tension decrease over time due to a progressive accumulation of surface active material leading to higher densities. Here, the first step is the formation of a surfactant layer at the oil-water interface (Figure S4a, left) from the ambient solution by diffusion followed by adsorption. The transfer of SA molecules to the solid substrate starts as soon as the surfactant layer forms at the O/W interface, and this transfer is considered to occur along the oil-water contact surface i.e., surface of the spherical cap. We define  $N_1$  as the number of molecules adsorbed in the O/W interface while  $N_2$  is the number of molecules adsorbed on the substrate (from the O/W interface) in a rim of width w just outside the contact line. This width is assumed to be of the order of the size of an SA molecule. The area of the O/W interface is A and the length of the contact line is  $L = 2\pi r$  where r is the radius of the circular contact line. Furthermore, we define the surface densities  $\Gamma_1 = N_1/A$  and  $\Gamma_2 = N_2/(wL)$ . The autophobing drops are considered to be of sphreical cap geometry where the contact angle  $\theta$  is supposed to increase from a minimum value  $\theta_{\min}$  to a maximum value  $\theta_{\rm max} \approx 60^{\circ}$  after the autophobing. Following the arguments presented in the main text, we can write the instantaneous contact angle in form of the Young's equation:

$$\cos\theta(t) = \frac{\gamma_{so}(t) - \gamma_{sw}}{\gamma_{ow}(t)} \tag{5}$$



Figure S4: Stearic acid adsorption occurs first from bulk ambient alkane phase to the oil-water interface (a, left) and then subsequently the molecules get deposited on the solid substrate (a,right). The enlarged depiction of this deposition process is shown on b, right. (b, left) stearic acid coverage (hatched area) on a solid substrate for an autophobing drop. The initial three-phase contact line is depicted by the dashed line, while the receding contact line is shown by the solid line.

We consider the autophobing a quasi-ideal process, where the interfacial tension  $\gamma$  and the coverage density  $\Gamma$  linearly related:  $\gamma_{ow} = \gamma_{ow,0} - \alpha_1 \Gamma_1$  and  $\gamma_{so} = \gamma_{so,0} - \alpha_2 \Gamma_2$ . Hence, we can write:

$$or, \cos\theta(t) = \frac{\gamma_{so,0} - \alpha_2 \Gamma_2 - \gamma_{sw}}{\gamma_{ow,0} - \alpha_1 \Gamma_1} \tag{6}$$

$$or, \cos\theta(t) = \frac{\gamma_0 \cos\theta_0 - \alpha_2 \Gamma_2(t)}{\gamma_0 - \alpha_1 \Gamma_1(t)}$$
(7)

We can now formulate the following rate equations:

$$\frac{dN_1}{dt} = A(J_{\text{ads}} - J_{\text{des}}) - Lj \tag{8}$$

$$\frac{dN_2}{dt} = Lj + \dot{r}L\Gamma_2 \tag{9}$$

where,  $J_{ads}$  and  $J_{des}$  are the adsorption and desorption fluxes of SA from the bulk oil phase to the O/W interface, respectively, and j is the outward SA flux along the contact line for deposition from O/W to the S/O interface. The

term  $\dot{r}L\Gamma_2$  represents the molecules that leave the contact line area as the drop autophobes because they stick to the substrate and do not move with the contact line inwards. The fluxes are defined by:

$$J_{\rm ads} = ck_1(\Gamma_\infty - \Gamma_1) \tag{10}$$

$$J_{\rm des} = k_2 \Gamma_1 \tag{11}$$

$$j = k_3 \Gamma_1 - k_4 \Gamma_2 \tag{12}$$

where c is the concentration of the molecules in the oil phase near the water-oil interface and  $k_n$  are rate constants.

In order to solve Eqs. (8) and (9), a relation needs to be established between  $\theta$  and  $\Gamma_1$  and  $\Gamma_2$ . We define the function F as:

$$F(\Gamma_1, \Gamma_2, \theta) = \cos \theta - \frac{\gamma_0 \cos \theta_0 - \alpha_2 \Gamma_2}{\gamma_0 - \alpha_1 \Gamma_1} = 0$$
(13)

From this expression we observe that autophobing  $(\cos \theta < \cos \theta_0)$  is only possible if  $\alpha_2 \Gamma_2 > \alpha_1 \Gamma_1 \cos \theta_0$ . Using Equation (13) we can relate  $\dot{\theta}$  with  $dN_1/dt$ and  $dN_2/dt$ :

$$\frac{\partial F}{\partial \theta} \dot{\theta} + \frac{\partial F}{\partial \Gamma_1} \frac{d\Gamma_1}{dt} + \frac{\partial F}{\partial \Gamma_2} \frac{d\Gamma_2}{dt} = 0$$
(14)

or:

$$\dot{\theta} = C_1 \frac{d\Gamma_1}{dt} + C_2 \frac{d\Gamma_2}{dt} \tag{15}$$

where,

$$C_1(\Gamma_1, \Gamma_2, \theta) = \left(\frac{\partial F}{\partial \Gamma_1}\right) \left(-\frac{\partial F}{\partial \theta}\right)^{-1} \qquad C_2(\Gamma_1, \Gamma_2, \theta) = \left(\frac{\partial F}{\partial \Gamma_2}\right) \left(-\frac{\partial F}{\partial \theta}\right)^{-1}$$
(16)

Finally  $\dot{A}$  and the velocity of the contact line  $\dot{r}$  are given by:

$$\dot{A} = \frac{dA}{d\theta} \dot{\theta}$$
 and  $\dot{r} = \frac{dr}{d\theta} \dot{\theta}$  (17)

We can replace  $N_1 = A\Gamma_1$  in the rate equation 8:

$$\frac{d(\Gamma_1 A)}{dt} = Ack_1(\Gamma_\infty - \Gamma_1) - Ak_2\Gamma_1 - L(k_3\Gamma_1 - k_4\Gamma_2)$$
(18)

$$or, \frac{d\Gamma_1}{dt} = \left[ck_1(\Gamma_\infty - \Gamma_1) - k_2\Gamma_1 - \frac{L}{A}(k_3\Gamma_1 - k_4\Gamma_2)\right] - \frac{\frac{dA}{dt}}{A}\Gamma_1$$
(19)

Similarly, from Equation 9, we obtain:

$$\frac{d\Gamma_2}{dt} = \frac{k_3\Gamma_1 - k_4\Gamma_2}{w} + \frac{\dot{r}\Gamma_2}{w} - \frac{\Gamma_2}{L}\frac{dL}{dt}$$
(20)

Summarizing the results so far:

$$\frac{d\Gamma_1}{dt} = B_1 - \frac{A'}{A}\Gamma_1 \left(C_1\frac{d\Gamma_1}{dt} + C_2\frac{d\Gamma_2}{dt}\right)$$
(21)

$$\frac{d\Gamma_2}{dt} = B_2 - \frac{(w-r)r'}{wr} \Gamma_2 \left( C_1 \frac{d\Gamma_1}{dt} + C_2 \frac{d\Gamma_2}{dt} \right)$$
(22)

where we defined:

$$B_1(\Gamma_1, \Gamma_2, \theta) = ck_1\Gamma_1^{\infty} - (ck_1 + k_2)\Gamma_1 - L/A(k_3\Gamma_1 - k_4\Gamma_2)$$
(23)

$$B_2(\Gamma_1, \Gamma_2, \theta) = k_3 \Gamma_1 / w - k_4 \Gamma_2 / w \tag{24}$$

$$A' = \frac{dA}{d\theta}$$
 and  $r' = \frac{dr}{d\theta}$  (25)

Rearranging the terms in Equation (21) and (22) gives:

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} \dot{\Gamma}_1 \\ \dot{\Gamma}_2 \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$$
(26)

with

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = \begin{pmatrix} 1 + \Gamma_1 C_1 A' / A & \Gamma_1 C_2 A' / A \\ \Gamma_2 C_1 (w - r) r' / (wr) & 1 + \Gamma_2 C_2 (w - r) r' / (wr) \end{pmatrix}$$
(27)

Inversion of Equation 26 results in:

$$\begin{pmatrix} \dot{\Gamma}_1 \\ \dot{\Gamma}_2 \end{pmatrix} = \frac{1}{[M]} \begin{pmatrix} M_{22} & -M_{12} \\ -M_{21} & M_{11} \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$$
(28)

where  $[M] = M_{11}M_{22} - M_{12}M_{21}$  is the determinant of the matrix  $\{M\}$ . If we have values for the parameters  $k_n$  and  $\alpha_n$ , we can use Equation 28 to solve  $\Gamma_1$ ,  $\Gamma_2$  and  $\theta$  as a function of time.