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

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20 The properties of liquid dispersions, such as foams or emulsions, depend strongly on the volume
20 fraction ϕ of the continuous phase. Concentrating on the example of foams, we show experimentally
20 and theoretically that ϕ may be related to the fraction ϕ_s of the surface at a wall which is wetted by the
20 continuous phase – given an expression for the surface energy or osmotic pressure of the bulk system.
20 Since the surface fraction ϕ_s can be readily determined from optical measurement and since there are
20 good general approximations available for surface energy and osmotic pressure we thus arrive at an
20 advantageous method of estimating ϕ . The same relationship between ϕ and ϕ_s is also expected to provide
20 a good approximation of the fraction of the bubble or drop surface which is wetted by the continuous
20 phase. This is a parameter of great importance for the rheology and ageing of liquid dispersions.

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30 1 Introduction

30 Liquid dispersions, such as foams or emulsions, consist of
30 individual gas bubbles or liquid droplets, respectively, which
30 are dispersed in a continuous liquid matrix. The volume
30 fraction ϕ of the continuous phase ranges from zero in the
30 limit of tightly compacted, polyhedral bubbles/droplets, to a
35 critical value ϕ_c , in the limit where the bubbles/droplets are
35 spherical and come apart.^{1–3} Most physical properties depend
35 strongly on ϕ – for example, the shear modulus of disordered
35 liquid dispersions decreases to zero at ϕ_c .^{1,2,4–6}

40 A number of different experimental techniques exist for the
40 determination of the value of ϕ , based, for example, on the
40 measurement of electrical conductivity⁷ or capacity,⁸ optical
40 transmission⁹ or X-ray techniques.¹⁰ Here we show that ϕ is
45 readily determined from a simple optical measurement of the
45 surface fraction ϕ_s , that is, the fractional area of the continuous
45 liquid phase which wets the surface of the vessel holding the
45 dispersion. We will show that the relationship between the
45 volume and the surface fraction depends on the surface energy
45 E of the dispersion which is proportional to the interfacial area
45 created between the immiscible fluids. Various expressions
50 exist for E in the literature (ref. 11 and references therein)
50 based on approximate theory or semi-empirical fits.

30 Previous work on surface properties of foams has focussed
30 on the relationship between the bubble size or the bubble size
30 distribution of the surface and the bulk structure.^{12,13} Here we
30 concentrate entirely on the question of the relationship
30 between the volume and surface fraction, ϕ and ϕ_s , which is
30 quite insensitive to the detailed structure of the dispersions, as
30 will be shown later. In what follows we will refer to bubbles
35 making up a foam. However, the nature of the physical argu-
35 ment and comparison with data on emulsions from the litera-
35 ture shows the general validity of our proposed relations.

40 2 Experimental set-up

40 In the experiments we use foams generated from aqueous
40 solutions of the anionic surfactant Sodium Dodecyl Sulfate
40 (SDS, 6 g L⁻¹) with some additional glycerol (0.5 wt%) and
45 dodecanol (0.06 g L⁻¹) in order to improve foam and solution
45 stability. In order to obtain foams over a wide range of different
45 bubble radii R (0.1 < $\langle R \rangle$ < 2 mm) and polydispersities $\sigma =$
50 $\frac{\sqrt{\langle R^2 \rangle - \langle R \rangle^2}}{\langle R \rangle}$ (1–64%) we use different foaming techniques
50 (Sections A and B in the ESI†). Monodisperse foams ($\sigma < 2\%$)
50 are generated using microfluidic techniques or bubbling from a
50 needle. Polydisperse foams of low polydispersity ($\sigma < 20\%$) are
55 generated by bubbling from a porous sparger ($\sigma \approx 5\%$ poly-
55 dispersity), while larger polydispersities are obtained by the

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sparger polydispersity?²
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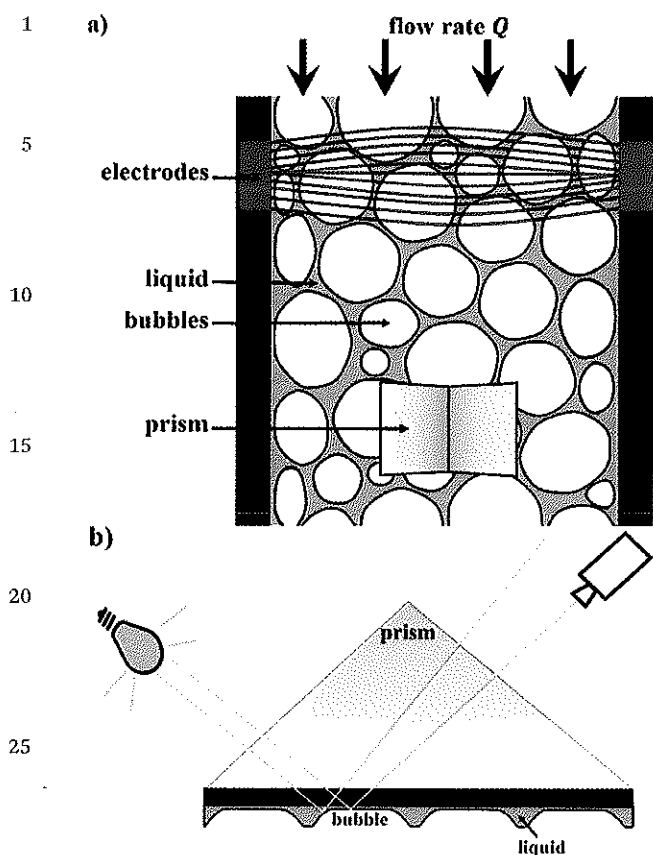


Fig. 1 (a) Scheme of the experimental setup: the foam is contained in a glass column of square cross-section (FoamScan by TECLIS). A pair of electrodes (in red) is used to measure the local electrical conductivity of the foam (and hence the volume fraction ϕ). Foaming solution is injected at constant, controlled flow rate Q in order to ensure a homogeneous volume fraction throughout the foam. (b) Sketch of ray paths passing through a prism is used to observe bubbles at the wall.

double syringe method¹¹ ($\sigma \approx 40\%$) or by shaking the solutions in a closed container ($\sigma \approx 50\%$).

The foaming gas is nitrogen or air with traces of C_6F_{14} to slow down gas diffusion between bubbles. The generated foams are then filled into the glass column of the commercial FoamScan device (TECLIS, Lyon, France) which has a square cross-section (25×25 mm) and is 200 mm tall. Adding surfactant solution at a constant flow rate at the top of the column (forced drainage), as sketched in Fig. 1a, results in a uniform distribution of the volume fraction.⁴ Its value is obtained by measuring the electrical conductivity across the column using pairs of electrodes integrated into opposing walls of the cell (Fig. 1a). This procedure rests on a general empirical relation for conductivity which is now well established and is subject to a relative experimental error of about 5% in volume fraction ϕ .⁷

The surface fraction ϕ_s is obtained by imaging light reflected from the foam surface with a telecentric lens through a prism with a 45° angle, as shown in Fig. 1b. Light reflected from the flat wetting film which separates a bubble from the glass surface is then received by the camera (and appears white), while light

Monodisperse $\sigma \approx 5\%$ Polydisperse $\sigma \approx 64\%$

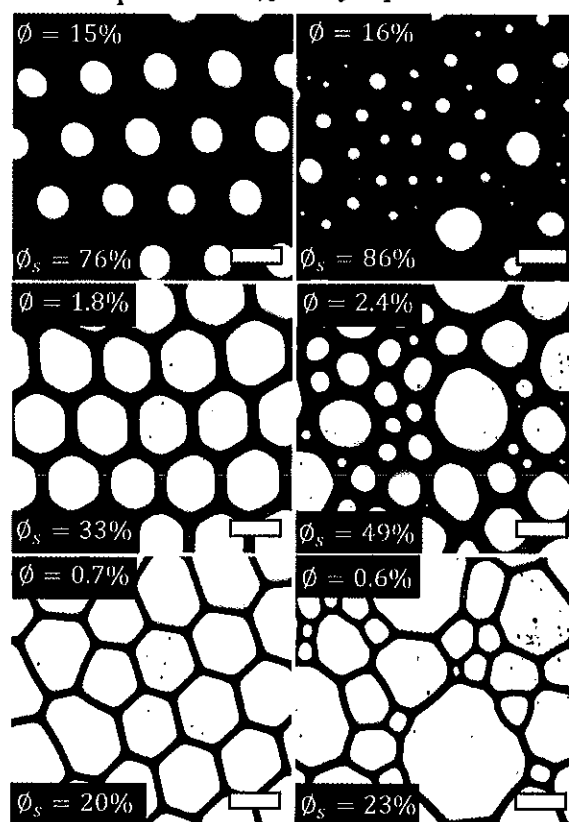


Fig. 2 Examples of photographs taken at the surface of the foam through the prism (Fig. 1b) for three different volume fractions and for two different polydispersities σ . The scale bars are equal to 1 mm.

reflected by a curved interface is not detected by the camera (and appears black). This technique was first developed in the 1990s for determining bubbles size distributions.^{14,15} Here we expand this application to surface fraction measurements. Examples of the resulting photographs for different volume fractions and polydispersities are shown in Fig. 2. Using ImageJ software,¹⁶ these photographs are readily converted into a surface fraction ϕ_s by taking the ratio of the black area to the imaged surface (Section C in the ESI†). The relative error made in the surface fraction measurement is of the order of 5% with a systematic tendency to underestimate ϕ_s due to a combination of uncertainties in the optical path selection and in the image treatment.

3 Experimental results

Fig. 3 shows the experimental data for surface fraction ϕ_s as a function of volume fraction over one order of magnitude of bubble sizes ($0.1 < \langle R \rangle < 2$ mm) and a wide range of polydispersities ($1\% < \sigma < 64\%$). For the filled data points, measurements were taken once the foam was in equilibrium, *i.e.* once the volume fraction was constant for a given flow rate Q of the injected liquid (forced drainage experiments). Each data point is

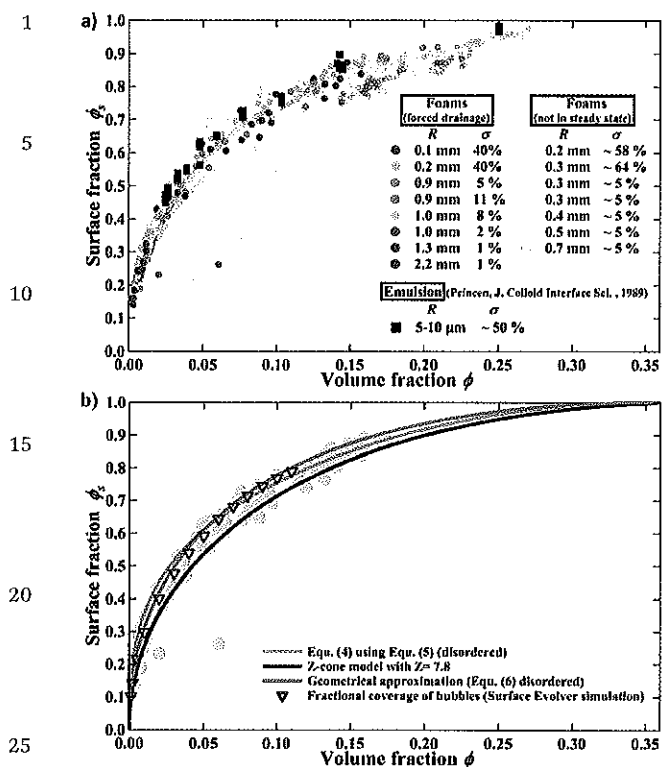


Fig. 3 (a) Experimental data relating the surface fraction ϕ_s to the volume fraction ϕ over a wide range of bubble sizes $\langle R \rangle$ (0.2–2 mm) and polydispersities σ (1–64%). We have also added a data set which was obtained by Princen¹⁷ using emulsions of $\langle R \rangle \approx 5$ –10 μm and $\sigma \approx 50\%$. (b) A variety of theoretical models are consistent with the experimental data. The relationship $\phi_s(\phi)$ also describes the fraction of the bubble surface which is wetted by the continuous phase for a Kelvin foam, as obtained from Surface Evolver simulation (kindly provided by A. M. Kraynik and D. A. Reinelt, unpublished).

obtained by averaging ϕ_s over 10 images, taken at a foam height of 5 cm from the bottom, and by averaging ϕ over the 10 values measured at the moment when these images were taken. The open symbols are taken under dynamic conditions, *i.e.* while the volume fraction changes with time. This arises for example, once the flow rate is stopped, or upon increasing the flow rate. Here, each data point corresponds to one single measurement. The latter results are therefore more prone to errors from dynamic effects or simple lack of statistics. Nevertheless, it can be seen that the data generated by both protocols fall onto what seems to be a single curve without any systematic dependence on bubble size, polydispersity or measurement protocol. We have also added a data set obtained in 1984 by H. Princen for emulsions with much smaller droplet sizes ($\langle R \rangle \approx 5$ –10 μm) and in the same range of polydispersities ($\sigma \approx 50\%$).¹⁷ His data set coincides with our data on foams, indicating a common underlying relationship.

4 Modelling and interpretation

In order to interpret this experimental observation let us consider the main pressure relations in a foam. Since we will

focus on an area at fixed height we can neglect the hydrostatic pressure. Forced drainage leads to a homogeneous volume fraction throughout the foam, we thus treat the liquid pressure P_l as homogeneous in the measured zone. In a disordered foam with modest polydispersity the gas pressure P_g varies only slightly between bubbles.^{1,2} Since this variation is small in comparison with $P_g - P_l$, we will treat P_g as constant throughout the foam, also for the bubbles in contact with the wall. Comparison with our experimental data below seems to justify this assumption, but future work needs to quantify the consequences of this approximation. P_g is also sufficiently small ($P_g < 1000$ Pa) in order to consider the gas as incompressible. This then implies a constant capillary pressure $P_c = P_g - P_l$ throughout the foam.

The bubbles in contact with the wall create a flat film with the solid surface (which appears white in the photographs of Fig. 2). This film is drained by the capillary pressure P_c until P_c is balanced by the repulsive force between the bubble surface and the solid wall (the so-called disjoining pressure which arises from the presence of the surfactants¹⁸). In equilibrium, a bubble therefore exerts a force on the wall which is given by the product of the capillary pressure and the area of its contacting film. A wall in contact with a foam with a surface fraction of ϕ_s therefore experiences an overall pressure of $(1 - \phi_s)P_c$.

This macroscopic pressure exerted by the bubbles of a foam on a flat wall is also known as the osmotic pressure Π , which was introduced by H. Princen.⁵ For a bulk foam it is defined as⁵

$$\Pi(\phi) = - \left[\frac{\partial E}{\partial \phi} \right]_{V_g = \text{const}}, \quad \Pi = - \left(\frac{\partial E}{\partial V} \right)_{V_g} \quad (1)$$

where V_g is the gas volume, which is kept constant, and E is the surface energy. We therefore have

$$(1 - \phi_s)P_c = \Pi(\phi). \quad (2)$$

The capillary pressure P_c and osmotic pressure Π of a foam of volume V have been shown to be related^{19–21} via

$$\Pi(\phi) = (1 - \phi)P_c - \frac{2E}{3V}. \quad (3)$$

Based on our approximations we can therefore write a simple equilibrium relation for the foam bubbles which are pressed against the wall,

$$\frac{(1 - \phi)}{(1 - \phi_s)} = 1 + \frac{2E}{3\Pi V}. \quad (4)$$

Weaire and Hutzler stated an approximate form of this equation valid near the dry limit (eqn (3.42) in ref. 1). Let us note that in the case of an ordered, two-dimensional foam, eqn (4) can be derived rigorously, leading to the same expression in which the prefactor 2/3 is replaced by 1/2 to account for the different dimensionality (Section D in the ESI†). Eqn (4) (together with eqn (1)) suggests that we need to know $E(\phi)$ or $\Pi(\phi)$ for a given sample in order to relate surface to volume fraction. Both $E(\phi)$ and $\Pi(\phi)$ have been found to be remarkably independent of the detailed structural properties of the foam

1 for a wide range of different samples, based on experimental
and computational results (ref. 11 and references therein). It
follows that one may choose a representative function for either
 $E(\phi)$ or $\Pi(\phi)$, whereupon an estimate of the surface-volume
5 relation can be deduced. In what follows we will highlight two
possible choices.

R. Höhler and co-workers^{22,23} suggested a semi-empirical
expression for the osmotic pressure

$$10 \quad \Pi = K \frac{\gamma}{R_{32}} \frac{(\phi_c - \phi)^2}{\sqrt{\phi}}, \quad (5)$$

where $R_{32} = \frac{\langle R^3 \rangle}{\langle R^2 \rangle}$ is the Sauter mean bubble radius. The

15 prefactor K depends on the critical volume fraction ϕ_c of the
foam. $K \approx 3.2$ for disordered, polydisperse foams ($\phi_c \approx 0.36$)
with modest polydispersity and $K = 7.3$ for ordered, mono-
disperse foams ($\phi_c = 0.26$).^{22,23} Numerical integration of eqn (5)
gives the surface energy $E(\phi)$, and thus the evaluation of the
20 relation between surface and volume fraction *via* eqn (4).

The resulting predictions for $\phi_s(\phi)$ for ordered and disor-
dered foams are plotted in Fig. 3b, together with a shaded
representation of our data obtained from forced drainage
experiments, showing that both expressions describe the data
25 very well up to $\phi = 0.15$. For higher ϕ , $K = 3.2$ (the values
corresponding to disordered foam) leads to better agreement
with the data. While this is expected for the polydisperse foam
samples, it may seem surprising with respect to the monodis-
perse foams shown in the left column of Fig. 2, which seem to
30 hint at nearly perfect order. However, this is a well-known
boundary effect,²⁴ due to the presence of the flat wall which
encourages order in its vicinity while the foam remains dis-
ordered in the bulk. In the case of polydisperse foams one
might also expect that some segregation of bubble size occurs
35 at the surface, so that its size distribution is different from that
of the bulk. However, this has no effect on the derivation
of eqn (4), if the assumption of constant gas pressure
remains valid.

Another expression of eqn (4) may be obtained using the
40 recently developed Z-cone model²⁵⁻²⁷ which approximates the
geometry of a Z-faced bubble as being composed of Z equal-
volume cones. This provides analytical expressions for energy
and osmotic pressure as a function of volume fraction for a
given number Z of contacts of a bubble. These expressions are
45 advanced and are therefore not stated explicitly here, but they
can be found in the Appendix A of ref. 26. The model is derived
for an ordered monodisperse foam but should provide a
reasonable approximation also for the disordered polydisperse
foams studied in this article with an appropriate choice of Z .
50 Fig. 3b shows that the variation of surface fraction with volume
fraction is well described for a choice of $Z \approx 7.8$ over the entire
range of data. This is a value somewhere between the average
numbers of neighbours of a random monodisperse foam in the
limits of low and high ϕ , where $Z = 13.4$ and $Z = 6$, respectively.
55 The corresponding expressions for $\phi_s(\phi)$ are shown in Section E
in the ESI.†

5 Geometrical approximation

The comparisons in Fig. 3 show that there is clearly sufficiently
close agreement to justify surface measurements for the esti-
mation of the volume fraction. Since the use of currently
5 available models for $E(\phi)$ and $\Pi(\phi)$ in eqn (4) leads to rather
complex expressions, we wish to close our analysis with the
suggestion of a simple approximation which is based on purely
geometrical arguments. These are stimulated by the fact that
eqn (4) may be rewritten in terms of surface area and volume/
10 surface fraction only, using $E = \gamma S$ and eqn (1). In the simple
model of a foam as a network of liquid channels of character-
istic width w and characteristic length close to the bubble
radius R ,^{1,2} the volume fraction scales as $\phi \propto w^2 R / R^3 =$
 $(w/R)^2$. For the surface fraction we may write the scaling
15 $(1 - \phi_s) \propto (1 - w/R)^2$. Combining both equations and requiring
that $1 - \phi_s = 0$ when $\phi = \phi_c$, gives the simple relationship

$$20 \quad 1 - \phi_s = \left(1 - \sqrt{\frac{\phi}{\phi_c}}\right)^2. \quad (6)$$

This kind of relationship has already been proposed by
Princen^{5,17} and Hilgenfeldt,²⁸ but with slightly different pre-
factors. Eqn (6) is plotted in Fig. 3b, showing that this provides
25 a rather good approximation to the experimental data – and to
the other models. The simplicity of this relationship may seem
surprising at first sight, but the fully analytical calculations
(Appendix I in ref. 17) for an ordered 2D foam gives the same
relationship with power “1” instead of “2”. For most practical
30 purposes the use of this simple relationship, eqn (6) may
therefore prove sufficient.

6 Conclusion

In summary, our experimental measurements clearly show that
there is a simple relationship between the bulk and the surface
fraction of a liquid dispersion. We demonstrate that this
relationship can be modelled by relating the different pressures
acting in the dispersion and on its surface, leading to eqn (4).
40 This expression is, at least roughly, independent of polydisper-
sity and bubble size. A dependence on the polydispersity is
expected to occur close to the critical volume fraction ϕ_c , but
the precision of our experimental set-up does not allow us to
draw any quantitative conclusion.

Taking photographs of liquid dispersions in contact with a
transparent wall may therefore replace more tedious techni-
ques, including measurements of electrical conductivity,
weight measurements or various kinds of tomography. A
further advantage is also that a simple imaging technique
50 imposes less requirements on the sample conditions (not
negligible conductivity, density contrast *etc.*). For most practical
purposes, the simple relationship provided in eqn (6) may be
used to relate both fractions with fairly good precision –
especially in dispersions with $\phi < 0.15$ (which captures most
55 of the commonly encountered foam samples).

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References

- 1 While, for simplicity, we have concentrated our experiments and the discussion on the example of foams, our arguments are valid for all liquid dispersions in which interfacial tension is constant and the relevant energy is surface energy. This is consistent with the agreement with data on emulsions from Princen¹⁷ shown in Fig. 3a.
- 5 A physically closely related question of great relevance to dispersion science is that of the average "surface fraction" or "wetting fraction" of the bubbles or droplets within the bulk dispersion, *i.e.* what fraction of the bubble/droplet surfaces is covered by the continuous phase? Or, inversely, what fraction of the bubble/droplet surfaces is not covered by the continuous phase and therefore correspond to thin films? This is a parameter of great importance for the description of rheology and ageing phenomena in dispersions. In Fig. 3b we plot this average surface fraction for a periodic Kelvin foam, obtained by Surface Evolver simulations (the data was kindly provided by A. M. Kraynik and D. A. Reinelt). We notice an excellent agreement between this data and the models derived for the surface fraction on the container wall. Moreover, expressions similar to eqn (6) have already been successfully used in the modelling of bulk foam ageing.²⁸ This seems to indicate that our derivation for the surface fraction on container walls may be extended, at least to a good approximation, to the derivation of the surface fraction on the bulk bubbles/droplets. Further analysis of this question is in progress.
- 15 In conclusion, in-depth investigations of dispersions in contact with solid surfaces may therefore help in answering numerous pending questions in relation to their interfacial energy (and osmotic pressure) over a wide range of volume fractions,¹¹ and, in relationship with this, the description of the non-pairwise interaction potentials between soft grains such as drops or bubbles.^{21,22}
- ## 35 Acknowledgements
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- 55
- 1 D. L. Weaire and S. Hutzler, *The Physics of Foams*, Clarendon Press, 2001, p. 246.
- 5 I. Cantat, S. Cohen-Addad, F. Elias, F. Graner, R. Höhler, O. Pitois and F. Rouyer, *Foams: Structure and Dynamics*, OUP Oxford, 2013, p. 280.
- 10 M. van Hecke, *J. Phys.: Condens. Matter*, 2010, 22, 033101.
- 10 R. Höhler and S. Cohen-Addad, *J. Phys.: Condens. Matter*, 2005, 17, R1041-R1069.
- 10 H. M. Princen, Background, *Encyclopedic Handbook of Emulsion Technology*, 2001, p. 243.
- 15 B. Bink, *Modern Aspects of Emulsion Science*, 1998, p. 430.
- 15 K. Feitosa, S. Marze, A. Saint-Jalmes and D. J. Durian, *J. Phys.: Condens. Matter*, 2005, 17, 6301-6305.
- 15 S. Hutzler, G. Verbist, D. Weaire and J. a. V. D. Steen, *Europhys. Lett.*, 1995, 31, 497-502.
- 20 M. U. Vera, a. Saint-Jalmes and D. J. Durian, *Appl. Opt.*, 2001, 40, 4210-4214.
- 20 E. Solórzano, S. Pardo-Alonso, J. de Saja and M. Rodríguez-Pérez, *Colloids Surf., A*, 2013, 438, 159-166.
- 25 W. Drenckhan and S. Hutzler, *Adv. Colloid Interface Sci.*, 2015, 224, 1-16.
- 25 H. C. Cheng and R. Lemlich, *Ind. Eng. Chem. Fundam.*, 1983, 22, 105-109.
- 25 Y. Wang and S. J. Neethling, *Colloids Surf., A*, 2009, 339, 73-81.
- 30 J. H. S. J. Garrett, P. R. and P. Whittal, *Report prepared for Uniflavor R & D*, 1993. Q6
- 30 S. Mukherjee and H. Wiedersich, *Colloids Surf., A*, 1995, 95, 159-172.
- 35 <https://imagej.nih.gov/ij/>, ImageJ website.
- 35 H. Princen, *J. Colloid Interface Sci.*, 1985, 105, 150-171.
- 35 J. N. Israelachvili, *Intermolecular and Surface Forces: Revised Third Edition*, 2011, p. 704.
- 35 H. M. Princen, *Langmuir*, 1988, 4, 164-169.
- 40 N. D. Denkov, S. Tcholakova, K. Golemanov, T. Hu and a. Lips, *AIP Conf. Proc.*, 2008, 1027, 902-904.
- 40 R. Höhler, private communication.
- 40 A. Maestro, W. Drenckhan, E. Rio and R. Höhler, *Soft Matter*, 2013, 9, 2531.
- 45 R. Höhler, Y. Y. C. Sang, E. Lorenceau and S. Cohen-Addad, *Langmuir*, 2008, 24, 418-425.
- 45 A. J. Meagher, D. Whyte, J. Banhart, S. Hutzler, D. Weaire and F. García-Moreno, *Soft Matter*, 2015, 11, 4710-4716.
- 45 S. Hutzler, R. P. Murtagh, D. Whyte, S. T. Tobin and D. Weaire, *Soft Matter*, 2014, 10, 7103-7108.
- 50 D. Whyte, R. Murtagh, D. Weaire and S. Hutzler, *Colloids Surf., A*, 2015, 473, 115-122.
- 50 R. Murtagh, D. Whyte, D. Weaire and S. Hutzler, *Philos. Mag.*, 2015, 95, 4023-4034.
- 55 S. Hilgenfeldt, S. Koehler and H. Stone, *Phys. Rev. Lett.*, 2001, 86, 4704-4707.