# **Microfluidics with foams**

Philippe Marmottant\* and Jan-Paul Raven\*

### DOI: 10.1039/b903276b

Lab-on-a-chip devices can handle very tiny amounts of fluids, as small as a picolitre. Samples of gas are conveniently encapsulated and transported within bubbles. The generation of these calibrated bubbles involves specific microfluidic devices that we describe. When the bubble concentration is high enough in a channel, they come into contact, and they flow as a crystalline foam. The flow of the foams depends strongly on the arrangement of bubbles within the channel, which entails original dynamical behaviours such as super-stability of the flow, or on the contrary spontaneous oscillations.

#### **Motivations** 1

Why study microfluidics with foams? Foams consist of a dispersion of gas bubbles in a liquid, stabilized by surfactant molecules. They are closely related to emulsions, a dispersion of liquid droplets in an other liquid. Together with emulsions, they are of huge importance in numerous applications, such as coatings, cosmetics and even gastronomy.

Recently, a lively activity focused on the development of microfluidic methods to generate bubbles/drops. They are based on channels, micrometric in size, with specific geometries to mix two fluid phases.<sup>1</sup> These methods produce extremely well controlled bubble/drop sizes. These tiny elements are well suited for a bottomup assembly of a foam. Furthermore,

Lab. Spectrométrie Physique CNRS - UMR 5588, Université Grenoble I, B.P. 87, F-38402, St Martin d'Hères Cedex, France. E-mail: philippe.marmottant@ujf-grenoble.fr; janpaulraven@gmail.com

creating bubbles and foams is of interest within the concept of lab-on-a-chip. Indeed bubbles (and similarly droplets) can be seen as tiny volume samples, typically of one picolitre,2 that can be manipulated and analyzed within a miniature lab.3

On a fundamental point of view, foams are a model complex material, made of simple elements. Furthermore, this material is highly confined when it flows in microfluidic channels: the discrete composition of the foam appears through original features, as we will see further when looking at their flow. Foams therefore suggest a new research area in microfluidics, coined 'discrete microfluidics'.4

#### Microbubble generation 2

Foams are generated bubble by bubble within microchannels. These channels, a few dozens of micrometres in width, are easily manufactured by 'soft lithography'5 in a transparent and flexible silicon such PDMS material as (polydimethylsiloxane). The method consists of forming a PDMS replica of a mold, the mold being manufactured by traditional photo-lithography.

While centimetric bubbles are produced by 'bubbling', that is simply by injecting air through a tube exiting in a liquid pool, obtaining micrometric bubbles requires a different strategy. In the centimetric bubbling process, buoyancy detaches bubbles that were linked to the inlet tube by capillarity. However, at small scales buoyancy forces (proportional to the volume) are inefficient compared to capillary forces (proportional to the perimeter), the volume to perimeter ratio being much smaller.

An active method is needed to produce tiny bubbles. The bubble detachment can be achieved at small scales with the help of a co-flowing liquid stream. This is the 'flow-focusing' method,<sup>6</sup> where the liquid stream focuses the gas jet through a tiny



**Philippe Marmottant** 

Philippe Marmottant is Chargé de recherche at CNRS in Laboratoire de Spectrométrie Physique, Grenoble, France since 2004. In 2001 he defended a PhD thesis on spray formation, under the supervision of Prof. Emmanuel Villermaux, within the laboratory LEGI of the Institut National Polytechnique de Grenoble. He then went for a post-doctoral stay at the University of Twente in the Netherlands, studying microbubbles driven by ultrasounds, with Prof. Detlef Lohse and Prof. Sascha Hilgenfeldt.



Jan-Paul Raven

Jan-Paul Raven currently works for a consulting firm. In 2007 he defended a PhD thesis on foams in microfluidics at the Laboratoire de Spectrométrie Physique in Grenoble, France under the supervision of Philippe Marmottant and François Graner. Jan-Paul has a Masters degree in Applied Physics from the University of Twente in the Netherlands.



**Fig. 1** Microfluidic set-up for 'flow-focusing' of a gas jet by liquid streams into an orifice. Here the orifice width is  $w_{\rm or} = 100 \ \mu \text{m.}^{30}$  Bubbles are then conducted to an exit channel.

orifice, a method popularized with axisymmetric capillary tubes by Alfonso Ganan-Calvo.<sup>7,8</sup> It was first developed with microfluidic tools for droplets,<sup>9</sup> and then implemented for bubbles by Piotr Garstecki.<sup>10</sup> A typical set-up is represented in Fig. 1. There are two control parameters: the gas pressure  $P_g$  and the liquid flow rate  $Q_{\rm l}$ .

Note that a second type of geometry is also used, with a 'T-junction': the vertical branch of the 'T' stands for gas inlet, while the horizontal branch stands for the liquid stream.<sup>11-13,1</sup>

The mechanism of bubble formation follows from the periodic pinch-off of the gas jet by the liquid stream.<sup>14</sup> Pinch-off occurs in the small orifice, see Fig. 2.

Flows are much more reproducible at microfluidic length-scales than at (human) macroscopic scales: viscous forces are dominant over inertial forces (*i.e.* the Reynolds number of the flow is small), which smoothes flows and prevents instabilities. The pinch-off process is thus metronomic and produces accurate bubble sizes: the measured standard deviation in bubble size is as little as 0.1%.<sup>15</sup> However, note that inertial forces

may appear at high liquid flows,<sup>16</sup> which induce chaotic bubble production.

The bubble size is tuned by the gas and liquid flux. Indeed, the pinch-off frequency f is proportional to the liquid flux.<sup>14</sup> This results in a bubble volume that scales like  $V_b = Q_g/f \sim w_{or}^3 \times Q_g/Q_l$ , with  $Q_g$  the gas flow rate and  $w_{or}$  the orifice width.<sup>17</sup> We emphasise here that  $Q_g$  is not fixed, since control is on the gas pressure  $P_g$ . When the exit channel is already densely populated, each new bubble has to push the bubbles already present in the exit channel. We will see that the resulting flow rate  $Q_g$  depends on the drag of the foam structure that is already present in this channel (section 5).

## 3 Self-assembly of the foam in the channel

When the density of bubbles is high enough, a foam is formed in the exit channel (see Fig. 3). Because sizes are monodisperse, bubbles promptly selfassemble in ordered patterns described as 'flowing crystals'<sup>18</sup> or 'microfluidic crystals'.<sup>19,24</sup> Each bubble is added in a selfrepeating way to the foam, that acts as



**Fig. 2** Snapshots of the flow-focusing at work in the orifice. The gas jet first enters the orifice (a). It is then squeezed inwards from the sides by the surrounding liquid (b). This regime is sketched in magnified cross section of the orifice in (c). The gas thread experiences finally a fast pinch-off (d), where it is squeezed radially in the cross section (e).<sup>15</sup>

a template in the exit channel, with a periodic distribution of bubbles.

Ordered hexagonal patterns are named by the number of bubble rows in the channel width:<sup>18</sup> *hex-one*, *hex-two*, *hexthree* and so on. More complex (nonhexagonal) patterns were also observed<sup>18</sup> and computed.<sup>20</sup>

#### 4 Foam liquid fraction

The liquid fraction is defined as  $\Phi_1 = V_1/(V_1 + V_g)$  from the actual volumes of liquid  $V_1$  and gas  $V_g$  present in the channel. At first glance, one could think that liquid fraction reflects the fraction of *injected* liquid  $\alpha_1 = Q_1/(Q_g + Q_1)$ . However this statement does not completely hold. Liquid can flow through the foam at an average velocity  $\langle u_1 \rangle$  faster than the bubble's average velocity  $\langle u_g \rangle$ ,<sup>17</sup> because bubble motion is retarded by the drag exerted by the walls. This phenomenon is known as relative drainage, and explains why the liquid fraction  $\Phi_1$  can be smaller than  $\alpha_1$ .

At high liquid fraction, foams are wet with their bubbles nearly round (see closeup Fig. 4a), and foams are good analogs of crystalline materials.<sup>21</sup> But when the liquid fraction is small, foams are dry and their bubbles assume polyhedral shapes (Fig. 4b). Dry foams are usually amorphous (*i.e.* irregular), except in microfluidic devices since foams were accurately produced by placing regularly each new bubble.

### 5 Flow and discrete effects

The flow rate of the foam is a highly nonlinear function of the applied pressure.<sup>17</sup> Foams are not Newtonian fluids, while paradoxically it is the case of the liquid and gas that take part in their composition. We approximate the foam flow rate using the gas flow rate  $Q_g$ , which induces a little error at low liquid fraction. The gas flow rate is easily extracted using the recorded velocity of the bubbles, while it is much more difficult to measure the liquid velocity because of relative drainage.

A typical flow rate to applied pressure curve is displayed on Fig. 5. The salient features of the flow behaviour are the following: first, foams flow only above a *threshold pressure*  $P_{cap}$ . This pressure is interpreted as the pressure necessary to overcome capillarity through the orifice.<sup>17</sup>



Fig. 3 Foam structure when bubble size is increased by turning up the gas pressure (from top to bottom).<sup>24</sup>



Fig. 4 (a) 'Wet' foams and (b) 'dry' foam, both with three rows (type F3). Their thickness is 8  $\mu$ m and they flow in a channel whose width is 400  $\mu$ m.<sup>17</sup>

Second, the flow rate is a *power-law* in applied pressure,  $Q_g \propto \Delta P^{1/\alpha}$ , with  $\Delta P = P_g - P_{cap}$  the pressure over threshold and  $\alpha \approx 2/3$ . This law is reminiscent of the flow of a single bubble within a capillary tube.<sup>22</sup> Foams definitely do not flow as Newtonian fluids, for which flow is proportional to pressure. Finally, strong *discontinuities* occur, due to the discrete nature of the foam: when the structure of the foam changes, the flow jumps to another curve, *via* a transition region (grey area on Fig. 5).

The power-law behaviour has been rationalised by Isabelle Cantat<sup>23</sup> who enlarged the application of the Bretherton law<sup>22</sup> for single bubbles in a cylindrical tube to foams in a channel: the proposed law is

$$\Delta P = n\lambda \frac{\sigma L_{\rm proj}}{S} C a^{\alpha}$$

with *n* the number of bubbles,  $\lambda$  a prefactor depending on the liquid fraction,  $\sigma$ the surface tension, *S* the channel section,  $L_{\text{proj}}$  the total length of the liquid films touching walls, projected in the direction of flow (transverse size), and  $Ca = \mu \langle v_{\text{foam}} \rangle / \sigma$  the capillary number constructed with the liquid viscosity  $\mu$  and foam velocity  $v_{\text{foam}} = \langle u_g \rangle$ . An exponent  $\alpha \simeq 2/3$  was derived analytically for single bubbles<sup>22</sup> and still applies, to a certain extent, for foams.

Discontinuities are also explained by the previous formula. When bubbles arrange in a different pattern the friction length  $L_{\text{proj}}$  suddenly changes. For instance, it is clear from Fig. 3 that *hex*one bubbles take the whole channel width w (therefore  $L_{\text{proj}} = w$ ), while *hex-two* bubbles present a reduced transverse width ( $L_{\text{proj}} < w$ ). Coming back to Fig. 5, we therefore understand the sharp slow down of the flow when a foam transits from *hex-two* to *hex-one* at comparable bubble volume: the *hex-one* bubbles have a much larger projected length, and therefore an increased resistance to flow.

## 6 Stability of production: rearrangements within the foam

In between the regimes with a continuous production of an homogeneous structure, transition regimes produce several structures, as first observed by ref. 18. These intermediate regimes are associated with rich dynamical behaviour, and result in a structure that varies over space, over time or both. We distinguish three



Fig. 5 High non-linear behaviour of a flowing foam.<sup>17</sup>



**Fig. 6** Intermediate regimes with a mix of structures. The vertical bar indicates a rearrangement front and the arrow its velocity in the laboratory frame. Movies are available at ref. 31.

transition regimes, controlled by the foam velocity  $v_{\text{foam}}$ .<sup>24</sup>

• (a) At intermediate foam velocity, the foam continuously rearranges in another structure at a fixed position,<sup>24</sup> see Fig. 6a on which a structure hex-one rearranges to a structure hex-two. The fixed position is a consequence of the presence of a wave of rearrangements (rearrangements are called T1's within foams<sup>25</sup>) that travels relative to the foam with a velocity  $v_{T1}$ . In this regime, the velocities exactly compensate each other  $v_{\text{foam}} = -v_{\text{T1}}$ . This wave is stationary in the reference frame of the laboratory. Remarkably, in this regime the foam velocity and bubble size are 'super-stable', locked to a fixed value whatever the driving pressure. This selfregulated flow differs considerably from the behaviour of homogeneous structures that have a strong dependence on applied pressure. This specificity might be helpful to achieve enhanced stability in bubble production, since volume changes due to pressure variations are smoothed out.

• (b) At higher foam velocity,  $v_{\text{foam}} > -v_{\text{T1}}$ , the transition regime presents rearrangements waves that are not stationary but convected out of the channel, see Fig. 6b.

• (c) At lower foam velocity,  $v_{foam} < -v_{T1}$ , the foam spontaneously oscillates between two structures, with a well-defined time period. Applied pressure is kept constant:<sup>26</sup> the oscillation is self-driven. Indeed rearrangement perturbations can travel back to the orifice, which creates a retroaction loop with a defined period.

These types of transition regimes can be classified using the language of non-linear instabilities. Indeed each foam structure (*hex-one* or *hex-two*) is linearly stable, but can be non-linearly unstable when a large amplitude perturbation is applied. Here *hex-one* has a higher energy than *hex-two*, *i.e. hex-one* is metastable, and the rearrangement wave triggers a large amplitude perturbation, large enough to cross an energy barrier and relax towards the low energy state *hex-two*. The observed regimes therefore reflects (a) stationary, (b) convected and (c) absolute non-linear instabilities.

#### 7 Perspectives

We have described the spontaneous generation and flow of foams within microchannels. A further step in the microfluidic control of foams would be the active manipulation of foams: operations such as bubble sorting, break-up or coalescence are still to be performed.

Another perspective is the mixture of these foams with other liquids. Bubbles can be mixed with droplets.<sup>27</sup> The advantage of introducing bubbles in between droplets is to enlarge the produced volumes. Bubbles also act as spacers to separate droplets and prevent contamination from each other.

Besides their use within the channels of a lab-on-a-chip device, these perfectly calibrated foams are well suited for the assembly of meta-materials<sup>28</sup> with well defined structure. Crystalline volumes of liquid foams can be generated.<sup>29</sup> These foams may serve as a template for new solid materials.

### References

- 1 G. F. Christopher and S. L. Anna, J. Phys. D: Appl. Phys., 2007, 40, R319.
- 2 T. M. Squires and S. R. Quake, *Rev. Mod. Phys.*, 2005, **77**, 977.
- 3 G. M. Whitesides, *Nature*, 2006, **442**, 368–373.

- 4 W. Drenckhan, S. Cox, G. Delaney, H. Holste, D. Weaire and N. Kern, *Colloids Surf.*, A, 2005, 263, 52–64.
- 5 D. Duffy, J. McDonald, O. Schueller and G. Whitesides, *Anal. Chem.*, 1998, **70**, 4974–4984.
- 6 C. S. Smith, J. Appl. Phys., 1949, 20, 631–631.
- 7 A. M. Gañán-Calvo and J. M. Gordillo, *Phys. Rev. Lett.*, 2001, **87**, 274501.
- 8 A. M. Ganan-Calvo, M. A. Herrada and P. Garstecki, *Phys. Rev. Lett.*, 2006, **96**, 124504–4.
- 9 S. L. Anna, N. Bontoux and H. A. Stone, *Appl. Phys. Lett.*, 2003, 82, 364–366.
- 10 P. Garstecki, I. Gitlin, W. DiLuzio, G. M. Whitesides, E. Kumacheva and H. A. Stone, *Appl. Phys. Lett.*, 2004, 85, 2649–2651.
- 11 T. Thorsen, R. W. Roberts, F. H. Arnold and S. R. Quake, *Phys. Rev. Lett.*, 2001, **86**, 4163.
- 12 P. Guillot and A. Colin, *Phys. Rev. E*, 2005, **72**, 066301.
- 13 P. Garstecki, M. J. Fuerstman, H. A. Stone and G. M. Whitesides, *Lab Chip*, 2006, 6, 437–446.
- 14 P. Garstecki, H. A. Stone and G. M. Whitesides, *Phys. Rev. Lett.*, 2005, 94, 164501.
- 15 B. Dollet, W. van Hoeve, J.-P. Raven, P. Marmottant and M. Versluis, *Phys. Rev. Lett.*, 2008, **100**, 034504–4.
- 16 P. Garstecki, M. J. Fuerstman and G. M. Whitesides, *Phys. Rev. Lett.*, 2005, 94, 234502.
- 17 J.-P. Raven, P. Marmottant and F. Graner, *Eur. Phys. J. B*, 2006, **51**, 137–143.
- 18 P. Garstecki and G. M. Whitesides, *Phys. Rev. Lett.*, 2006, **97**, 024503–4.
- 19 T. Beatus, T. Tluskty and R. Bar-Ziv, *Nat. Phys.*, 2006, 2, 743.
- 20 P. Garstecki and G. M. Whitesides, *Phys. Rev. E*, 2006, **73**, 031603–10.
- 21 W. L. Bragg and J. F. Nye, Proc. R. Soc. London, Ser. A, 1947, 120, 474.
- 22 F. P. Bretherton, J. Fluid Mech., 1961, 10, 166–188.
- 23 I. Cantat, N. Kern and R. Delannay, Europhys. Lett., 2004, 65, 726–732.
- 24 J.-P. Raven and P. Marmottant, *Phys. Rev. Lett.*, 2009, **102**, 084501–4.
- 25 D. Weaire and S. Hutzler, *The physics of foams*, Oxford University Press, Oxford, 1999.
- 26 J.-P. Raven and P. Marmottant, *Phys. Rev. Lett.*, 2006, **97**, 154501–4.
- 27 M. Hashimoto, S. S. Shevkoplyas, B. Zasońska, T. Szymborski, P. Garstecki and G. M. Whitesides, *Small*, 2008, 4, 1795–1805.
- 28 R. M. Walser, Introduction to Complex Mediums for Optics and Electromagnetics, ed. W. S. Weiglhofer and A. Lakhtakia, SPIE Press Book, 2003.
- 29 A. van der Net, G. W. Delaney, W. Drenckhan, D. Weaire and S. Hutzler, *Colloids Surf.*, A, 2007, **309**, 117–124.
- 30 J. P. Raven, PhD thesis, University Joseph-Fourier, 2007.
- 31 P. Marmottant, 2009, http://www-lsp.ujfgrenoble.fr/equipe/dyfcom/marmottant/ Microfoams.html.