Monodisperse foams in one to three dimensions
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A B S T R A C T
Most major recent advances in the physics of monodisperse foams are centred around the ability to generate them with excellent control of bubble sizes down to a few micrometers thanks to the development of appropriate micro- and millifluidic techniques. As a natural consequence, monodisperse liquid and solid foams are playing an increasingly important role in fundamental research and in the development of industrial applications. In this review, we will address the different properties of monodisperse foams, comparing them to the more standard polydisperse foams.

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1. Introduction

Foams consist of closely packed gas bubbles surrounded by a continuous liquid or solid phase. Due to their complex properties, foams play a very important role in soft-matter research and industrial applications [¹, ²]. Needless to say that nature discovered their virtues long before us. Most foams are polydisperse and disordered, containing a wide range of bubble sizes which are randomly packed together. As our understanding of foams and foamed materials advances, bubble size distribution and foam structure become increasingly important control parameters. Excellent control is provided by using monodisperse foams which contain only equal-volume bubbles. These foams are special also in that they have the tendency to self-order into periodic structures under gravity or conﬁnement (Fig. 1 and Section 3.1.2).

Monodisperse foams have lived a quiet life for a surprisingly long time. This is why an unusually large number of the references in this article will date back quite far. By most researchers they were considered too removed from “real foams” and also too transitory in character, suffering from film rupture (coalescence, Section 5.3) and gas exchange (coarsening, Section 5.1) between adjacent bubbles, both processes leading ultimately to polydispersity in bubble size. In recent years, the disinterest in foams composed of equal-volume bubbles has literally metamorphosed into an enthusiasm for the subject for a range of reasons, of which we shall list here some of the most important:

• New bubbling techniques (Section 2) allow the straightforward generation of extremely monodisperse foams at high production rates and down to micrometric bubble sizes. Foams created from such small bubbles maintain a homogeneous liquid content due to the presence of strong capillary forces which outweigh gravity and hence inhibit drainage of liquid. This provides an inexpensive microgravity scenario on earth and precursors for the development of solid foam materials with unequalled structural control (Section 7).
• Computer power and algorithms have advanced sufﬁciently to perform experiments on physically realistic “numerical” foams (in terms of properties and size) on a desktop computer (in particular Section 3, Section 6 and Section 7) and hence circumvent a number of problems which tend to complicate experiments. This increased computer power also has an important impact on the automated analysis of the often complex foam experiments.
• Monodisperse, periodic foams provide extremely useful models for simulation and theory in that the description of the otherwise very complex foam structure is reduced to that of a single unit cell with periodic boundary conditions. Many fundamental properties of liquid and solid foams can be captured that way and often apply to a good approximation to disordered and polydisperse foams.
Both, well-controlled bubbling techniques and computer simulations, are now making possible that bubble size distribution has become an important control parameter in various domains of foam research. Monodisperse foams, ordered or disordered, present an important limit in these investigations.

3D imaging techniques (such as magnetic resonance imaging, optical tomography and other tomography techniques, such as X-ray tomography) in conjunction with efficient 3D-data handling have advanced sufficiently in terms of resolution, acquisition time and cost to provide the long-lacking access to structural properties of solid, and increasingly also liquid foams [3–7].

Research into the physical chemistry of foams has advanced sufficiently so that monodisperse foams can now be produced which are stable against coalescence and coarsening for weeks, even months (Section 5).

In 1994 Weaire and Phelan [8] managed to beat a more than 100 year-old conjecture on the optimal structure of monodisperse foams. Important mathematical breakthroughs in closely related problems followed, which incited a true race for optimal foam structures (Section 3.1.2).

Some of the main driving forces come from very applied questions, the first one being the creation and manipulation of bubbles as discrete gas-samples in fully automated microfluidic Lab-on-a-Chip design (Section 6) [9,10]. The second one being triggered by the desire to turn the increasingly well understood and controlled structure of liquid foams into templates for the development of porous materials (polymers, metals, ceramics...) with well-defined structural properties (Section 7).

Monodisperse foams find many profound analogies in physics (for example in crystallography, colloids, granular media, astrophysics, cellular systems), in mathematics (minimal surface problems), chemistry, biology (cellular 2D and 3D structures) or geology (crack patterns) where individual, identical elements or grains interact in complex manners.

Last but not least, a non-negligible element of the recent success of monodisperse foams is certainly their beauty. At times where scientific outreach has become of high value and interdisciplinary relationships between the sciences and the arts (including architecture) an appreciated element of scientific culture, the simultaneous elegance and “practicality” of periodic foam structures with their slightly curved edges attract a lot of attention. The most outstanding example is certainly the Olympic swimming pool “water cube” in Beijing (Fig. 1b), whose architecture was based on Weaire’s and Phelan’s structure (above and Section 3.1.2).

The topic of monodisperse foams covers an intriguing number of subjects ranging from purely mathematical questions of minimal surface structures to physico-chemical problems of foam stability. In what follows, we shall review the recent progress in the field of mostly liquid monodisperse foams by considering separately their key physical and physico-chemical properties. After an introduction to the generation of monodisperse foams (Section 2), we shall analyse their structure (Section 3), their osmotic pressure (Section 4), their stability and their rheology (Section 6). We conclude with a section on monodisperse solid foams (Section 7).

The research on liquid foams has a long and successful history of generating simplified systems by confining foams to quasi-one or two dimensions, as described in more detail in Section 3. For clarity, we tried to keep the division into (quasi)1D, (quasi)2D and 3D foams throughout each section. Within this classification, we shall only consider foams in which at least one dimension is much larger than the bubble size. A lot of interesting work has been done on monodisperse bubble clusters (down to two equal-volume bubbles), but this will not be considered here.

The polydispersity p of bubbles in a foam has a significant influence on a number of its overall properties, in particular its structural (Section 2) and rheological (Section 6) properties. p is commonly defined as the normalised standard deviation \( \sigma_p \) of the distribution of the “equivalent bubble radii \( R_b \), i.e. the radii the bubbles would have if they were spherical (\( V_b = 4\pi R_b^3/3 \)).

\[
p_d = \frac{\sigma_p}{R_b} = \left( \frac{R_b^2}{{\langle R_b^2 \rangle}^{1/2}} - 1 \right)^{1/2}
\]

which is also the definition we will use throughout this article — unless otherwise stated. In some cases, more subtle definitions seem be more appropriate and have occurred throughout the literature. One of the more recent examples includes a definition proposed by Kraynik et al. [11] which is based on the Sauter mean bubble radius \( R_{32} = \langle R_b^3 \rangle / \langle R_b^2 \rangle \).

\[
p_{32} = \frac{R_{32}}{\langle R_b^2 \rangle^{1/3}} - 1.
\]

Whatever the definition of \( p_d \), an ideal monodisperse foam has \( p = 0 \). In most experimental situations, however, \( p \) is only close to zero and in this article we shall refer to a monodisperse foam when \( p_{32} \approx 5\% \).
Another key parameter in the description of liquid foams is its liquid fraction \( \phi \), the ratio of the liquid volume to the total volume of the foam. 

Infinitely dry foams (\( \phi = 0 \)) are much-considered idealised foams in which polyhedral bubbles with (generally) curved interfaces are tightly packed. The equilibrium rules describing the structure of such “mathematical” foams are well understood and described in detail elsewhere [17]. We consider foams as dry for liquid fractions up to a few percent (top of Fig. 1a). In such foams, the films between neighbouring bubbles remain effectively very thin, while junctions of films (so-called Plateau borders) swell to accommodate the liquid. The structure of such foams is generally considered equivalent to that of an infinitely dry foam with “decorated” Plateau borders (this holds certainly true in 2D [12] but is slightly more complicated in 3D [17]). With increasing liquid fraction (wet foams), bubbles become increasingly spherical and turn into full spheres in the wet limit. If these spherical bubbles are organised in hexagonally close-packed structures (such as seen at the bottom of Fig. 1a and discussed in more detail in Section 3.1.2.1), \( \phi \approx 26\% \). If the bubbles are randomly close packed, \( \phi \geq 36\% \). Beyond this liquid fraction, bubbles lose contact and we generally speak of a bubbly liquid instead of a foam. The physics of monodisperse bubbly liquids is also very rich but, again, shall not be considered here.

Research on monodisperse foams finds much analogy with that on monodisperse emulsions, whose importance is being greatly boosted by the recent advances in microfluidic techniques and numerous emerging applications, for instance in biochemical screening. Emulsions are dispersions of oil and water which are stabilised by the same kind of stabilising agents as foams (small molecular weight surfactants, proteins, polymers or particles). They form structures identical to those of foams and their properties are in many respects very similar — but can also be quite different. For example, foams experience a much faster gravity-driven drainage of the continuous liquid phase due to a larger density difference with the dispersed phases; foams coarsen faster due to the solubility of gases in water being much higher than the mutual solubilities of oil and water; and foams are governed by larger surface tensions, making it more difficult to generate bubbles of very small sizes.

### 2. Generation of monodisperse foams

Monodisperse foams can be generated using a range of techniques, the choice depending on the desired bubble size, production rate and the flexibility required in varying the bubble sizes within the same device. The most classical technique is the **bubbling technique** (Fig. 2a) in which gas is blown at constant pressure \( \Delta p \) into the foaming solution through a (commonly circular) nozzle of radius \( r \). At sufficiently low gas flow rates, the bubble generation goes through a series of quasi-static states and the final bubble radius \( R_b \) is determined by equilibrating the surface tension force, attaching the bubble at the nozzle, and the buoyancy force, giving

\[
R_b \propto \sqrt{\frac{\Delta p}{\gamma}}
\]

where \( g \) is the gravitational acceleration, \( \sigma \) the surface tension and \( \Delta p \) the density difference between the solution and the gas. In the quasi-static limit this fixes one bubble size per nozzle size and bubble sizes are of the order of millimetres. Larger bubble sizes and higher production rates can be obtained from the same nozzle by going to higher gas flow rates, such that viscous forces enter the bubble formation and surface tension becomes negligible. In this case, bubble sizes can be controlled over up to an order of magnitude by the gas flow. Even larger bubbles can be obtained by placing the nozzle under an inclined surface to generate large bubbles. (left foam of Fig. 3c). Control over the bubble size towards smaller volumes can be achieved by moving the nozzle through the solution to exert a viscous drag facilitating bubble detachment [14].

Despite being satisfactory for many purposes, these traditional methods neither reach the small bubble sizes nor the production rates required by many modern research efforts and industrial applications. Following an unfortunately rarely acknowledged early leap of C.S. Smith [15] (who was blowing monodisperse bubbles for Braggs bubble crystals [14]), the recent microfluidics-buzz has generated ample solutions (Fig. 2c–e) for those seeking to generate in an extremely reliable manner: bubble sizes between a few and several hundred micrometers, at a polydispersity down to 2%, produced at up to thousands per second and, above all, at well-controlled liquid fractions [16", 17", 19"]! While surprisingly straightforward to use, these techniques offer insight into a hitherto little explored domain of interfacial hydrodynamic instabilities at small length scales. As a consequence, the last 10 years have seen the appearance of a large number of experimental and theoretical studies, trying to synthesise observations and predictions for different device geometries and flow conditions used by various research groups across the world. Thanks to an even more intense search for comprehension for the generation of monodisperse emulsions [16”] and to the development of increasingly powerful computational techniques, which can handle the dynamic boundary conditions of these flow problems [20,21], researchers are beginning to lay their hands on the decisive parameters controlling these systems. We shall briefly describe them here, keeping in mind that many of the arguments also apply to geometries of millimetric dimensions as long a gravitational forces can be neglected (i.e. sufficiently below the capillary length \( L_c = \sigma/(\rho g) \)). For more detailed descriptions we refer the reader to some excellent review articles [16", 17", 19”].

As sketched in Fig. 2c–e, the principal idea is to inject gas and liquid simultaneously at constant pressure or constant flow rate into a narrow hydrophilic channel system of micro- (or milli-) fluidic dimensions in which the gaseous phase breaks up into extremely monodisperse bubbles under laminar flow conditions and without the influence of gravity. Depending on the geometry of the channel
system, one generally distinguishes between confined co-flow (Fig. 2c), flow-focussing (Fig. 2d) or cross-flow (Fig. 2e) techniques. Even though different in detail, the overall behaviour of the break-up in these geometries may be described by three distinct regimes: the squeezing regime, the dripping regime and the jetting regime. For example, the transition from the squeezing to the dripping and then the jetting regime can be evoked by a successive increase of the liquid flow rate at constant (appropriate) gas flow rate [16–20]. All devices and regimes have in common that bubble sizes are well-controlled by the dimensions of the device and some power law of the ratio of the flow rates (or pressures), which makes it an easy-to-use technique for the common user. They differ, however, with respect to: the range of accessible bubble sizes and liquid fractions, monodispersity, production rate, or the stability of flow for solutions with non-aqueous viscosities. Even though the final pinch-off of the gaseous thread seems a common feature to all processes in the sense that it is axisymmetric and controlled by inertial forces [22,23], the regimes (and final bubble sizes) are well distinguished by how the system gets to this point.

Currently, the most widely used is the squeezing regime, which occurs at low capillary numbers \( Ca = \mu U/\sigma \) (ratio of viscous to surface tension forces with: \( \mu \) - solution viscosity, \( U \) - solution velocity, and \( \sigma \) - surface tension ). Several years of discussion seem to have confirmed Garstecki’s hypothesis [24] that in this regime the system goes through a series of pressure-driven equilibrium states in which the bubble blocks the narrow channel, leading to a pressure built-up in the liquid and a quasi-static squeezing of the bubble neck until it breaks. The squeezing rate being proportional to the liquid flow rate, the final bubble volume \( V_B \) is generally well described by the simple relationship

\[
V_B = V_o \left[ 1 + \alpha \frac{Q_g}{Q_l} \right]
\]

where \( V_o \) is the critical bubble volume at which the channel starts to be blocked, \( Q_g \) and \( Q_l \) are the gas and the liquid flow rates, respectively, and \( \alpha \) is a constant which is mostly related to the device and channel geometry (relative size of channel branches and geometry of the channel cross-section). It is important to note that neither the liquid viscosity nor the surface tension enters this relationship, making it particularly easy for the user to calibrate the device. It is also important to note that the size of bubbles generated in this regime will be of the order of (but bigger than) the channel cross-section. Furthermore, especially in the flow-focussing configuration (Fig. 2d), this regime allows the generation of very dry foams with liquid fractions down to 1% [10,25,26].

For larger capillary numbers \( Ca \), viscous stresses become increasingly important and begin to influence bubble detachment in the dripping regime, in which the gas thread remains in the bubble-forming channel but breaks at constant frequency at its inlet. For increasing Re and We numbers, i.e. as inertial forces gain importance over those exerted by surface tension and viscosity, the gas thread begins to penetrate into the channel in form of a jet (jetting regime) which breaks at the end. Foams generated in these two regimes tend to have a larger liquid content, bubble sizes smaller than the channel dimensions and less perfect monodispersity.

For those interested in intriguing fluid dynamic problems, just as well as for those trying hard in the lab to make monodisperse bubbles, it is important to know that at intermediate Weber numbers \( We \), i.e. when inertial and interfacial forces are of similar orders of magnitudes, these bubble-generating devices tend to display a chaotic behaviour [17,27] (period doubling, irregular bubbling, etc.) in analogy to the classical dripping faucet.

A synthesis of the large number of studies published in recent years is rendered difficult by the fact that people work with flow-rate-controlled or pressure-controlled systems [28]; many even with a mixture of both, in which they control liquid flow rates but gas pressures. Normally, if the hydrodynamic resistance of the channel
remains unchanged, pressure and flow rate are well related, but controlling one or the other may lead to different relaxation times and therefore a different device performance. Experimentalists seem to find that controlling gas pressures gives more reliable device performance, but for the moment we consider this an open question. Such questions certainly touch a sensitive point of these techniques: foam flowing in narrow channels is highly dissipative and depends strongly on the liquid fraction and the structure of the flowing foam [29,30]. Hence, the hydrodynamic resistance of the devices is rarely constant, leading easily to artefacts in device calibration and lack of device flexibility; but also to interesting physical questions [10,31,32].

A sensitive point of such rapid bubble generation techniques is that the surface active species (low molecular weight surfactants, proteins, polymers, particles...) used to stabilise the bubbles against coalescence, need time to go to and adsorb at the bubble surface. Adsorption time and bubbling frequency therefore need to be carefully matched, which often leads to the requirement of using very high surfactant concentrations and in many cases fails completely. The latter point is complicated by the fact that many species, especially proteins, polymers or particles, need to overcome non-negligible energy barriers in order to arrive at the gas/liquid interface. Despite the rapidness of the microfluidic techniques, they are strongly laminar (low Re) and often cannot provide the energy input required to sufficiently coat the bubbles. Hence, other mechanisms need to be integrated in order to avoid bubble coalescence. A very elegant solution to this problem in the case of particle coated bubbles has very recently been suggested by Park et al. [33], who used pH-sensitive particles and CO2-filled bubbles which dissolve rapidly in the microfluidic channel. In this case, the CO2 dissolution renders the environment of the bubble increasingly acidic and hence drives the particles to the interface where they need time to go to and adsorb at the bubble surface. Despite the rapidness of the microfluidic techniques, they are strongly laminar (low Re) and often cannot provide the energy input required to sufficiently coat the bubbles. Hence, other mechanisms need to be integrated in order to avoid bubble coalescence.

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For monodisperse foams, very crude bounds on this parameter can be found by taking the sphere as the lower and the cube as an upper limit, giving \((36\pi)^{1/3} \approx 4.8360 \times \varepsilon \times 6\). In real foams, this range is only of the order of a few percent [38,39], which illustrates that the packing efficiency of bubbles does not depend very strongly on the bubble shapes, hence rendering the comparison of analytical estimates challenging. Additionally, the experimental investigation of extended 3D-foam structures with sufficient accuracy is only now becoming feasible due to the availability of appropriate non-invasive imaging techniques [3]. Results of systematic experimental studies of 3D monodisperse foams are therefore few and far between, referring nearly always to the heroic efforts undertaken by Matzke [40], who placed and measured hundreds of equal-volume bubbles.

As a result of these analytical and experimental challenges, most of the advances in the search for an understanding of the structure of monodisperse foams have been pushed forward by

1. computer simulations, driven by the ever increasing computer power and the availability of reliable algorithms and softwares. A particularly important role in this process has been and is being played by the Surface Evolver Software [41], generously provided to the research community by K. Brakke.

2. concentrating on “simplified foams”, such as periodic foam structures in 3D (Section 3.4.1.2) or confined foams (Section 3.4.2 and Section 3.3), which are more accessible to traditional imaging and analysis techniques.

Investigations into the structure of foams are challenging due to the fact that they have highly complex energy landscapes. Finding the structure which corresponds to the global energy minimum therefore tends to be possible only for small bubble clusters or (some) periodic structures. While computer simulations can employ somewhat non-physical annealing-type algorithms (for example through forced vertex movements) to drive the system towards lower energies [41,42], the energy of re-arranging bubbles in real foams is orders of magnitudes higher than thermal fluctuations and therefore does not occur spontaneously. As a consequence, the structure of monodisperse foams generated in the lab tends to be more controlled by the history of their formation than by energetic arguments. In order to relax these structures to an energetically more optimal configuration, repeated shear cycles have proven to be very useful [43]. This is also the case in computer simulations [11].

3. The structure of monodisperse foams

We shall review in this section some recent developments concerning the structure of monodisperse foams under various conditions (disordered vs ordered foams, confined vs unconfined foams, and wet vs dry foams), trying simultaneously to sketch some of the historical background. Many of the discussed problems refer to well-known historical conjectures, some of which were proven mathematically only very recently!

The structure of foams is above all controlled by the minimisation of their interfacial energy \(E_B\), which corresponds to the total area of the gas/liquid interfaces multiplied by the interfacial tension \(\sigma\). In order to compare foam structures, one tends to consider their normalised energy density, which, for a 3D foam, is written as

\[
\hat{\sigma}_B = \frac{\langle V_B \rangle^{1/3} E_B}{\langle V_B \rangle^{2/3}} = \frac{\langle S_B \rangle}{\langle V_B \rangle},
\]

where \(V_B\) is the total foam volume and \(\langle S_B \rangle\) and \(\langle V_B \rangle\) the average bubble surface area and bubble volume, respectively. This parameter is very intuitive, as it measures how spherical the bubbles are on average by relating the average surface area of the bubbles \(\langle S_B \rangle\) to that of a sphere having a volume equivalent to the average bubble volume \(\langle V_B \rangle\). Researchers tend to give different names to this dimensionless number; we shall call it here the “packing efficiency”. For monodisperse foams, very crude bounds on this parameter can be found by taking the sphere as the lower and the cube as an upper limit, giving \((36\pi)^{1/3} \approx 4.8360 \times \varepsilon \times 6\). In real foams, this range is only of the order of a few percent [38,39], which illustrates that the packing efficiency of bubbles does not depend very strongly on the bubble shapes, hence rendering the comparison of analytical estimates challenging. Additionally, the experimental investigation of extended 3D-foam structures with sufficient accuracy is only now becoming feasible due to the availability of appropriate non-invasive imaging techniques [3]. Results of systematic experimental studies of 3D monodisperse foams are therefore few and far between, referring nearly always to the heroic efforts undertaken by Matzke [40], who placed and measured hundreds of equal-volume bubbles.

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3.1. 3D monodisperse foams

3.1.1. Disordered monodisperse foams
For disordered polydisperse foams in the dry limit, Kraynik et al. \[11\] recently established computationally that the packing efficiency can be expressed very simply by

$$\hat{E} = \hat{E}_K(1 + p_{2d})^{-1}, \quad (6)$$

where $p_{2d}$ is the polydispersity of the foam defined in Eq. (2). By fitting this relationship to their computational results they found that $\hat{E}_K \approx 5.32$, which corresponds to the packing efficiency in the mono-
disperse limit. This is already very close to what people find for
periodic structures, which is put in perspective in Section 3.4.1.2.

Like polydisperse foams, dry monodisperse foams are generally
highly disordered (Fig. 3a) containing typically more than 36 different
cell topologies \[40,41,42\]. Recent years have seen experiments \[40\] and simulations \[42\] converge to a coherent picture, which estab-
lishes the average number of faces of the bubbles at $\ell \approx 13.70$ and $\hat{E} \approx 5.32$. In particular, the most commonly observed bubbles have $12– 16$ faces with mostly 4, 5, and 6 edges with a strong preference for pentagonal faces. The most abundant cell \[app. 20\%\] found in random
monodisperse foams is one with 13 faces, containing one four-sided
face, 10 pentagons and 2 hexagons — a close cousin of the pentagonal
dodecahedron (which is not space filling). Kraynik et al. \[42\]
suggested recently to call this the Matzke cell in honour of his
contributions to the subject.

An interesting question to ask in future simulations would be how
the interfacial energy of random monodisperse foam structures
changes with liquid fraction. It is likely to be a function very similar
to that suggested by Hoehler et al. for periodic foams \[44\]
(Section 3.1.2.3) and is of great importance for the description of
the osmotic pressure (Section 4) and dilatancy (Section 5.2) in foams.

3.1.2. Ordered monodisperse foams

3.1.2.1. The wet foam limit.
In the wet foam limit, bubbles are spherical and pack together under the influence of gravity. The search for optimal foam structures in this limit therefore corresponds to that of the search for the densest packing of spheres \[46\], i.e. there is no consideration of the interfacial energy involved. The first official
formulation of this problem and proposition of a solution is commonly
attributed to Kepler, who conjectured in 1611 that the optimal
solution corresponded to the face-centred cubic (fcc) structure (and
its hexagonally close-packed cousins) with $\phi = 0.2596$. This seem-
ingly simple problem remained one of the oldest unsolved problems
in discrete geometry until recently, when Hales \[47,48\] came for
rescue, announcing in 1998 that he “had it”. But considering the
complexity of the proof — which contains a large computational part — it took until 2006 that it was accepted and published \[47,48\].

Unlike in the mathematical world, perfect order in real foams is
restricted to grains of finite extent, which elegantly join each other in
grain boundaries of different orientation or packing order \[44,49\] —
just as we know it from solid state physics. This fact was much
exploited by Bragg \[14\], who discovered this system by chance when
gardening and who used it extensively ever after as a demonstration
for grain boundaries, grain boundary motion, stacking faults or
dislocations in atomic crystals (and so did Feynman in his famous
lectures). After Bragg, the subject of ordered bubble crystals remained
surprisingly untouched. Initially, it resurfaced mostly in the search for
the ideal foam structure \[50\] and as a “side product” in the attempt
to generate well-controlled foam samples \[51,52\]. Only a few years
ago, their structure and formation began to be investigated more
systematically \[44,49,53,54\], bringing up a range of interesting obser-
vations and questions. One of the most intriguing — and yet
unexplained one — being the fact that despite the equivalent packing
density of all hexagonally close-packed structures, experimentalists
independently confirm a clear pre-dominance of Kepler’s (fcc)
structure \[44,49,54\] (left of Fig. 3e).

Even though spherical bubble packings find many analogies with
other systems from the arrangement of atoms, via colloidal to
granular systems, they differ significantly with respect to the forces
which control the bubble interaction (negligible friction between and
the easy deformability of bubbles, negligible influence of thermal
energy). “Bubble colloids” should therefore take an important place in
helping to understand the static and dynamic properties of colloidal/
granular-type systems. For example, researchers are increasingly
interested in studying wet bubble systems in analogy to “granular
materials” (Section 1, \[55\] and references therein). However, lack of
static friction and deformability in conjunction with strong buoyancy
forces mean that in trying to minimise their potential energy, wet
monodisperse foams do not jam in random close-packed structures as
do solid grains, but they find easily close-packed structures. This
provides us with highly ordered crystal structures which are of
interest by themselves (Section 3.1.2 and Section 4) and serve as
templates for material development (Section 7); but at the same time
they lose a certain generality due to their order and the properties
which derive from it (Section 6). Putting wet foams in space, i.e. into
microgravity conditions, is therefore at the heart of recent research
activities \[56\] aiming to study random (monodisperse) wet foams and
especially their transitions from bubbly liquids to foams with
decreasing liquid fraction.

3.1.2.2. The dry foam limit.
The quest and first conjecture for the optimal infinitely dry, monodisperse foam structure officially dates back to Lord Kelvin (1887), who, in search for the possible structure of the ether proposed that the most optimal space-filling bubbles were the Wigner–Seitz cells of a body-centred cubic (bcc) structure (left of Fig. 3b) \[57\]. This gives a truncated octahedron as bubble shape with
slightly curved edges to accommodate Plateau’s laws of equilibrium
\[1\] for a foam. Unlike the quest for the optimal packing of spheres (Section 3.1.2.1), this still remains an open one!

Two reasonably recent events in parallel with the availability of
ever increasing computer power incited a real race for structures
which beat Kelvin’s. After Matzke had shown that a real monodisperse
foam has on average $\ell = 13.7$ faces \[40,46\], Isern et al. \[58\] provided
the research community in 1992 with the suggestion of an “imaginary
ideal zero-mean curvature bubble” which would have $\ell = 13.4$ faces
and $\hat{E} = 5.254$. This bubble neither exists, nor it is space filling, but it
provided a well-defined lower limit on the packing efficiency and
together with Matzke’s work a guidance for the search: the average
number of faces of the optimal real structure should be close to $\ell =
13.4$, which corresponds to the faces having on average $n = 5.1$ sides
$\langle \ell \rangle = 12/(6(n-1))$ \[1\]. As a consequence, the search broke loose for
bubbles with pentagons \[59,60\]. Inspired by this, mathematicians and
physicists started looking intensely for possible candidates among
the tetrahedrally close-packed structures (TCP) \[59,61,62\], known as
clathrate structures, which only have pentagonal and hexagonal faces
(13 1 3 ≤ $\ell$ ≤ 13.5). In 1994 this search turned out to be successful with
Weaire and Phelan \[8\] announcing that the clathrate A15 structure
(Scott. 3c) with its two different cell shapes had 0.3% less
interfacial energy than that of Kelvin! Since then, several of the TCP
structures and their hybrids \[7\] have been shown to beat Kelvin’s
structure (Fig. 5 in \[42\]), but the one chosen by Weaire and Phelan
still remains unbeaten — with Weaire taking bets that this will remain
the case. Table 1 summarises a small selection of structures proposed
in the race to beat Kelvin, and now to beat Weaire–Phelan. The Kelvin
structure may, however, remain the best one for identical bubbles.

An important element in this search may have changed dramat-
ically recently: Until now, the search for the ideal structure was
dominated by lending structures known from crystallography, which
involved the guessing and testing of possible structures one by one. In

Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ref.</th>
<th>Faces</th>
<th>Interfacial Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weaire–Phelan</td>
<td>8</td>
<td>5.1</td>
<td>~0.3%</td>
</tr>
<tr>
<td>Clathrate A15</td>
<td>1</td>
<td>5.4</td>
<td>~0.3%</td>
</tr>
<tr>
<td>Kelvin</td>
<td>1</td>
<td>5.254</td>
<td>~0.3%</td>
</tr>
<tr>
<td>Other candidates</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
remain quite qualitative since not even the ideal structure for the dry
have been made in the past [51, 66, 67], but necessarily needed to
different structures as liquid is removed or added? Some propositions
intermediate liquid fractions and how does a foam transition between
are sure to have different optimal structures (Kepler vs Kelvin,
structure, remain still unwittnessed. Those who want to see the
tational domain. Whilst Kelvin cells can be generated in experiments
at least 50 years. This may provide the reader with an idea of the
bubbles loose contact) at a liquid fraction of about 11% [51, 66]. I n
3.1.2.3. Between the limits. Up to now we have discussed only the wet
and the dry limits of 3D monodisperse ordered foams — both of which
are sure to have different optimal structures (Kepler vs Kelvin,
respectively). A natural question arises here: what happens between
those limits, i.e. what are the optimal structures for foams at
intermediate liquid fractions and how does a foam transition between
different structures as liquid is removed or added? Some propositions
have been made in the past [51, 66, 67], but necessarily needed to
remain quite qualitative since not even the ideal structure for the dry
limit is known.
In the case of the Kelvin (bcc) structure (Fig. 3b) it is generally
assumed that the transition with increasing liquid fraction progresses
via the shrinkage of its four-sided cells to zero (i.e. neighbouring
bubbles loose contact) at a liquid fraction of about 11% [51, 66]. In
cylindrical foam columns (Section 3.2) with internal Kelvin cells such
kind of transitions are regularly observed [68]. The first systematic
investigation of this question in the other direction, i.e. upon
decreasing the liquid fraction of a monodisperse foam initially created
in the wet foam limit was put forward in 2007 by Hoehler and co-
workers [44] (Fig. 3e). Combining simulations and experiments they
found a transition from the Kepler (fcc) to the Kelvin (bcc) structure at
≈ 6% and confirmed previous predictions [69, 70]. They also
observed a clear co-existence region (≈ 6 ± 2%) of the two structures,
which is well confirmed by the argument that at these liquid fractions
a mixture of both structures is energetically more favourable. van der
Net confirmed these observations qualitatively [71].
A combination of the above-mentioned results by Weaire et al. and
Hoehler et al. suggests the presence of a strong hysteresis in these
transitions, which is a natural consequence of the discrete foam
structure in which faces and edges need to shrink to zero in order to
allow transitions without additional energy input. A similarly
pronounced hysteresis is known from transitions of cylindrical foam
structures [72]. These observations touch upon an important question
in foam physics: how relevant exactly are the energetic arguments to
the real foam systems which are so sensitive to how they are made?
Particularly ordered foams generally need to be generated starting
from wet foams to allow bubbles to self-order before draining them
into dry foam structures, which clearly acts as a template. To what
kind of structures do we have access this way, and will we ever be able
to find structures, such as the Weaire–Phelan structure, which,
despite its optimality has never been seen in experiments? Can we
influence these transitions by perturbing the foams, for example
under shear, without destroying the order?
3.2. Quasi-1D monodisperse foams in channels and tubes
Quasi-1D monodisperse foams are obtained by introducing equal-
volume bubbles into narrow tubes whose cross-section does not
exceed a few bubble-diameters. Under such a strong confinement
bubbles pack neatly into well-defined periodic structures whose
 topology depends on the geometry of the tube cross-section and the
ratio of the bubble and tube dimensions. Some of the most classic
examples are shown in Fig. 3c for the case of cylindrical tubes in which
the bubbles form hexagonal surface patterns wrapped around the
cylinder surface at different angles. After the pioneering work by
Weaire and co-workers [73], work based on such simplified foam
systems returns regularly in the search for well-controlled con
figurations to study specific foam and bubble structures [68, 74–76], or to
investigate their drainage (Section 5.2) and flow properties (Section 6).
An even simpler system is provided by quasi-2D tubes or channels,
in which one channel dimension is much smaller than the bubble
diameter. Such kind of monodisperse foams, especially their flow, is of
particular relevance in the development of a discrete micro-
or millilfluidics (Section 6). But just like their 3D equivalent, they pose
a large number of interesting fundamental questions, in particular
in relation to tiling problems in the presence of boundaries. Garstecki
and Whitesides [77] recently combined experiments and simulations
to mark the fact that this simple system is everything else but trivial.
Their work leaves us with two convincing-sounding, yet unproven,
postulates: one giving a lower bound on the minimal interfacial
energy of possible structures, the other stating that “there is no
periodic, equal-area tessellation of a stripe, which would yield a
smaller perimeter than one of the hexagonal tilings.”
Even more recently, investigations of monodisperse foam
structures in tubes of square cross-sections by Hutzler and co-workers [75]
revealed significantly less variety of possible structures than known
from cylindrical tubes. Particularly interesting is that all structures are
composed of sections of (or entire) Kelvin bubbles (Section 3.1.2.2),

<table>
<thead>
<tr>
<th>Structure</th>
<th>Year</th>
<th>$\bar{\ell}$</th>
<th>$\bar{\ell}/f_{\ell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams [65]</td>
<td>1968</td>
<td>5.337</td>
<td>14</td>
</tr>
<tr>
<td>Disordered [40, 42]</td>
<td>1946/2003</td>
<td>≈ 5.33</td>
<td>≈ 13.7</td>
</tr>
<tr>
<td>Kelvin</td>
<td>1887</td>
<td>5.3063</td>
<td>14</td>
</tr>
<tr>
<td>P42a [63]</td>
<td>2009</td>
<td>5.303</td>
<td>13.7</td>
</tr>
<tr>
<td>Weaire–Phelan (A15) [87]</td>
<td>1994</td>
<td>5.2883</td>
<td>13.5</td>
</tr>
<tr>
<td>Ideal bubble [58]</td>
<td>1992</td>
<td>5.254</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 1
Selection of monodisperse foam structures (mostly periodic) with the year of first
publication, their normalised packing efficiency $\bar{\ell}$ (Eq. (5)), and the average number
of faces $f_{\ell}$ of the bubbles.
potentially pointing towards the possibility of considering the tubes as unit cells of periodic multi-disperse 3D foam structures.

Problematic (or interesting) is, that quasi-1D foam structures are particularly sensitive to their history of generation [78], giving rise to a range of interesting transitions between structures with varying liquid content or under compression/dilation [51,72,79–81], generally including strong hysteresis effects. This raises once more the question of the potential "over-emphasis" of the interfacial energy as the structure-controlling parameter for real foams.

Cylindrical foam structures have also offered play-grounds for the exploration of foams which respond to external stimuli, such as those made from magnetic liquids (ferrofluids) [82–84].

3.3. 2D monodisperse foams

By creating a monolayer of equal-volume bubbles one obtains a quasi-two-dimensional (quasi-2D), monodisperse foam. Such a layer can be created easily by: floating bubbles on the surface of a surfactant solution (the "bubble raft" pioneered by Bragg and Nye [14]), by trapping the bubbles between a glass plate and the surfactant solution (the "liquid/plate configuration"), or by trapping the bubbles between two parallel glass plates ("plate/plate" or "Hele–Shaw configuration").

Such quasi-2D foams seem oversimplified systems, but their physics has proven to be extremely rich. They continue to provide important insights into fundamental static and dynamic properties of foams thanks to the simplicity of their topology/geometry [17] and the visibility of their cellular structure, which allows to make reasonably straightforward links between local and global foam properties. A very illustrative example was recently given by Janiaud et al. [85], showing how monodisperse 2D foam structures made from ferrofluid deform under the influence of magnetic fields. Other recent examples concern particularly problems in foam rheology (Section 6). 2D foams are often used to suppress the effect of gravity by placing them horizontally. However, including gravity by placing them vertically are often used to suppress the effect of gravity by placing them vertically.

In order to remove liquid from foams, bubbles need to be deformed which costs energy. This is expressed by the concept of the osmotic pressure [69*], which relates the work required to remove a volume of liquid dV from the foam to the corresponding change in interfacial area A:

$$\Pi dV = \alpha dA$$

It is important to note that this osmotic pressure is of energetic, and not of entropic origin.

4.1. 2D foams

In ordered, monodisperse 2D foams (hexagonal structure), the osmotic pressure can be calculated analytically [69*] and is given by

$$\Pi = \frac{\sigma}{R_B} \left[ \frac{1}{1-\varphi_c} \right]^{1/2} \left[ \varphi_c \left( \frac{1/2}{\varphi} - 1 \right) \right]$$

where \(\varphi_c = 1 - \pi / 2\sqrt{3} = 0.093\) is the critical liquid fraction in the wet limit (Section 1) and \(R_B\) is the equivalent bubble radius. Since the interfacial area \(A_1\) of a foam depends much more strongly on its liquid fraction than on its detailed structure, the above relation can be applied to disordered and reasonably polydisperse foams for most practical cases — especially for dry foams [87].

4.2. 3D foams

In 3D foams, the subject is more difficult to approach as until recently it was not even known how the structure and therefore interfacial energy of an ordered monodisperse foam changes with liquid fraction \(\varphi\) over the entire range. Hoehler and co-workers [44] have come to rescue and provided the first unifying picture for foams and emulsions over the entire range of the liquid fraction. Building on
the excellent agreement between their simulations and experiments, the authors provide an empiric relationship for the osmotic pressure

\[ \Pi(\phi) = 7.3 \frac{(\phi - \phi_c)^2}{R_B \sqrt{\phi}} \]  

(8)

where \( \phi_c = 0.24 \) is the liquid fraction of the wet limit (fcc packing of spheres, Section 3.1.2). This relationship agrees very well with previously established approximations. As in the case of 2D foams, we would suggest that this relationship can be applied for most practical purposes in the case of disordered monodisperse foams (with \( \phi_c = 0.36 \) for the wet limit of random close-packed bubbles) and probably even for moderately polydisperse foams (with some care in the wet limit). Evidence of this is given, for example, by the very good agreement of this relationship with data obtained for polydisperse emulsions [44].

To sum up: in two and three dimensions we now have well-working relationships at hand to describe the osmotic pressure of reasonably monodisperse foams to a good approximation, which is very useful for the analytical description of liquid fraction profiles of wet foams under external forces, such as gravity or applied pressure gradients. Up to now, most models have been restricted to either the dry or the wet limit. The next step will be to understand in more detail the osmotic pressure under shear, which is related to the concept of dilatancy [98,99], as briefly discussed in Section 5.2.

5. Stability

The stability of foams is governed by three different key processes [11]: drainage leads to the thinning of films between bubbles followed by coalescence (film rupture) when a critical film thickness is reached [108,109], and coarsening captures the growth of the average bubble size in time due to gas exchange between the bubbles. Film rupture due to evaporation also occurs if foams are left in the open atmosphere. Drainage can be slowed down using viscous foaming solutions or by gelification/solidification. Film rupture occurs more easily for larger bubbles, the probability of rupture being proportional to the film area, and decreasing with increasing surface compression elastic modulus of the surface layers [102]. Coarsening can be slowed down by using gases of poor solubility in water such as fluorinated gases; this simultaneously slows down drainage, since drainage is faster when bubbles are larger [103]. When foams with small initial bubble sizes are prepared using air, water and a surfactant which forms rigid surface layers, the above processes are well separated: the foam first drains, then coarsens and once a critical bubble size is reached, film rupture proceeds and leads to foam destruction [104].

5.1. Coarsening

Coarsening occurs because bubbles in a foam are at different pressures which drive inter-bubble gas diffusion [11,22]. Since the pressure in a bubble decreases with increasing number of neighbours, smaller bubbles (who tend to have fewer neighbours) are at higher pressures. Hence, with time, larger bubbles grow at the expense of smaller bubbles, leading to a continuous increase of the average bubble size of the foam.

A monodisperse foam with identical bubble topologies (such as the honeycomb or the Kelvin structure) would never coarsen since all bubbles are at the same pressure. But real monodisperse foams always contain topological defects and therefore — sooner or later — follow the same fate as their polydisperse cousins in that they head to a now well-accepted scaling state [105\textsuperscript{a}], in which only the average bubble size changes, whilst the normalised size distribution remains unchanged [106]. For a description of the pioneering work on foam coarsening (mostly in 2D), the reader may want to consult the excellent review of Stavans [106].

An interesting question is how exactly monodisperse foams, ordered or disordered, get to this scaling state [107]. As the reader shall see, much of the reported literature (mostly on 2D foams) has focused on this question by using monodisperse foams with various kinds of “perturbations”.

5.1.1. 2D foams

Glazier and co-workers [108] studied the coarsening of reasonably monodisperse foams between glass plates (Fig. 4a). They showed that in initially disordered systems the state of area growth increases smoothly and monotonically, whereas in initially ordered systems coarsening rate and disorder first overshoot and then decrease to the long-term values of the scaling state. Unexpectedly, the overall times needed to reach a fully disordered state were fairly independent of the initial order. Ruskin and Feng investigated in more detail the influence of the initial order/disorder of the foam and identified a quasi-scaling state for the highly ordered cases [107]. Earnshaw and co-workers studied later wetter and ordered foams containing isolated defects starting with bubble rafts covered with glass plates [109–111]. They observed that the bubble size distribution differed from that of the usual scaling state found when starting with many topological defects. However, it is likely that statistical equilibrium was not achieved during the experiments. Within the same setup, the authors also investigated the evolution of various types of defects and grain boundaries. They showed that the disorder introduced by defects propagates into the adjacent region of ordered foam, leading in some cases to a temporary overshoot in disorder, in line with the observations of Glazier et al. [108]. The possibility that the system could evolve to a different scaling state depending on the initial conditions was investigated through detailed simulations by Jiang et al. [112] and Tam [113] using a single defect (large bubble) in an ordered, monodisperse 2D foam as in the experiment of Ref. [111]. These authors suggested the existence of different scaling states. The influence of the nature of the defects appears therefore very important in the coarsening process of initially monodisperse foams.

5.1.2. 3D foams

Ganan Calvo et al. [52] studied the coarsening of wet monodisperse foams generated with a flow focusing device (\( \varphi \approx 25\% \)) (Section 2). They found that the bubble radius \( R_B \) stays first constant, then increases slowly. The bubble size distributions are close to log-normal, and an extended tail of larger bubbles develops as time goes on. Polydisperse foams with similar initial bubble size show a different behaviour: \( R_B \) increases from the beginning. In both cases, similar sizes are achieved after some time. This is in line with the 2D results.

van der Net et al. [114] described recently a self-organising effect in wet crystalline bubble structures exposed to air. As shown in Fig. 4b and c, due to the escape of gas from the bubbles in the top surface layer, bubbles shrink and create space for the bubbles of the lower layers to interpose themselves at the top, until an ordered bi-disperse top layer is formed (Fig. 4c). This kind of process can be followed for several episodes of elimination of surface layers, undergoing cycles of disorder and re-occurring order (Fig. 4b). The crystalline orientation influences the speed of shrinkage and formation of the bi-disperse top layer. Compared with diffusion of a single bubble or monodisperse monolayer on top of a liquid pool, the diffusion is much faster. This may be accounted for by the extra buoyancy force leading to a larger exposure of the bubbles at the surface.

Other studies have addressed coarsening in monodisperse foams under forced drainage (i.e. liquid is injected at a constant rate at the top of the foam) with the aim to keep the liquid fraction constant. Hutzler and Weraire [115] used initially monodisperse bubbles and monitored the bubble size by measuring the velocity of an additional drainage pulse. They found that the bubble size increased as the
square root of time after an initial regime in which there is little coarsening. Feitosa et al. [116,117] studied foams which were initially reasonably monodisperse and found (as in 2D) a temporary overshoot of polydispersity which is associated with the temporary development of a bi-disperse population of bubbles (as in 2D foams, see the second picture of Fig. 5a). The authors provided a simple description combining and solving analytically the coarsening and drainage equations providing bubble radius and liquid-fraction profiles.

Another aspect which has not yet been investigated is the influence of the stabilising chemicals which may bring interesting specificities. Finally, the transition from dry to wet foams should be addressed, even though the transition is expected to show non-universal features pertaining to specific systems [106]. Note that this last remark also applies to polydisperse foams, where an understanding is slowly emerging [3].

5.2. Drainage

Drainage is concerned by how the liquid phase flows through a foam, driven by capillary or external forces, such as gravity. The subject has advanced significantly in recent years and may be considered as quite well understood, particularly for reasonably dry foams [27,18,19]. Monodisperse foams served relatively little in the development of this field, mostly for the generation of foams with well-controlled and reproducible bubble sizes but generally with complete disinterest in the precise role of the bubble size distribution [51,116,118–122]. However, monodisperse foams have been — and are — at the centre of two fundamental drainage problems. The first one concerns drainage in ordered cylindrical foam structures (Section 3.2) and the nature of the transition of foam structures as a function of liquid fraction under forced drainage (constant applied flow rate at the top of the foam) [51,79,80] (Section 3.1.2.3). More recently, the simplest of these structures, the “Bamboo foam” (left in Fig. 2c) has surprised foam physicists with unexpectedly rich drainage behaviour. Below a well-characterised critical tube radius, no measurable drainage takes place in a bamboo foam. Above this radius, however, a gravity-driven instability opens up discrete liquid channels which allow liquid to pass [123]. Interestingly, these channels follow an intriguing variety of flow-rate dependent static and dynamic patterns [124]. Their explanation has been attempted by Carrier and co-workers [124] but still awaits full comprehension.

The second problem concerns a particularly complex one which couples drainage with rheology (Section 6) and is therefore at the centre of modern foam research, which seeks to integrate the various, interdependent dynamic properties of foams in a coherent picture. Here we are thinking of the subject of convective instabilities in foams.

Fig. 4. (a) A highly ordered, nearly monodisperse 2D foam transitions to the scaling state via an overshoot in polydispersity as ordered grains need to be destroyed [from 108]). (b) An ordered monodisperse 3D foam in contact with air going through cycles of order and disorder in the top layer, the ordered stage containing a (c) bi-disperse top layer (courtesy of Antje van der Net).
(2D or 3D), i.e. the motion of bubbles in a foam, which occurs under forced drainage above a critical flow rate and/or under inhomogeneous liquid input [125–128]. Of particular concern is the origin of this instability and the nature of the various types of steady, convective rolls observed in the foam. Since the bubbles of polydisperse foams size-sort under this motion [129], monodisperse foams have been the answer to maintaining a homogeneous sample and to facilitate modelling [130]. It is clear at this stage, that the instability is driven by inhomogeneities in the liquid fraction of the foam, but the central question concerns what generates, and especially what stabilises the significant variations in liquid fraction required to shear a foam beyond its yield stress under the effect of gravity. Whilst static dilatancy [98] (“Sheared foams are wetter than unsheared ones in order to minimise interfacial energy”) should certainly be present in the problem, its magnitude is now generally considered to be too small (less than 2% difference in liquid fraction [98,99]), to be at the heart of the problem. More seriously considered are now the effects of dynamic dilatancy (liquid fraction depends on strain rate of the foam) [130] and anisotropic drainage of sheared foams [131]. The latter of these may sustain up to 20% differences in liquid fraction and can be well approximated using an analytical model of a hexagonal 2D foam [131]. In particular, it predicts well the liquid fraction $\phi_C$ at the onset of the convective instability of a monodisperse foam as a function of the inverse bubble radius $R_0$: $\phi_C \sim R_0^{-4/3}$ [132,133]. In general, the interplay between these various effects leads to a self-amplification phenomenon: an inhomogeneous liquid fraction causes shear under gravity, which amplifies the inhomogeneity of the liquid fraction; either through anisotropic drainage or through dilatancy (likely both), which in turn increases the shear, etc. Even if the individual ingredients of this process seem to be emerging increasingly clearly, it is their precise interplay which needs to be elucidated in the future and tightly coupled with questions of yielding or shear banding (Section 6) in foam rheology. This undertaking should include at some point, a systematic investigation of the influence of the polydispersity of the foam on the onset of the instability and also a better understanding of the size sorting. Both questions are very important for applications, in particular for foam flotation, which is used extensively in the mining industry.

5.3. Coalescence

Let us now discuss the coalescence process, which is the most poorly understood. In order to advance in this understanding, monodisperse foams will have to play a central role in making a link between the rupture of well-controlled isolated liquid films and complex foam structures. With all bubbles being identical in ordered monodisperse foam structures, the probability of film rupture will be the same for all neighbouring bubbles, the film thicknesses being identical too. In the case of emulsions, a well-defined coalescence threshold in size was first identified in high internal volume fraction monodisperse emulsions [134]. Note that these emulsions were not strictly monodisperse ($\Delta R/\bar{R} \approx 10\%$ see Eq. (1)).

5.3.1. 2D foams

Experiments by Abd el Kader et al. [135] starting with monodisperse bubble rafts covered by a glass plate did not evidence coalescence events, probably because the films between bubbles were thick.

Later, monolayers of monodisperse bubbles between glass plates were investigated [136]. Coalescence was initiated through gentle heating. At a “critical break time”, a cascade of film ruptures is observed, leading to a rapid disintegration of the foam, as commonly observed in 2D foams. Later on, simulations were performed by Hasmy et al. [137], assuming that the probability of film rupture is proportional to the film length (instead of film area in 3D), which closely reproduced these observations.

More recently, monodisperse bubble rafts were studied by Ritacco et al. [138] (Fig. 5). Different surfactants were used in order to vary the viscoelastic properties of the gas/liquid interface. Surprisingly, the characteristic time for film rupture was independent of the surfactant used, but depended appreciably on the bulk viscosity of the foaming solution: for small viscosities, rapid cascades of film ruptures were
seen as in [136,137], whereas for higher viscosities, the coalescence events remained isolated, the convection motion created by the coalescence event being rapidly damped.

5.3.2. 3D foams

To our knowledge, no experiments of the stability of truly monodisperse foams have been reported due to the difficulty of rapidly producing a sufficiently large amount of monodisperse bubbles. Instruments producing foams with reasonable monodisperse bubbles \( \phi_B \approx 10\% \) and at high production rates (1 L/s) have recently been designed [139]. With these moderately monodisperse foams a clear separation between the coarsening and coalescence steps was observed, coalescence starting above a critical bubble size depending on the surfactant used, as expected [104]. In other moderately monodisperse foams \( \phi_B \approx 20–30\% \), coalescence was observed during drainage [140]. It was postulated that coalescence is due to redistribution of surfactant during bubble rearrangements caused by the drainage.

It is important to comment here on the fact that monodisperse foams can be stabilised for months against coalescence and coarsening using partially hydrophobic particles as stabilising agents. Unfortunately, they tend to be very difficult to generate, as discussed in Section 2. For one of the rare examples see the work by Cervantes-Martinez et al. [141].

6. Rheology

Rheology describes the response of a material to a mechanical stress. In the case of foams, there is a crucial distinction between monodisperse ordered foams whose behaviour can be described in terms of grain boundary motion, and monodisperse disordered foams, who behave like a continuous material with collective bubbles motion. Disordered monodisperse foams have almost the same behaviour as polydisperse foams: they are elastic for small deformation, plastic for large deformation and flow at large deformation rates. But some subtle differences exist in the shear modulus and the onset of plasticity [142,143].

6.1. Linear regime (quasi-static)

The elastic properties in the linear regime are described by bulk and shear moduli. The bulk modulus is dominated by the enclosed gas, and therefore of the order of 1 atm, several orders of magnitudes larger than the shear modulus. As a consequence, foams can be considered as incompressible in many practical contexts. When the bubbles are closely packed, they distort into polyhedra and store elastic energy: the surface tension \( \sigma \) provides the restoring force in response to small strains. The elastic shear modulus should then scale as \( \sigma \), \( R_B \) being an average bubble radius. Although this argument gives a remarkably correct estimation, it is very difficult to achieve more complete descriptions.

Another straightforward result is the evolution with increasing liquid volume fraction \( \psi \): when \( \psi \) reaches values at which the bubbles are spherical (or circular in 2D), the elastic energy vanishes and the shear modulus becomes zero. This transition is called “rigidity loss” or “jamming transition”. For ordered monodisperse 3D foams this happens around \( \psi_B = 36\% \), the volume fraction of randomly close-packed spheres being 64%, for ordered monodisperse foams this value is \( \psi_B = 26\% \) (Section 3.1.2.1).

6.1.1. 2D foams

The elasticity of the honeycomb lattice was first evaluated by Princen [69]. In the case of dry foams, when three adjacent bubbles are considered (the angle between the films remaining equal to 120° during the application of shear) the deformation is not affine. When the shear strain is increased, the central film shortens until four films meet: this situation is unstable, the bubble rearranges and a new film is generated in the so-called T1 process [17]. Below the critical or yield strain, the stress is proportional to the strain, their ratio being the shear modulus \( G \) (although small non linearities were predicted by Princen). The stress reaches a maximum value called yield stress and vanishes after the T1 process. Princen extended the model to finite liquid fractions. \( G \) is zero above \( \psi_B \approx 0.1 \) (corresponding to the close-packing of discs); below \( \psi_B \), there is a discontinuous jump, followed by a weak increase (as \( 1 - \psi^{-1/2} \)). In the dry limit, the shear modulus \( G \) equals the yield stress and \( G \approx 0.5 \eta / R_B \). Khan and Armstrong [144] later considered the effect of the orientation of the unit cell relative to the shear direction. For dry foams they found that the modulus is unaffected, but that the yield stress is sensitive to the orientation [145]. The influence of disorder was investigated by Hutzler et al. [146]: as the number of polydisperse bubbles in the simulation is increased, the jumps in stress associated with T1 rearrangements become less noticeable, the stress increases smoothly with increasing strain until a plateau is reached which can be identified as the yield stress. The variation of the yield stress with \( \psi \) is therefore different to that of \( G \); although the values for \( \psi = 0 \) are close. The rigidity loss occurs at \( \psi_B = 16\% \), the random packing fraction of polydisperse discs being 84%. A number of experiments are reported in the literature, but their interpretation is rendered difficult by the phenomenon of shear banding, which is discussed in more detail later.

6.1.2. 3D

The elasticity of ordered foams (mostly Kelvin foams) was investigated by Reinitz and Kraynik [147,148]. The structures being anisotropic are characterised by two moduli. The orientation-averaged results are surprisingly close to the 2D prediction; \( G \approx 0.5 \eta / R_B \). The influence of disorder is non-negligible on the yield stress and on the variation of \( G \) with \( \psi \). In particular, \( G \) does not follow the linear variation in \( \psi - \psi_c \), which was experimentally observed for relatively \( \phi_B \approx 10\% \) monodisperse emulsions [149] or foams [150,151]. Foams with still smaller polydispersities have also been investigated (up to volume fractions of 6%) but their properties are similar [151].

6.2. Non-linear regime and dissipation

As already observed by Bragg and Nye [14], the deformation of ordered monodisperse foams is similar to that of crystalline solids, i.e. they distort plastically through gliding dislocations.

Due to their periodic nature, topological transitions in ordered monodisperse soap froths are very different to those in disordered and polydisperse foams. As mentioned earlier, ordered cylindrical foam structures in tubes show sequences of structural transitions upon uniaxial compression/dilatation (i.e. deformation involving also shear). After recompression, the foam recovers its initial structure, but there is a significant hysteresis: sequences of intermediate structures upon dilation and upon compression are different [81]. Rosa et al. studied monodisperse bubble rafts upon compression/dilatation (in the plane of the raft) and evidenced an elastic limit at which dislocations nucleate and glide [152,153]. Glide changes the number of close-packed layers of cells perpendicular to the axis of strain. These changes do not occur at the critical strains at which the energies of the initial and final configurations are the same; considerably overtaking of the equi-energy strain is required to nucleate and/or move the dislocations. Again as mentioned in Section 3.2, energy is most likely not the pertinent control parameter here.

The transition from 2D foams to 3D foams through the “wine-bottle” instability has been recently demonstrated: it was shown that upon stretching perpendicular to the bubbles layer, a hexagonal structure remains stable, whereas in the presence of defects (bubbles with less than 6 sides) a monolayer of bubbles will transform into a bilayer [154].
The occurrence of shear bands is due to the viscous drag forces exerted on the details of the model. Later, Katgert et al.\cite{163,164} concluded that experiments, simulations exhibit different behaviour depending on the application of shear. In their paper, they quoted that as with the placing a glass plate on top of the bubble raft gave rise to a band upon exposure to air, the velocity varied linearly with the strain, whereas \cite{161} obtained clear evidence of shear-banded bubbles trapped between two parallel glass plates. Debrégeas et al.\cite{166} proposed a simple model assuming that the drag force exerted by the plate scales linearly with the flow velocity and that the bulk stress varies linearly with strain rate. This model accounted for shear rate independent velocity profiles. Kargert et al.\cite{163,164} showed that the introduction of disorder modifies this result: the velocity profiles change with \(v\), and the drag force varies much faster with \(v\) at the bubble scale than at the bulk level.

6.3. Flow regime

6.3.1. Quasi-1D: ordered foam structures in channels and tubes — towards a discrete microfluidics

The flow of ordered foam structures in tubes and channels provides well-controlled rheology experiments on the scale of a few bubbles, which can be combined more easily with theoretical and computational modelling. As such it was used recently to determine the bubble/wall dissipation\cite{9,29,30,157} and in particular its dependence on the bubble velocity \(v\). When this velocity is small, the motion of foam structures in channels can be described by quasi-static models using the Laplace equation. At higher velocities, however, dissipative forces become non-negligible (leading, for example, to the deformation and topological transitions of the foam structures) and need to be integrated into appropriate models. The simplest of these is the so-called Viscous Froth Model\cite{158,159} which adds a term proportional to \(v^2\) to the standard Laplace model. As in the shear banding problem of monodisperse 2D foams (see below), this model is able to account for the deformation and topological transitions of monodisperse, ordered foam structures flowing around bent tubes at high velocities\cite{9,10,31,32}.

Beyond the fundamental interest of ordered foam flow in tubes and channels lies a strong applied one which concerns the development of “discrete micro- or milliliuidic techniques” which allows the fully automated manipulation of gas-samples within a Lab-on-a-Chip. Using, for example, the interaction between channel geometry and flowing foam structures, “bubble operations” such as the swapping, splitting, merging or re-arranging of bubbles can be integrated within a simple channel network\cite{9,10,18,160}. An example of one of these elements in which two rows of bubbles are split and afterwards re-united is shown in Fig. 6a. In such systems, the coupling of the foam flow in the channel (structure-dependent pressure built-up in the channel) and the bubble generation at the channel inlet can lead to a complex dynamic behaviour\cite{31,32}, which needs to be understood for technical applications.

6.3.1.1. 2D: shear banding

In recent years, a variety of studies have addressed the formation of shear bands in disordered monodisperse (and reasonably monodisperse) quasi-2D foams. Using a layer of bubbles trapped between two parallel glass plates, Debrégeas et al.\cite{161} obtained clear evidence of shear-banded flow profiles. Later, Dennin and co-workers\cite{162} showed that in the case of bubble rafts (exposed to air), the velocity varied linearly with the strain, whereas placing a glass plate on top of the bubble raft gave rise to a band upon application of shear. In their paper, they quote that as with the experiments, simulations exhibit different behaviour depending on the details of the model. Later, Katgert et al.\cite{163,164} confirmed that the occurrence of shear bands is due to the viscous drag forces exerted by the confining glass plates. While initially it was believed that for slow flows the effect of these drag forces would be negligible, they have turned out to be crucial. Already for a bubble sliding past a solid wall, Bretherton showed that the drag force does not vary linearly with bubble velocity \(v\)\cite{165}, so the problem is quite complex.

Janiaud et al.\cite{166} proposed a simple model assuming that the drag force exerted by the plate scales linearly with the flow velocity \(v\) and that the bulk stress varies linearly with strain rate. This model accounted for shear rate independent velocity profiles. Kargert et al.\cite{163,164} showed that the introduction of disorder modifies this result: the velocity profiles change with \(v\), and the drag force varies much faster with \(v\) at the bubble scale than at the bulk level.

6.3.1.2. 2D: flow around objects

Flow around objects in 2D monodisperse foams has been studied in order to access the foam viscosity in analogy to the classical Stokes experiment. It was observed that an asymmetric obstacle (cambered airfoil profile, Fig. 6b) experiences a downwards lift, opposite to the lift usually known (in a different context) in aerodynamics\cite{167}. It was argued that such an inverse lift should be common to complex fluids with elasticity. The data for a variety of objects of different size and shape show two contributions to the drag: a yield drag and a flow-rate dependent contribution\cite{168,169}. Contrary to the yield stress or yield strain, which are intrinsic properties of the foam, the yield drag depends on the geometry of the flow: the relation between yield stress and yield drag is non-trivial and \(v\)-dependent\cite{88}.

Studies of the motion of a large bubble in a monodisperse 2D foam made of smaller bubbles showed an instability above a certain flow velocity: the large bubble moves then faster than the small ones\cite{170,171}. This is due to the fact that is dissipates less energy sliding between the plates than the smaller bubbles, being another indication of the importance of wall-slip in 2D-foam flow problems. It again emphasises the importance of the presence of one or more defects in an otherwise monodisperse foam, a question which was also addressed in recent studies of viscous foam relaxation between plates\cite{172,173}.

Graner et al.\cite{174,175} used foams to build a link between microscopic and macroscopic deformations. They were able to quantify the discrete pattern’s local distortion and rearrangements, making the link the behaviour at large scale, describing the foam as a continuous medium. This enabled them to formulate elastic,
plastic, fluid behaviours in a common, self-consistent modelling using continuous mechanics [174,175].

Let us finally mention that the flow of bubble rafts on inclined plates has demonstrated analogies with granular flow: dense bubbles rafts can be considered as “ideal” granular media with negligible friction [55,176,177].

6.3.1.3. 3D. Although the notion of surface drag has no counterpart in 3D foams, shear banding in polydisperse 3D emulsions (mayonnaise) was recently reported [178]. This could be special to polydisperse emulsions in which shear produces a size segregation of the drops. Localisation was also reported in a rather monodisperse foam, but the phenomenon was associated to dynamic dilatancy: the shear is localized in the wetter regions [179].

7. Monodisperse solid foams

Most foams around us are of solid and polydisperse nature. They are porous materials, which, unlike liquid foams, can have closed or open cells, the latter of which leading to a sponge-type material with interconnected air channels. The properties of solid foams are strikingly complex — many of them being extremely useful and largely exploited by industry and nature. The properties of foamed solids are mostly controlled by the foamed material, the foam structure (average bubble size, bubble size distribution, and isotropy) and the foam density. These properties include: large surface to volume ratios (catalysis and heat exchangers), rigidity despite low weight (transportation and space industry), excellent energy (shock) absorption (mechanical damping materials), acoustic and thermal insulation, filtering, etc... In order to well-control these properties and to open up pathways to new applications, researchers are continuously looking for ways to foam new materials. (More or less) routinely foamed materials now include diverse substances such as polymers, metal [180], glass (Chapter 2.7 in [181]), concrete or ceramics [182,183]. Equally important is the ability to control the structure and the density of these foams. Unfortunately, most of the currently used foaming techniques provide little of this, being statistical in nature (nucleation and growth) and often tightly coupled with foam solidification (for example in extrusion). An increasing number of researchers and companies are therefore looking into sufficiently separating the generation of a well-controlled liquid foam templates and their solidification [34,35,90,184–186]. Monodisperse foams play a very important role in this undertaking, as they not only provide ultimate control over the pore size, but if liquid viscosities are sufficiently low they also tend to self-organise (Section 3) to form highly ordered porous materials. For illustration, Fig. 7a shows a monodisperse metal foam obtained by bubbling through nozzles (Section 2) and Fig. 7b shows polymerised ordered foam threads (Section 3.2) obtained using millifluidic flow-focussing techniques [90]. Such an approach not only leads to the improvement of more traditional foam materials, but also has the potential to take foams into new domains, which require very tight control over structural properties. A particularly promising direction is that of scaffolding for controlled tissue engineering [187] or for the 3D-growth of cell cultures [185] (Fig. 7c).

Fig. 7. Examples of monodisperse solid/gelified foams for the controlled development of complex materials: (a) Tomography image of an aluminium foam (courtesy of Metcomb); (b) polymerised cylindrical foam structures [90]; (c) Alginate scaffold from [186]; (d) Magnetic foam stretches in the presence of a magnet [34].
With the requirement of starting solidification from a sufficiently stable liquid foam template, researchers are touching upon a range of old, yet often unsatisfyingly explored questions. These include: How to generate and stabilise well-controlled foams under extreme conditions, such as heat? How to generate and stabilise non-aqueous foams or aqueous foams of complex chemical composition? Additionally, how to ensure the generation of monodisperse foams from liquids which are highly viscous or non-newtonian?

We have no doubt that the near future will see the increasing versatility of well-controlled foam structures through the addition of “passive” components (such a carbon nano-tubes to enhance mechanical properties and conductivity), or “responsive” components which can be manipulated through control parameters such as heat or (electro)magnetic fields. First successful attempts have been demonstrated by Sang et al. [34], who added magnetic particles to a monodisperse, gellified alginate foam (Fig. 7d). By combining structural and external control in this kind of way, we may see before long the development of “intelligent” foam materials, used, for example as artificial muscles?

A significant part of the development of highly structured solid foams will naturally be dedicated to their mechanical properties. This subject has a long history, but turns out to be everything but an “old hat”. In fact, much in analogy with the research on liquid foams, it has experienced a completely new boost with the development of 3D imaging, computer simulations and the appearance of “new” foams. A number of recent advances in attempting to link the micro-structure of foams to their overall properties seem to make clear that some of the traditionally accepted models need to be modified — some overthrown — and that surprisingly many questions remain open. A more detailed review of this subject would be beyond the scope of this article due to its complexity and diversity. We therefore direct the reader to recently published books such as that by N. Mills [187], which comprises a large number of recent references on the subject. We shall simply emphasise here that monodisperse, ordered foam structures (especially honeycombs in 2D and Kelvin foams in 3D) have always served as model systems in this subject but, unfortunately, in 3D without much counterpart in experimental investigations due to the lack of sufficiently well-controlled, structured samples. The recent advances in generating such samples may help overcome this shortcoming [34,35,90,186]. Questions to be posed here are again very similar to those raised for liquid foams: What is the effect of order vs disorder on the foam properties (elastic moduli, buckling behaviour, air transport, acoustic properties, etc.)? What is the influence of polydispersity on the same parameters? How do monodisperse, ordered foam materials behave in the presence of isolated or multiple defects?

8. Conclusions

Since we have discussed specific details of the subject in the respective sections we shall leave the reader at this point with a very general remark: We hope to have been able to show that even though monodisperse foams are in some sense simplified foams, their physical and physico-chemical properties are everything else but trivial — and in many cases still poorly understood. In fact, in most sub-domains of the physics of foams, monodisperse foams have been much less exploited up-to-date than they probably should have been in view of the control over the foam properties which they provide. As a consequence, truly systematic investigations into almost all of their properties are few and far between even though they carry the promise of important fundamental insight. We therefore hope that this article may inspire some of its readers to take a part of the subject at hand so that the near future will see a response to some of the questions we have raised here (and to those we did not), and that new questions emerge in this old, yet excitingly new subject!

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References

Kraynik AM, Reinelt DA, van Swol F. Structure of random monodisperse foam.

Raven JP, Marmottant P. Periodic microfoams.


van der Net A. Generation, characterisation and solidification of crystalline microfoams, in School of Physics. Dublin: University of Dublin, Trinity College; 2008.


