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The surface tells it all: Relationship between volume and surface fractions of liquid dispersions†

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A foam generation

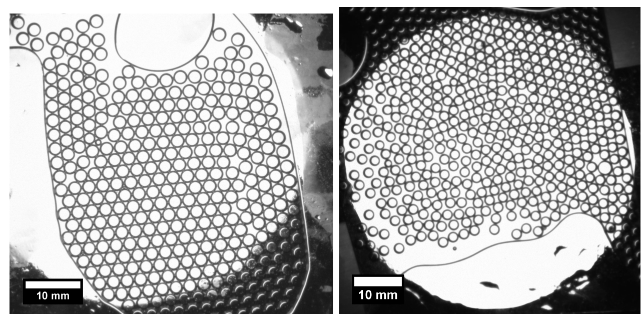
We use multiple technique to generate our foams. The FoamScan which is a commercial device (TECLIS) is a 200 mm tall column with a square cross-section of 25×25 mm. At the bottom, there is a porous disc which can be used to generate the foam. The gas is injected into the porous disc which is submerged in the solution. Bubbles rise from the bottom to create the foam. With this method we create foams with a polydispersity $\sigma \approx 5-10$ % and a bubble size $<R> \approx 1$ mm. The foam can also be created by shaking the liquid in a closed container. This technique gives very polydisperse foam ($\langle R \rangle \approx 3$ mm, $\sigma \approx 60$ %).

For monodisperse foams, we use two techniques. The simplest one is to inject the gas in the solution with a needle (with a diameter of 0.4 mm) which is placed at the bottom of the FoamScan column. The bubble radius is then of 0.3 mm and the polydispersity is around 5 %. The second method is a microfluidic technique which is the flow focusing though a T-junction. The solution is injected in the first branch and the gas in the second one. They meet at the junction where they create equal-volume bubbles which flow out of the third branch. The FoamScan is filled with this foam through an opening at the top of the column. With this method, it is possible to generate a wide range of bubble sizes ($1-2$ mm) with a polydispersity of $1-2$ %.

B bubble size and polydispersity

To measure the bubble size and the polydispersity of the foam, we take a sample in the column of the FoamScan and dilute it with the same solution between two glass plates which are separated by a known gap which is smaller than the bubble diameter. Diluting the foam sample in allows to separate the bubbles from each other and to see all of them individually as shown in Fig. 1. A camera is positioned above the sample which is illuminated from below with a circular light source to take pictures of the bubbles.

On these pictures, the edges of the bubbles appear in black (see Fig. 1). With a basic image processing in ImageJ software[1], we obtain the inner radius of the bubbles, R_c, as described in detail in[2]. Knowing the distance between the light and the sample, L_l, the radius of the light, R_l, the gap, h, between the two glass plates, the optical index, n, and the inner radius of the bubbles, we can calculate the real radius of the bubbles with Equ. (17) of reference[2].



(a) (b)

Fig. 1 Photographs of bubbles between two glass plates taken with a camera placed on top of the sample and enlighten with a circular light source below. (a) bubbles size of $\langle R \rangle = 2.2$ mm and a polydispersity of 1 %. (b) Bubbles size of $\langle R \rangle = 1$ mm and a polydispersity of 8 %.

Based on these pictures and on the calculation of the radii, we measure the polydispersity of the foam given by $\sigma = \frac{\sqrt{\langle R^2 \rangle - \langle R \rangle^2}}{\langle R \rangle}$. Hence, for the figure 1a, $\langle R \rangle = 2.2$ mm and $\sigma = 1$ % while for the picture 1b, $\langle R \rangle = 1$ mm and $\sigma = 8$ %.

C Measurement of the surface liquid fraction

The column of the FoamScan is provided with prisms which are glued on the container surface between successive electrodes as sketched in Fig. 1a. Pictures of the bubbles at the wall are taken though the prism (Fig. 1b) using a camera with a telecentric lens.

To obtain a sharp image of the bubbles at the wall, the angles between the wall and the light and between the wall and the camera must be positioned at an angle of 45 ° with respect to the container surface. That way the maximum intensity will arrive in the prism. Additionaly, we use a telecentric lens so that only the rays reaching the prism with an angle of 45° will be seen by the camera (Fig. 1b in the main article). So, if the light beam arrives on a plane surface (film against the wall), the light will be reflected in the axis of the camera and the film will appear in white on the photograph (Fig. 2a). On the contrary, if the beams

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is reflected by a curved surface, it will be reflected with another angle and will not be seen by the camera. This point will thus appear in black in the photograph (Fig. 2a). We therefore obtain a picture which is black, where the liquid wets the surface and white where the bubbles are pressed against the wall. We use the free software ImageJ to binarise and to invert the photographs (Fig. 2b). The surface fraction is then calculated with the ratio of the number of black pixels over the total number of pixels.

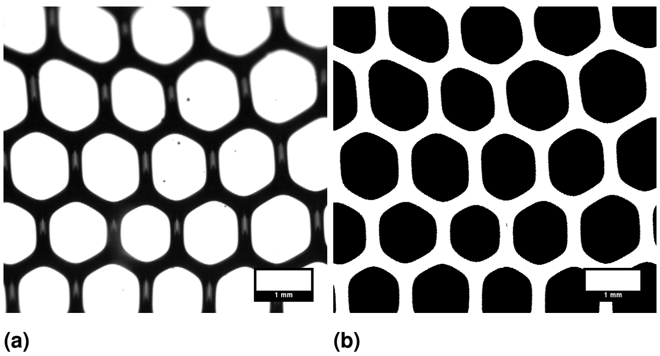

Fig. 2 Photographs of bubbles of the surface at the container wall. (a) Original photograph taken with a camera and a telecentric lens as shown in Fig. 1b. (b) Same photograph which has been binarised and inverted.

Fig. 2 shows an example of the surface of a foam with a volume fraction of $\phi = 1.8$ %. For this foam the surface fraction is $\phi_s = 34$ %. This measurement technique has the systematic tendency to underestimate slightly the surface fraction. On the one hand, the telecentric lens allows for a small variation in the angle of the detected light rays. On the other hand, the threshold, which is used to turn the photograph into a black-and-white picture has the tendency to cut slightly the boundary of the black zones. We estimate that the combination of both errors leads to an underestimation up to 5 % of the surface liquid fraction.

D Calculation of Equ. (6) for a 2D foam

In the case of a two-dimensional hexagonal foam one can derive rigourously the foam energy[3]

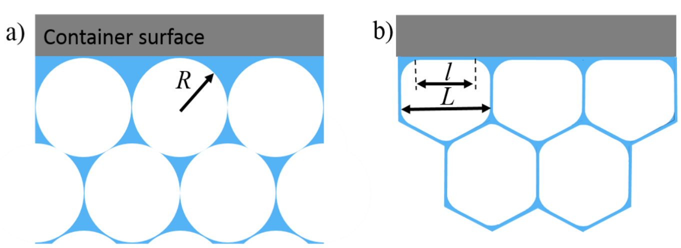

Fig. 3 2D foam (a) with undeformed bubbles of radius R and (b) with hexagonal shape bubbles of width L and length of film against the wall l.

$$E(\phi) = \gamma S(\phi) = \gamma S_0 \frac{(1-\phi^{1/2}\phi_c^{1/2})}{(1-\phi_c)^{1/2}(1-\phi)^{1/2}}, \tag{1}$$

where $S_0 = 2\pi R$ is the surface of the undeformed bubbles, which corresponds to a line length in two dimensions. R is the radius of the undeformed bubbles (Fig. 3a), γ the line tension, and ϕ the area liquid fraction. Similarly, one obtains for the two-dimensional osmotic pressure[3]

$$\Pi(\phi) = \frac{\gamma}{R}\frac{(1-\phi)^{1/2}}{(1-\phi_c)^{1/2}}\left[\left(\frac{\phi_c}{\phi}\right)^{1/2} - 1\right]. \tag{2}$$

The surface fraction in a 2D-foam (Fig. 3b) is given by (Appendix I in[4])

$$\frac{l}{L} = (1-\phi_s) = 1 - \sqrt{\frac{\phi}{\phi_c}}, \tag{3}$$

with l being the length of film against the wall and L the width of the bubble against the wall (Fig. 3b). Combining Equ.s (1)- (3) gives

$$1 + \frac{1}{2}\frac{E}{\Pi A} = \frac{1-\phi}{1-\phi_s} \tag{4}$$

which is the 2D analogy of Equ. (4) of the main article with $2/3$ replaced by $1/2$. Here A is the area of the foam, which is given by $A = A_B(1-\phi)$ with A_B being the bubble area.

E Comparison with the Z-cone model

The Z-cone model can be used to calculate the value of the osmotic pressure and the energy of the foam which are necessary to evaluate the Equ. (4). In this model a key parameter is Z which is the number of faces of a bubble.

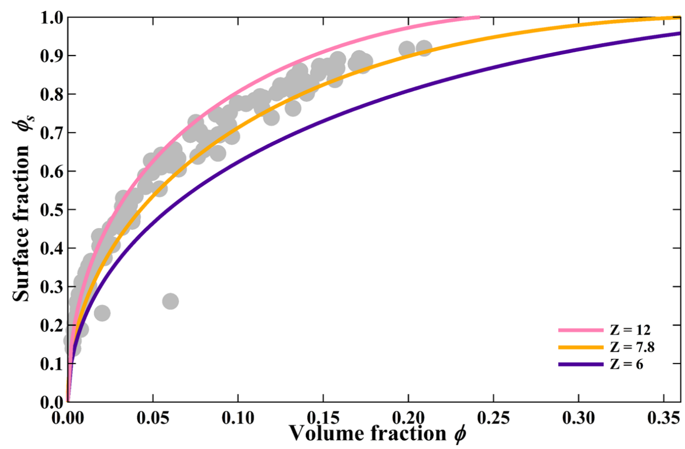

Fig. 4 Surface fraction versus volume fraction for the Z-cone model with 3 values of Z ($Z = 6, 7.8$ and 12). The gray points are the experimental data extracted from Figure 3a in the main article.

Z is derived for an ordered monodisperse foam but the model can be used for disordered polydisperse foams. Since Z represents the number of equal-sized cones or faces of the bubbles in the foam, it can also be seen as the number of neighbours of the bubble. For example, if $Z = 6$ it means that the bubbles have 6 neighbours and for bubbles with 12 neighbours $Z = 12$.

Fig. 4 shows the surface fraction, ϕ_s, versus the volume fraction, ϕ, $Z = 6$ in purple, $Z = 12$ in pink and $Z = 7.8$ in orange which is the values of Z allowing the better agreement with the data. The gray dots are the experimental data points (static foam in fig. **??**a). For $Z = 12$, there is a good agreement between the Z-cone model and the experimental points for small bulk liquid fractions. It is due to the fact that a bubble has a lot of neighbours in a dry foam. It is noticeable that a unique value of Z ($Z = 7.8$) allows to describe the entire range of data. This value is between the average neighbours of a random monodisperse foam in the limits of low and high bulk liquid fraction.

References

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