Droplet Initiated Rupture of High Viscosity Jets to Create Uniform Emulsions

Dimitris N. JOSEPHIDES *, Shahriar SAJJADI

* Corresponding author: Tel.: ++44 (0)207 848 2902; Email: dimitris.josephides@kcl.ac.uk
Department of Physics, Kings College London, UK

Abstract
Creating highly monodisperse emulsions of high viscosity fluids has long been a challenging task. Even with the advent of micro-engineered emulsification systems such as membranes and microchannels obtaining a good degree of uniformity is hampered as these systems are very prone to jetting. We present a method of increasing the range at which uniform droplets can be produced by the use of droplet initiated jet rupture. In this method, a third, low viscosity inner phase, is introduced in the dispersed phase forcing the dispersed phase to form a shell around each drop and effectively reverts the system from jetting to dripping. Formulations are chosen so that the resulting core-shell droplets are unstable and soon rupture to form highly monodisperse emulsions. The rate of internal droplet production is found to be the governing parameter in the system and must be below a critical frequency. This frequency is found to be well predicted by Plateau–Rayleigh instability theory of jet rupture, where the perturbations caused by internal drops are at a wavelength larger than the circumference of the would-be jet. This method is easy to implement in conventional microfluidic designs and equipment and greatly facilitates the ability to produce very uniform emulsions of high viscosity

Keywords: Monodisperse, Viscous Droplets, Micro Flow, Emulsion, Core-shell Templating, Dripping, Jetting

1. Introduction

Monodisperse emulsions and droplets have found uses in many fields such as in coatings, pharmaceuticals and more recently in lab-on-chip type devices. By far the most common method to produce monodisperse emulsions of high uniformity is by the use of micro-engineered devices such as membranes and microchannel systems (Vladisavljević et al., 2012). When creating droplets of high uniformity from such micro engineered devices, in almost all cases, they rely on a dripping flow regime (Abate et al., 2011; Nunes et al., 2013). This is where droplets are created "drop by drop" at either a nozzle or membrane pore. The extremely consistent and non-chaotic flow conditions involved result in uniform drops. However, if the same devices are used at elevated flow rates, or the viscosities of the fluids increased, jetting occurs. Jetting is characterized by a fluid jet emerging from a nozzle or pore which ruptures downstream to from drops and results in increasing polydispersity. When dealing with fluids of very high viscosities or low interfacial tensions, jetting becomes unavoidable at any appreciable flow rate and reducing its effect on monodispersity has been the subject of various studies. Systems have been employed (Huang et al., 2010; Sauret and Cheung Shum, 2012; Sauret and Shum, 2012; Song and Shum, 2012) such as feed pressure pulsation, vibrating nozzles and electric fields to reduce the onset of jetting in problematic systems (*Cv:* 3% to 10%), but all require substantial amounts of additional apparatus.

In this work we consider a different route to forcing a would-be jetting system into a dripping regime by the use of droplet initiated rupture. We show that if internal droplets are introduced into a jet, at frequencies bellow a critical value, it will force the system into a dripping mode, creating monodisperse core-shell type droplets. These core-shell droplets can be formulated to be highly unstable and thus rupture to create a highly uniform single emulsion. This technique is shown to be

extremely advantageous in the production of highly viscous emulsions where dripping is hard to achieve through conventional methods. This is based on work set out in (Josephides and Sajjadi, 2014)

1.1 Theory

The point at which a microfluidic device transitions from dripping to jetting has been the subject of many works and studies, and although no definitive equation exists to fully predict this point, it is generally understood to be a consequence of elevated continuous and dispersed capillary numbers (Ca_c, Ca_d), where they reach a value of order unity (Nunes et al., 2013). In a simple two-phase flow focused system, capillary numbers of the continuous and dispersed phase are defined as follows; $Ca_c = \mu_c U_c/\gamma$ and $Ca_d = \mu_d U_d/\gamma$ (where μ is the dynamic viscosity, U the velocity, γ the interfacial tension and subscripts c and d denoting continuous and dispersed phases, respectively). As the capillary number and viscosity of a system are directly proportional one can therefore see how such a system is sensitive to high viscosity fluids. If a high viscosity system is to be run at an appreciable flow rate, the resulting jet would have to be ruptured in a uniform and regular fashion to create a final emulsion of high monodispersity.

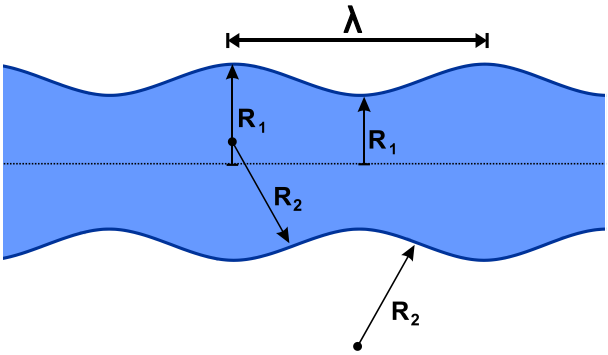

Fig.1. Rayleigh-Plateau instability on a jet

The most common phenomenon related to jet breakup is Rayleigh-Plateau instability (**Fig.1.**). This occurs because a jet is inherently unstable as the interfacial area between the jet and continuous phase is greater than that if the system existed as a spherical droplet (Rayleigh, 1878). When a jet ruptures due to Rayleigh-Plateau instability, capillary waves appear on the interface due to perturbations or noise in the system. These waves either decay or are amplified and propagate through the jet depending on their wavelength. Smaller wavelengths than $\lambda = \pi D_{jet}$ decay and larger ones propagate through the jet and lead to rupture (where D_{jet} is the diameter of the jet and λ is the wavelength) (Eggers, 1997). This is due to the relative difference between Laplace pressure at the peaks and troughs of capillary waves formed on jets at different wave lengths. This phenomenon is often exploited when attempting to rupture jets to desired droplet sizes by forcing a desired wavelength by use of vibration.

Forcing drop formation of a middle phase around an inner core drop has been observed in works concerning core-shell droplet production where the rate at which core droplets are created override the middle phase production rate (Shah et al., 2008; Shum et al., 2010), such works however have only concerned low viscosity fluids.

The principle behind the work expressed in this paper is to use an internal droplet feed at a constant wavelength to induce regular rupturing of a high viscosity jet thus creating uniform droplets at appreciable flow rates.

1.2 Experimental

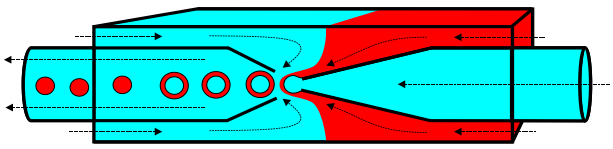

Fig.2. Schematic of the microfluidic device being used. The blue fluid represents the inner (i) and outer (o) phases, and the red fluid the middle (m) phase. Core shell drops are created which later destabilize downstream to create uniform single emulsions.

A glass capillary microfluidic device was used to conduct the experiments. Two cylindrical glass capillaries (1 mm *OD*) were pulled (Sutter P-1000) to fine tapered ends and their tapered ends cut to desired sizes (50 µm and 96 µm *ID*). These where then introduced and glued into opposite ends of a square cross-

sectional (1 mm x 1 mm) capillary tube, where the larger capillary became the so-called collector capillary and the smaller capillary the fluid port for the inner phase. Middle and outer phase fluids were introduced into opposite ends of the square capillary as illustrated in **Fig.2**. This is a common microfluidic set up for the creation of core-shell droplets [1].

The system was pumped via two syringe pumps (Harvard apparatus Pump 11 elite). the first pump controlled the flow rates of the outer and middle phases fixed to a constant ratio of 5:1 by the use of dissimilar syringes (1 ml and 5 ml Hamilton Air-tight), and the second pump independently controlled the flow rate of the inner phase. The resulting droplet production was observed under microscope (Zeiss Axiomat) and high-speed camera camera (Vision Research Phantom V7.1) where size and uniformity data was acquired.The inner phase consisted of pure water, the middle phase consisted of 100 cSt silicone oil (Dow corning 200 fluid), and the outer phase consisted of 90 % w/w glycerol (technical grade, Sigma-Aldrich) and 0.5 % w/w sodiumdodecylsulphate in water. The dynamic viscosities of these three fluids are 0.95 mPa·s, 106 mPa·s and 193 mPa·s respectively. Interfacial tensions between pure water and silicone oil, and aqueous solution of SDS and silicone oil are 40 and 4 mN/m, respectively. Experiments were carried out by varying two parameters: the middle flow rate was varied between 20 µl/hr to 2000 µl/hr (outer flow rate 100 µl/hr to 10000 µl/hr); and the inner flow rate between 0 µl/hr to 1000 µl/hr.

2 Results and Discussion

With the inner flow rate (Q_i) set to 0 µl/hr, the device behaved as a normal 2-phase flow focusing microfluidic cell for single emulsion production and at no flow rate was it possible to produce a stable dripping mode.

When the Q_i was set above 0 µl/hr the device behaved as a 3-phase system for core-shell droplet production (co-flow, flow-focused). Core-shell droplets were created at middle phase flow rates (Q_m) of between 100 to 200 µl/hr and Q_i of between 100 to 200 µl/hr.

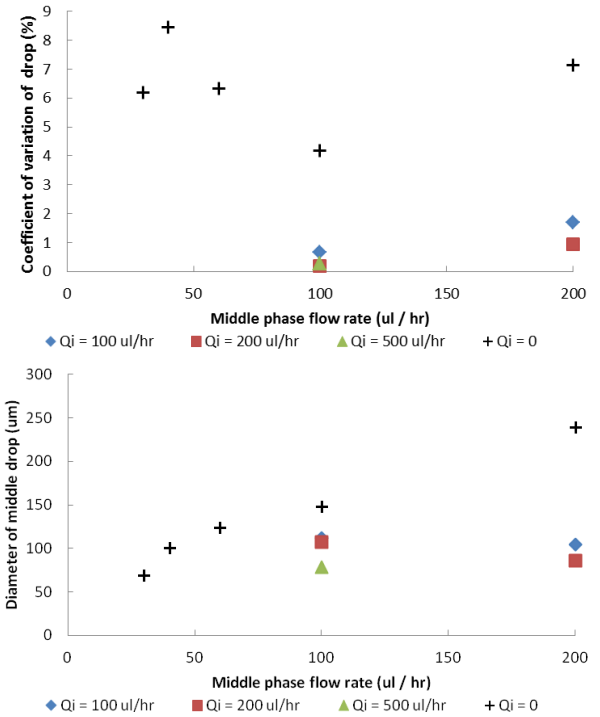

Fig.3. Uniformity and size of final emulsion produced. With no internal droplet feed (+) the system was always in the jetting regime and suffered from a decrease in uniformity whereas with the addition of a droplet feed uniformity is increased. Data for where the jet was not successfully ruptured is not shown on graphs

At higher values of Q_m the system moved into the jetting regime where resulting inner droplets did not rupture the jet and instead large oil drops were formed downstream containing many uniform drops of water. The final emulsions obtained when the device was producing core-shell droplets were highly uniform and consisted of a high viscosity continuous and dispersed phase (**Fig.3,** and **Fig4)**.

2.1 Critical frequency

At higher values of Q_i the device no longer produced uniform droplets but instead the internal droplets were unable to rupture the jet. To understand and predict under what regimes the device will work we must consider the rate of internal droplet production.

If we assume the critical wave length of jet perturbation (minimum wavelength to rupture

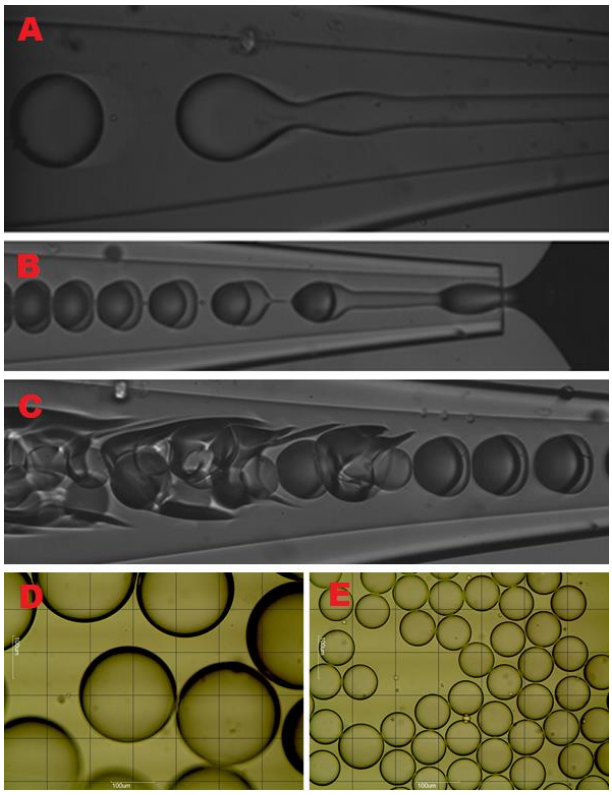

Fig.4. A and D show the device behaving in a standard 2-phase configuration (Q_m = 200 µl/hr, Q_i = 0) and the resulting emulsion. Due to the unavoidable jetting in the system the droplets are relatively non-uniform and large. B, C, and E show the device behaving in a 3-phase configuration (Q_m = 200 µl/hr, Q_i = 200 µl/hr). B shows rupture of the jet to create core-shell drops, C shows the subsequent rupture into single drops, and E the final emulsion. Due to the regular nature of jet rupture the resulting emulsion is highly uniform and relatively smaller.

a jet, see **Fig.1**) to be $\lambda_{crit} = \pi D_{jet}$, and the jet diameter at orifice of the collection capillary tube to be:

$$D_{jet} = 2\left(\frac{A_{cc}(Q_i + Q_m)}{(Q_i + Q_m + Q_o)\pi}\right)^{(1/2)} \qquad (1)$$

(where A_{cc} is the area of the collection tube orifice), we can calculate the minimum wavelength at which the jet needs to be perturbed to lead to rupture (D_{jet} calculation assumes a fully developed plug flow as fluids enter the orifice).

The dripping action of the inner phase in this system acts as the perturbation on the jet with $\lambda_i = v_m / f_i$ (where λ_i is the distance between each internal drop, f_i the frequency at which internal drops are produced, and v_m the

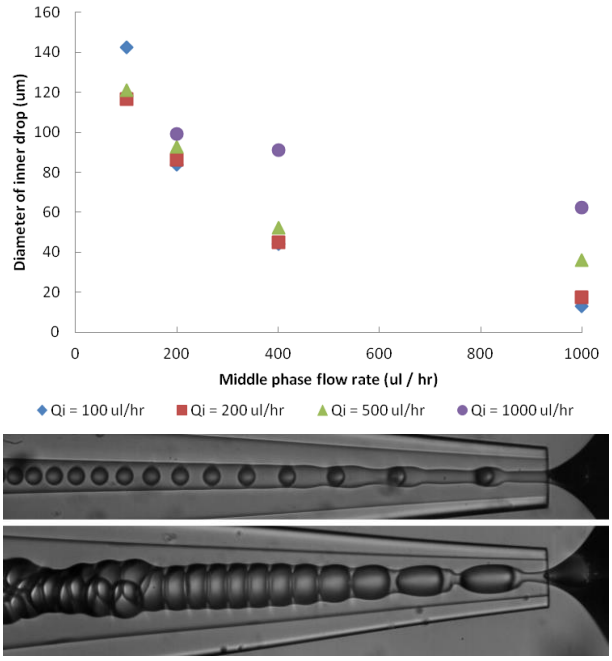

Fig.5. Graph showing the size of internal droplets at various flow rates. At all measured flow rates the internal droplets where highly uniform and dripping from the nozzle. The micrographs show two examples of a jets not being ruptured by internal droplets. The top picture (Q_m = 400 µl/hr, Q_i = 100 µl/hr) is just in the transition zone and the bottom picture is well within the jetting regime (Q_m = 200 µl/hr, Q_i = 1000 µl/hr).

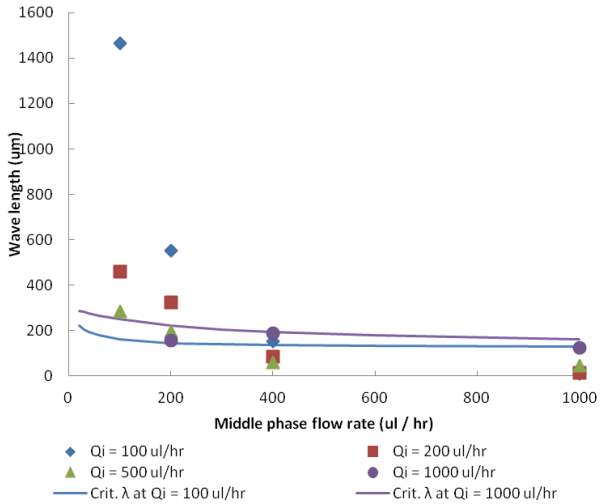

Fig.6. Measured internal droplet wavelength at various flow rates. The two solid lines show theoretical critical wavelengths for Q_i = 100 µl/hr, and Q_i = 1000 µl/hr calculated based on **Eqn. 1**. Data points above the theoretical lines predict when jet rupture shall occur and points below when jet rupture will not occur.

velocity of the middle jet) we can predict whether the perturbations caused by the inner phase will lead to jet rupture. We can calculate the frequency of internal phase drop production of the experimental data as $f_i = Q_i / V$ (where V is the volume of each internal drop). Comparing the measured λ_i to λ_{crit} for all measured flow rates we can see that $\lambda_i > \lambda_{crit}$ is true only for the lower flow rates (**Fig.6**). The area of the graph that shows values below λ_{crit} predicts the regions at which jetting occurred in experiments.

The actual onset of jetting (**Fig.3)** is well predicted by the Rayleigh-Plateau model (**Fig.6**) however it can be see that the model slightly over predicts flow rates at which jetting occurs. We attribute this inaccuracy to the geometry of the collector capillary. As the collector capillary instantly widens downstream from the orifice this has the effect of reducing the velocity of all fluids and widening the middle phase jet. This hampers jet rupture by two mechanisms, firstly the decrease in velocity results in a decrease of λ_i the further downstream one goes, and the widening middle phase jet results in an increase of λ_{crit}; both of which can be observed in the micrograph shown in **Fig.5**. As jet rupture via Rayleigh-Plateau instability is a dynamic process consisting of associated time constants, if the system changes from $\lambda_i > \lambda_{crit}$ to $\lambda_i < \lambda_{crit}$ before jet rupture occurs, the jet will stabilize and not be ruptured.

2.2 Increasing the rupture regime

In the above experiments only one fixed geometry and phase ratio was used but the results suggest that it is possible to create uniform viscous emulsions at greater flow rates. One possible method would be to decrease the frequency at which internal droplets are produced. The easiest method to do this would be to simply increase the nozzle diameter of the inner capillary tube so as to increase the internal droplet size for a given flow rate.

Another method would be to decrease the jet diameter for a given value of Q_m. This could either be done geometrically (decreasing the collection tube orifice) or by simply decreasing the phase ratio of the system (Q_i / Q_m). Further experiments were conducted to identify the onset of jetting in a system of the same geometry but a *phase ratio* = 0.1 at various viscosity ratios. Three dispersed viscosities were chosen (mixtures of silicone oils) of 5.5, 50 and 430 mPa.s so that the final emulsion had viscosity ratios of 0.1, 1, 8.5 respectively. It was found that highly uniform emulsions could be created at Q_i = 500, 400, and 175 µl/hr respectively. This is a great improvement on the 2-phase system.

3 Conclusions

Creating highly uniform viscous emulsions is known to be a problematic task even with the use of standard modern microfluidic techniques due to an early onset of jetting. We show that by the use of a third internal dripping phase we can dramatically increase the flow rates at which highly uniform single emulsions can be created. The internal dripping phase must be miscible and of a lower viscosity than the continuous phase. It is shown that highly uniform single viscous emulsions of various viscosity ratios are obtainable.

The mechanism behind this technique is the creation of unstable core-shell droplets by uniform jet rupture due to Rayleigh-Plateau instability. It is shown that the frequency of internal droplet production is critical to whether the jet will be ruptured and it is found that the perturbation wavelength generated by the internal feed must be greater than the circumference of the would-be jet.

The system is very easy to implement in most microfluidic systems without the need for additional equipment (ie. No vibrating stages or pulse feed systems) as it uses the same geometry used in standard core-shell drop production methods. The method offers a stable flow regime to produce high viscosity emulsions at appreciable flow rates.

4 Acknowledgements

We acknowledge the use made of the high speed camera which was borrowed from the EPSRC (Engineering and Physical Sciences

Research Council) Engineering Instrument Pool.

5 References

Abate, A.R., Kutsovsky, M., Seiffert, S., Windbergs, M., Pinto, L.F.V., Rotem, A., Utada, A.S., Weitz, D.A., 2011. Synthesis of Monodisperse Microparticles from Non-Newtonian Polymer Solutions with Microfluidic Devices. Adv. Mater. 23, 1757–1760. doi:10.1002/adma.201004275

Eggers, J., 1997. Nonlinear dynamics and breakup of free-surface flows. Rev. Mod. Phys. 69, 865.

Huang, S.-B., Wu, M.-H., Lee, G.-B., 2010. Microfluidic device utilizing pneumatic micro-vibrators to generate alginate microbeads for microencapsulation of cells. Sens. Actuators B Chem. 147, 755–764. doi:10.1016/j.snb.2010.04.021

Josephides, D.N., Sajjadi, S., 2014. Microfluidic method for creating monodisperse viscous single emulsions via core–shell templating. Microfluid. Nanofluidics 1–8. doi:10.1007/s10404-014-1439-2

Nunes, J.K., Tsai, S.S.H., Wan, J., Stone, H.A., 2013. Dripping and jetting in microfluidic multiphase flows applied to particle and fibre synthesis. J. Phys. Appl. Phys. 46, 114002. doi:10.1088/0022-3727/46/11/114002

Rayleigh, L., 1878. On the instability of jets. Proc. Lond. Math. Soc. 1, 4.

Sauret, A., Cheung Shum, H., 2012. Forced generation of simple and double emulsions in all-aqueous systems. Appl. Phys. Lett. 100, 154106. doi:10.1063/1.3702434

Sauret, A., Shum, H.C., 2012. Beating the Jetting Regime. Int. J. Nonlinear Sci. Numer. Simul. 13, 351–362. doi:10.1515/ijnsns-2011-0183

Shah, R., Shum, H., Rowat, A., Lee, D., Agresti, J., Utada, A., Chu, L., Kim, J., Fernandeznieves, A., Martinez, C., 2008. Designer emulsions using microfluidics. Mater. Today 11, 18–27. doi:10.1016/S1369-7021(08)70053-1

Shum, H.C., Sauret, A., Fernandez-Nieves, A., Stone, H.A., Weitz, D.A., 2010. Corrugated interfaces in multiphase core-annular flow. Phys. Fluids 22, 082002. doi:10.1063/1.3480561

Song, Y., Shum, H.C., 2012. Monodisperse w/w/w Double Emulsion Induced by Phase Separation. Langmuir 28, 12054–12059. doi:10.1021/la3026599

Sun, B.J., Shum, H.C., Holtze, C., Weitz, D.A., 2010. Microfluidic Melt Emulsification for Encapsulation and Release of Actives. ACS Appl. Mater. Interfaces 2, 3411–3416. doi:10.1021/am100860b

Utada, A.S., 2005. Monodisperse Double Emulsions Generated from a Microcapillary Device. Science 308, 537–541. doi:10.1126/science.1109164

Vladisavljević, G.T., Kobayashi, I., Nakajima, M., 2012. Production of uniform droplets using membrane, microchannel and microfluidic emulsification devices. Microfluid. Nanofluidics 13, 151–178. doi:10.1007/s10404-012-0948-0