Support Information

Microfluidic generation of a high volume fraction of bubbles in droplets

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Shape transitions of secondary droplets

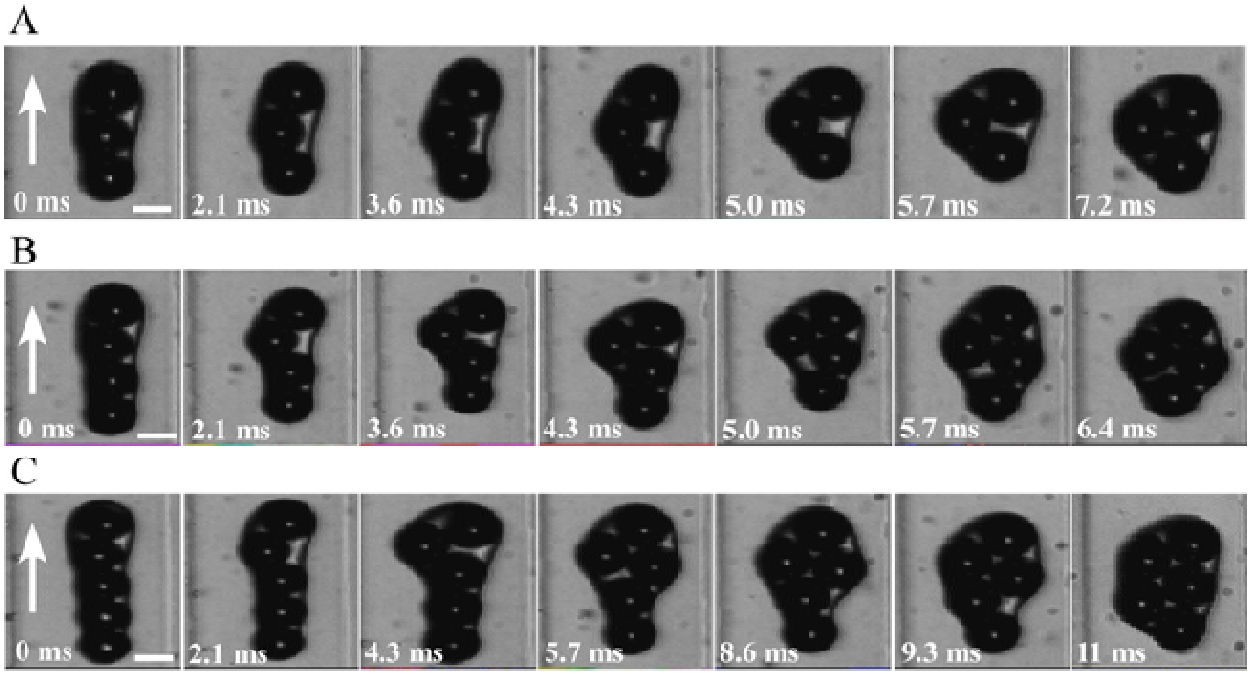

Fig. S1 Time-lapse images show the shape transitions of secondary water droplets with (A) three, (B) four and (C) five gas bubbles. The normalized surface area change, $\Delta A/A$, is 0.3, 0.28 and 0.26 for (A), (B) and (C) respectively. White arrows indicate the flow direction. Scale bar: 50 μm.

Calculation of gas volume fraction using a two-dimensional approximation

Since the diameter of droplets and bubbles is bigger than the height of channel, both droplets and bubbles appear as disk shapes inside the channel, as sketched in Fig. S2.

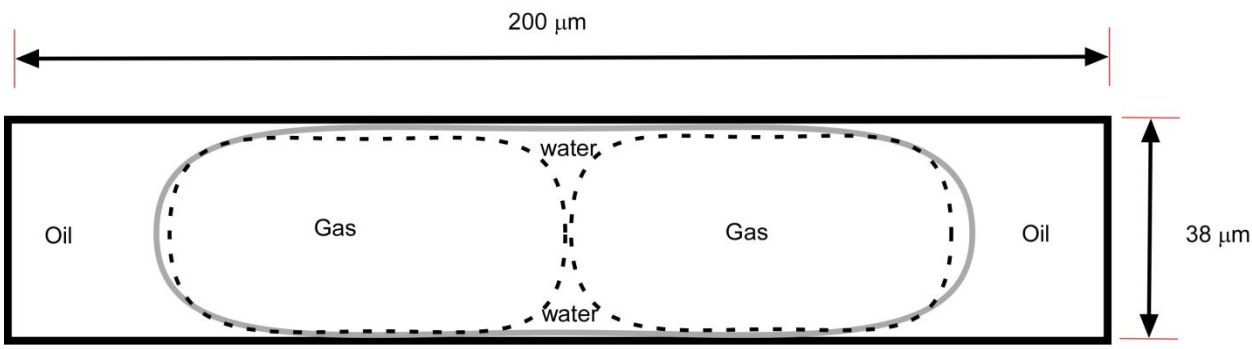

Fig. S2. Cross-sectional view of the gas-water-oil emulsions in a rectangular channel.

We therefore calculate the volume of gas bubbles and droplets by multiplying the height of the channel with the areas of bubbles and droplets based on 2D image analysis (Fig. S2). The gas volume fraction is subsequently obtained by dividing the total volume with the volume of the gas bubbles.

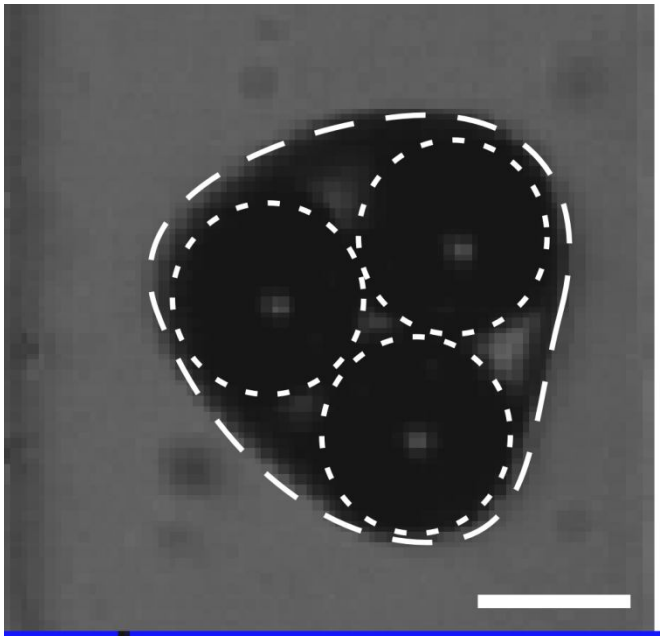

Fig. S3 Sketch of boundaries of bubbles and droplets for a 2D calculation of the gas fraction. Scale bar: 50 μm.

Development of an analytical solution for the size change of bubbles along a microfluidic channel

1. Gas bubbles flow in a cylindrical tube: We first consider a spherical gas bubble with radius of R_{gas} flowing in a channel, as sketched in Fig. S4.

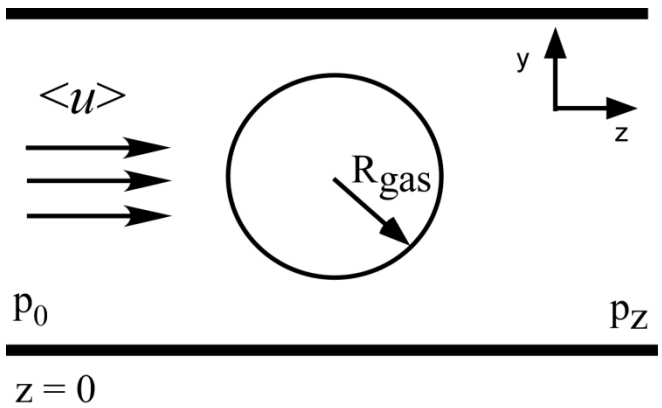

Fig. S4 Sketch of a spherical gas bubble (R_{gas}) flowing in a tube which has an average fluid velocity $<u>$.

The pressure drop along the channel can expressed using Darcy's law:

$$p(0) - p(z) = \frac{\mu <u>}{k} z \qquad (1)$$

where $p(0)$ and $p(z)$ are the pressures at positions $z = 0$ and z respectively. Also, μ and k are the viscosity of water and permeability of the channel, $<u>$ is the average velocity of the fluid, and z is the postion along the channel. For a rectangular channel with width (w) much larger than the channel height (h), $k = h^2/12$. The pressure inside the bubble, on the other hand, can expressed using the Laplace law:

$$p_{gas} - p_{out} = \frac{2\gamma}{R_{gas}(z)} \qquad (2)$$

where p_{gas} and p_{out} are the pressure inside and outside bubbles respectively, γ is the surface tension between gas and water, and $R_{gas}(z)$ is the radius of the gas bubble at position z. If the size of the bubble is small compared to the distance over which the pressure changes occur, then p_{out} approximately equals $p(z)$. We therefore combine equations (1) and (2) and get:

$$p_{gas} - p(0) + \frac{\mu <u>}{k} z = \frac{2\gamma}{R_{gas}(z)} \qquad (3)$$

Neglecting dissolution of gas in water and using the ideal gas law $p_{gas} = nR_gT/V_{gas}$, where R_g is the gas constant, T is temperature and V_{gas} is gas volume, we obtain:

$$nR_gT = \frac{4}{3}\pi R_{gas}^3(z)\left[\frac{2\gamma}{R_{gas}(z)} + p(0) - \frac{\mu<u>}{k}z\right] \quad (4)$$

Since nR_gT is constant, at $z = 0$ and some other z, equation (4) yields

$$R_{gas}^3(0)\left[\frac{2\gamma}{R_{gas}(0)} + p(0)\right] = R_{gas}^3(z)\left[\frac{2\gamma}{R_{gas}(z)} + p(0) - \frac{\mu<u>}{k}z\right] \quad (5)$$

Rearranging equation (5), we obtain

$$\frac{R_{gas}^3(0)}{R_{gas}^3(z)} = \frac{\frac{R_{gas}(0)}{R_{gas}(z)} + \frac{p(0)}{2\gamma/R_{gas}(0)} - \frac{\mu<u>z}{2\gamma k/R_{gas}(0)}}{1 + \frac{p(0)}{2\gamma/R_{gas}(0)}} \quad (6)$$

Assuming $R_{gas}(z) = R_{gas}(0)(1 + \delta)$, where $\delta << 1$, we apply a Taylor expansion and rearrange equation (6) to obtain

$$\delta \approx \frac{\mu<u>zR_{gas}(0)}{8\gamma k\left(1+\frac{p(0)}{2\gamma/R_{gas}(0)}\right)} \quad (7)$$

2. The calculation for a disk-shaped gas bubbles in a microfluidic channel

Now we consider how the shape of the gas bubbles will effect the obtained results. Considering $2R_{gas} > h$, where R_{gas} is the radius of the gas bubble observed from above and h is the height of the microfluidic channel, we then have the situation as sketched in Figure S2.

In this case, we have approximately

$$p_{gas} - p_{out} = \gamma\left(\frac{1}{R_{gas}} + \frac{2}{h}\right) \quad (8)$$

Combining with equation (1), we have:

$$p_{gas} - p(0) + \frac{\mu<u>}{k}z = \gamma\left(\frac{1}{R_{gas}} + \frac{2}{h}\right) \quad (9)$$

Using the ideal gas law $p_{gas} = nR_gT/V_{gas}$ and considering $V_{gas} = h\pi R_{gas}^2$ as the volume of a disk-shaped bubble, we follow the same steps as before and obtain:

$$\frac{R_{gas}^2(0)}{R_{gas}^2(z)} = \frac{\frac{\frac{1}{R_{gas(z)}}+\frac{2}{h}}{\frac{1}{R_{gas(0)}}+\frac{2}{h}} + \frac{p(0)}{\gamma(\frac{1}{R_{gas(0)}}+\frac{2}{h})} - \frac{\mu<u>z}{k\gamma(\frac{1}{R_{gas(0)}}+\frac{2}{h})}}{1+\frac{p(0)}{\gamma(\frac{1}{R_{gas(0)}}+\frac{2}{h})}} \qquad (10)$$

Assuming $R_{gas}(z) = R_{gas}(0)\,(1 + \delta)$, where $\delta << 1$, we apply a Taylor expansion and rearrange equation (6) to obtain

$$\delta \approx \frac{\mu<u>zR_{gas}(0)}{\gamma k(1+\frac{4R_{gas}(0)}{h}+\frac{2p(0)}{\gamma/R_{gas}(0)})} \qquad (11)$$

Equation (7) and (11) are similar except the additional term of $4R_{gas}(0)/h$ in equation (11). The linear relation between the change of bubble size and the position along the channel, however, still hold in for disk-shaped bubbles.

3. The calculation for gas bubbles encapsulated in droplets in a microfluidic channel

Now we take a further step and consider how the encapsulating the water droplets in oil will effect the size change of bubbles. Based on the Laplace law, the pressures inside the droplet and gas bubbles are

$$p_{droplet} - p_{out} = \frac{2\gamma_{wo}}{h} \qquad (12)$$

$$p_{gas} - p_{droplet} = \frac{\gamma_{gw}}{R_{gas}} \qquad (13)$$

where $p_{droplet}$ and p_{gas} are respectively the pressure inside the drop and bubbles. Also, p_{out} is the pressure outside the droplet, h is the height of the channel, and γ_{wo} and γ_{gw} are, respectively, the surface tensions of the water-oil and gas-water interfaces. Combining (12) and (13), we get

$$p_{gas} - p_{out} = \frac{\gamma_{gw}}{R_{gas}} + \frac{2\gamma_{wo}}{h} \qquad (14)$$

Equation (2) and (14) are the same except the additional term of $2\gamma_{wo}/h$ in equation (14). In our experiments, $\gamma_{gw} \approx 60 \times 10^{-3}$ N/m, $\gamma_{wo} \approx 20 \times 10^{-3}$ N/m, $R_{gas} \approx 30$ μm and $h \approx 40$ μm. If we substitute the values into equation (2) and (14), the additional term in equation (14) only

increase 1.5 fold the values in equation (2) and will not effect the final solution in order of magnitude. We thus consider the analytical solution we developed for gas bubbles is still applicable for order of magnitude estimates for bubbles trapped in droplets. Obviously, for more accurate estimates, equation (14) is better than equation (2) when proceeding to estimate the pressure change with position.