SURFACTANT EFFECTS IN LIQUID JETS: GR/M73194
FINAL REPORT

Principal Investigator: Dr. C. D. Bain, University of Oxford

1. Background

Strain rates of the order of 10–10^3 s^{-1} occur widely in jets and sprays, coating equipment, foams and bubbly dispersions. The transfer of species between bulk solution and the gas–liquid interface is an important characteristic affecting coalescence and break-up, coating uniformity and foam stability. The Investigators of this proposal, Dr. Colin Bain and Prof. Richard Darton had formed a successful collaboration to study Marangoni Effects (i.e. hydrodynamic flows driven by surface tension gradients) on an overflowing cylinder (OFC). The timescales accessible with an OFC (0.1–1s) are relevant for some applications, but there are other applications where higher strain rates (shorter timescales) need to be studied. To address the 1–100 ms timescale, we decided to apply some of the experimental techniques that we had developed for the OFC to a liquid jet, which resulted in this proposal. One of the attractive features of a liquid jet was that we expected very large strain rates to arise at the exit from the nozzle associated with the discontinuity in the stress boundary condition. These large strain rates would give rise to large surface tension gradients in surfactant solutions and hence to strong Marangoni effects. We did not realise at the outset quite how singular the behaviour near the nozzle would prove to be and the development of an analytical theory to explain the fluid dynamics near the nozzle has been one of the major achievements of this project.

2. Key Advances

- Development of a robust experimental rig for high precision measurements of flow velocities and surface concentrations of surfactants in liquid jets.
- First simultaneous measurements of surfactant distribution and velocity profiles in liquid jets. Conclusive demonstration of significant Marangoni effects in dilute surfactant solutions (0.1%).
- Development of a fully coupled finite-element model of the liquid jet incorporating hydrodynamics, mass transport and Marangoni stresses at the free surface.
- Identification of a singularity in the surface stress at the nozzle in a simple boundary layer treatment of a surfactant solution in a liquid jet. Derivation of an asymptotic solution that eliminates the singularity and allows quantitative predictions of fluid flow and dynamic surface excess / surface tension for simple adsorption isotherms.
- Development of quantitative mathematical models for adsorption of ionic surfactants at surfaces under pure dilation.

3. Detailed Report

The project had five stated objectives and we describe here the progress made towards each of these.

Objective 1. To design and construct a falling jet suitable for the study of liquid surfaces with surface ages of 1–100 ms.

A gravity-driven jet was constructed that provided a stable flow for between 5 and > 10 cm, depending on surfactant and concentration, before the onset of Rayleigh instabilities. Long nozzles ensured parabolic flow within the nozzle (see below). Typical internal radii of 1 mm and mean velocities of 1 m s^{-1} were employed, giving Reynolds numbers, Re = 1000–2000. Preliminary experiments with a pressurised reservoir showed that we could generate stable jets with radii down to the minimum radius studied of 250 μm. The ends of the nozzles were tapered to reduce wetting of the tip of the nozzle (see figure 1). Nevertheless, there remains a thin square-cut region (< 100 μm wide) at the end of the nozzle and wetting of this steel annulus may affect the hydrodynamics.

Attempts were made to eliminate wetting by silanisation or gold-coating followed by adsorption of a fluorinated alkanethiol. Elimination of wetting did not have a significant effect on downstream measurements, though there are undoubtedly effects very near the nozzle where experimental measurements are difficult. The hydrophobic coatings were not very robust and most experimental measurements were carried out with a wetting tip as seen in Fig. 1. The jet rig was mounted on an optical table screened with curtains. No instability in the surface of the jet was detectable in a laser beam reflected from the surface. Experimental measurements were stable over a period of many hours. (See [1] for full details)

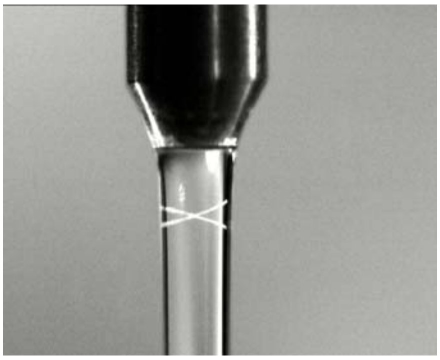

Figure 1: Aqueous jet emerging from 0.8-mm radius SS nozzle. The crossed laser beams are for laser Doppler velocimetry.

Objective 2: To interface jet to an ellipsometer and laser Doppler velocimeter and to demonstrate the ability to measure the surface concentration of surfactants with a precision of < 5% of a monolayer and the velocity profiles with a precision of < 10% and a spatial resolution of 20 μm.

The laser Doppler velocimeter (the LDV) was entirely home-built. A 17 mW HeNe laser was split, focussed and recombined to generate a set of interference fringes (Fig. 2(a)). Small particles (<2 μm TiO_2) seeded into the flow scatter the light, which is collected with a PMT (Fig. 2(b)). The signal from the PMT is digitised, Fourier-transformed and averaged (Fig. 2(c) – note logarithmic scale). From the peak frequency, the velocity normal to the fringes can be calculated. Achieving sufficient precision and stability required considerable effort, but the result was that the target performance was comfortably met or exceeded. The spatial resolution in the axial direction (obtained by counting the fringes) is < 10 μm and in the radial direction is ca. 20 μm (due to effects of refraction). The velocity precision is limited by the digital signal processing and not by the stability of the jet: it was usually set to ca. 1%. Full transverse profiles can be measured to within one jet diameter of the nozzle and the surface velocity to within 200 μm of the nozzle. There are no fundamental obstacles to improving the spatial resolution to < 5 μm (axial) if required.

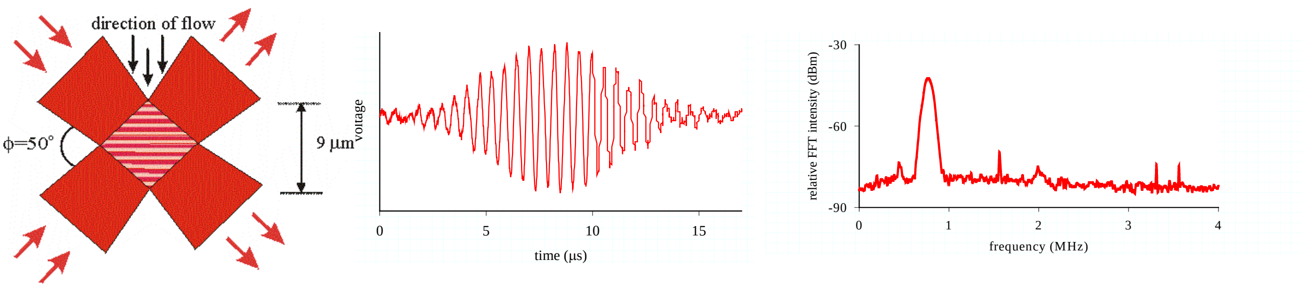

Figure 2. Laser Doppler Velocimetry. (left) crossed laser beams (centre) light scattered by probe particles (right) Fourier transform yields local velocity in probe volume.

Radial velocity profiles are shown in Figure 3 for pure water as a function of distance down the jet. The near perfect agreement with the solid lines obtained from our computational fluid dynamics (CFD) model for parabolic flow within the nozzle validates both the experiment and the computer model. Figure 4 shows the surface velocity, u_s, as a function of distance, z, down the jet for pure water and for 2.5 mM C_{16}TAB solution (a cationic surfactant). Pure water shows the expected $u_s \sim z^{1/3}$ dependence and the decrease in u_s due to the surface tension gradient (inset) in the C_{16}TAB solution is clearly evident.

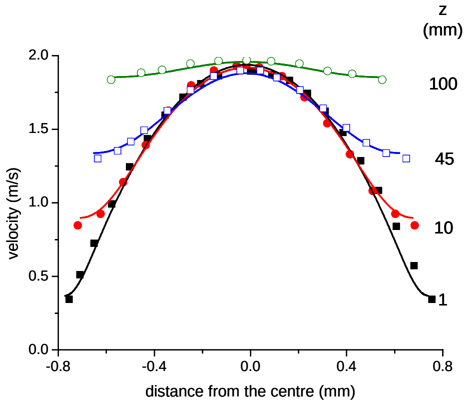

Figure 3. Radial velocity profiles (symbols) and predictions (lines) from cfd model assuming a parabolic profile well within the nozzle.

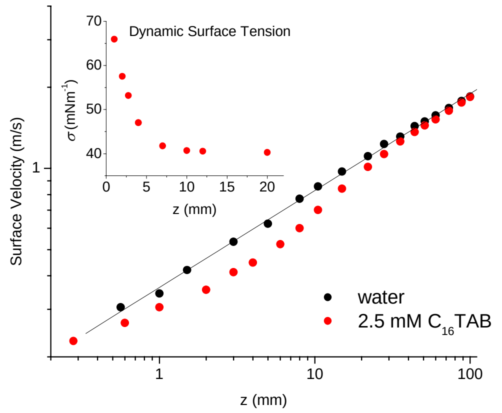

Figure 4. Comparison of surface velocity as a function of z for pure water and a 2.5 mM $C_{16}TAB$ solution.

The ellipsometer was constructed from components supplied by Beaglehole Instruments (Wellington, NZ). Obtaining accurate ellipsometric measurements from the curved surface of the jet proved a challenge. We eventually developed reproducible protocols based on calibration with solutions of known ellipticity. For $C_{16}TAB$, the precision of the measurements is about ± 3% of a monolayer downstream and ± 5% of a monolayer as the nozzle is approached. Within 1 mm of the nozzle the jet was too curved in the axial direction for us to obtain quantitative readings. To convert values of the ellipticity to surface excess, Γ, we conducted calibration experiments by neutron reflection on an OFC at the neutron spallation source, ISIS. Figure 5 shows the surface excess, relative to the saturation value, for $C_{16}TAB$ solutions of varying concentrations as a function of z. Note the steep decrease in Γ at low z due to the high strain rates near the nozzle. We will show below that Γ is expected to extrapolate to a low, but finite, value of Γ at the nozzle.

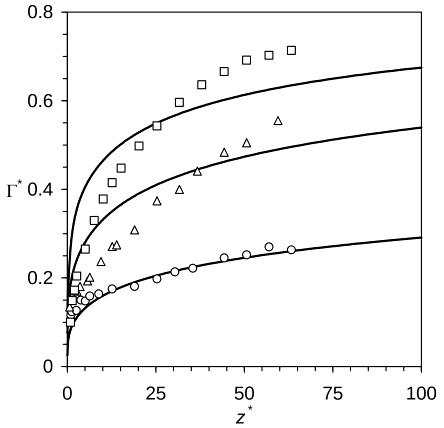

Figure 5: Surface excess of CTAB as a function of z for c = 0.3, 0.63 and 0.9 mM. R_0 = 0.79 mm; Re = 1950. Theoretical lines are described in the text

Measurements were made on a range of different chain lengths in the C_nTAB family, with and without salt and at various values of Re. Some measurements were made on the C_nE_m family on nonionics and these are now being extended. The recent theoretical developments referred to below will allow quantitative analysis of the adsorption kinetics in these systems.

Objective 3: To develop a validated hydrodynamic model of surfactant adsorption and Marangoni flow in liquid jets.

The velocity profile at the nozzle exit is that of fully developed laminar flow, with the usual no-slip condition at the wall. This no-slip condition is immediately relaxed when the fluid leaves the tube. In the absence of any surface shear (no surfactant present) a region of zero vorticity appears at the surface of the jet and, as the fluid travels downwards, the zero-vorticity region diffuses towards the centre of the jet, eventually equalising the velocity across the jet. The CFD code predicts this velocity profile, and its development with distance is in almost perfect agreement with the experiments (Fig. 3). Applying continuity and a momentum balance to the thin layer near the jet surface yields an expression for the surface velocity $u_s = (32\, u_0^2\, \nu z / R_0^2)^{1/3}$, where u_0 is the mean nozzle exit velocity, ν is the kinematic viscosity and R_0 the nozzle radius. This theoretical result, which is closely supported by experiment (Fig. 4), shows that, in the absence of surfactant, the surface strain rate at the nozzle (z = 0) is infinite. In the presence of surfactants there is rapid transfer to the surface caused by the high surface acceleration, and an argument based on asymptotics as $z \rightarrow 0$ shows that the leading order term in a Taylor expansion for Γ about z = 0 is a finite value Γ_0. Near the nozzle (in the region termed by us the "detachment region") the surface velocity increases linearly with distance so that the surface acceleration at $z = 0$ is finite. Shear stress at the surface is presumed to be continuous at the nozzle exit, so its value at the start of the detachment region is $4\mu u_0/R_0$, equal to the value inside the nozzle. A value for Γ_0 can be found from this theory, with some simplifying assumptions, and this is found to vary with the bulk concentration raised to the power 3/2. Outside the detachment region, as long as the surface is far from saturation, Γ is found to increase as $z^{1/3}$, like the velocity [2].

These theoretical considerations have formed the framework to a full solution of the flow and concentration fields in the jet, using FIDAP, one of FLUENT's general-purpose CFD solvers. The three-dimensional liquid jet is reduced to the axisymmetric case. The origin of the cylindrical coordinate system is located on the centre (symmetry) line of the jet in the nozzle exit plane. A short part of the long capillary nozzle is considered in the calculation, the flow profile being set parabolic at one nozzle radius upstream of the exit plane. The jet model ends at a downstream position sufficiently far away from the nozzle that the appropriate downstream boundary conditions may be applied. To keep the numerical size of the flow field to a minimum, we chose a length of $100 \times R_0$ for the free jet section. The distance from the row of surface nodes to the first row of nodes underneath the surface is only about 60 nm (for a nozzle radius of $R_0 = 0.79$ mm), to ensure the accurate computation of the concentration field within the diffusion boundary layer. The mesh consists of 12,012 elements in total, which results in average computation times of not more than 10 minutes for the water jet and not more than 30 minutes if the hydrodynamics are solved along with the coupled mass transfer problem on a Windows 2000 PC with 512 Mb RAM and a 1.0 GHz processor. A fully coupled Newton-Raphson iteration scheme, where the free surface position was updated at each iteration step, is employed to solve the governing set of equations [2].

A major challenge in coupling the flow field to the concentration arises from the singularity (slip/no-slip) at the surface at $z = 0$. The surface concentration drops precipitately at $z = 0$ and then increases; the numerical scheme, however, always calculated a finite, but extremely rapid decrease of surface concentration just following the nozzle exit plane. In turn this caused a very rapid increase in surface tension. When the two fields were coupled, this huge Marangoni stress caused a large acceleration, and convergence failed. Our solution of this problem is to superimpose the theoretical value of Γ_0 and the required finite shear stress at the nozzle exit plane. The resulting surface concentration profile in the detachment region is matched with the far field Γ values, to yield a surface concentration profile over the whole jet surface which can be returned to the flow field calculation as a surface tension profile. A small number of iterations, including updated matching, is then required to converge both flow and concentration fields. The result was numerically satisfactory, and gave good agreement with measurements of surface concentration with C_{16}TAB when the bulk concentrations were low (Figure 5). At higher bulk concentrations the agreement was reasonable, though the numerical solution suggested a more rapid rise in surface concentration with distance than is seen in the experiments.

Objective 4: To determine the role of kinetic barriers to adsorption for selected surfactants on the ms-timescale, including, where appropriate, quantitative measurements of rate constants.

We have incorporated both micellar diffusion and simple micelle break-down kinetics in the CFD code. The more general problem of analytical solutions has been pursued in two collaborative projects at Oxford: *Dynamics of Surfactant Adsorption* (GR/M83797) and *Mathematical Modelling of Surfactant-driven flows* (GR/R52190). In the first of these, we have demonstrated quantitative agreement with a diffusion-controlled model for C_nTAB surfactants below the cmc at strain rates up to 10^1 s^{-1}, and explored how high the strain rates would need to be to observe kinetic barriers arising from the electrical double layer [3]. This model suggests that kinetic barriers may be relevant very close to the nozzle, which is the region where we observe experimentally that the surface excess is lower than predicted theoretically (see figure 5 above). There are, however, other factors that could lead to this discrepancy and further work is required. In the second collaboration, we have very recently derived asymptotic solutions for the micellar case with finite breakdown kinetics and tested these models against data from the OFC [4]. The extension of these models to the faster timescales of the liquid jet is the next important step.

Objective 5: To apply validated models of surfactant adsorption and Marangoni flow to systems of industrial relevance including (i) coating flows, (ii) bubble coalescence, and (iii) interfacial mass transfer in turbulent dispersions.

An important strategy of this work was to use a commercially available CFD code as a platform for developing the numerical model solution. In this way we could develop an approach which is readily transportable to other free-surface flows involving surfactant adsorption, both below and above the cmc, and readily usable by other researchers. The full period of the grant has proved necessary to complete our model of the jet, so that only very preliminary work has been possible on the three other specific flows mentioned in Objective 5. Nevertheless, this work has indeed provided a basis on which these flows can be tackled, and indicated the problems that will arise. In particular, our experience has revealed the difficulties associated with finding a surface concentration boundary condition, which is essential to the solution of the flow, where there is no single place where the surface concentration is known *a priori*. Our collaborators Howell and Breward [5] suggested that in the OFC this situation could be tackled by a theory in which the surface concentration is zero (and the surface acceleration infinite) at the edge of the cylinder. In the jet problem we have been able to reach a solution by requiring the surface shear stress to be continuous at the nozzle exit. This then yields a finite surface concentration at the point of transition from confined to free-surface flow, and thus a finite surface acceleration. We believe that the same approach will be necessary in modelling the stretching flow that arises when a coating is laid down on a solid substrate (Objective 5(i)).

In contrast, in both bubble coalescence (Objective 5(ii)) and turbulent dispersions (Objective 5(iii)), the interfacial flow, and thus the surface concentrations and their associated Marangoni stresses, are not fixed by external geometry. Thus Breward and Howell [6] were able to find a number of theoretical solutions to the problem of drainage of a foam lamella, balancing capillary suction in the Plateau border with a Marangoni tension that arises between the border, where surfactant accumulates, and the lamella where the surfactant layer is stretched. In a numerical model of this flow, it will be necessary to take a maximum value of the surface concentration as a boundary condition, at the Plateau border, where flow becomes three-dimensional. It should then be possible to model foam stability as a function of bulk concentration. In a turbulent dispersion, any free surface is intermittently and randomly expanded by approaching eddies, and, just as in the jet, the presence of surfactant will act so as to reduce the surface acceleration. In this case a satisfactory boundary condition is probably that the adjacent stagnant surface is saturated. Surface strain rates in turbulent gas/liquid dispersions are around 30 s^{-1}, well within the range studied in this jet project.

4. Project Plan Review and Explanation of Expenditure

The post-doc employed on the project, Dr. Battal, resigned after 27 months to take up a faculty position in Turkey. With the agreement of the EPSRC, we used the remaining funds to invite him back as a Visiting Fellow for 3 months the following summer and to extend support for the project student on the grant.

5. Research Impact and Benefits to Society

We have learnt a number of lessons about how to solve problems involving Marangoni stresses, free surface flows and surfactant adsorption. These insights are extendable to other problems.

1) Methods for obtaining surface excess boundary conditions on the free surface
2) Meshing in CFD code near singularities in the flow
3) Incorporation of micelle diffusion and breakdown kinetics in mass transport problems
4) The importance of accurate adsorption isotherms for interpreting kinetic data

The code we have developed has been implemented in a commercial CFD package and is therefore accessible to other research groups.

The experimental measurements have attracted the interest of the ink jet industry and we are part of a large collaborative proposal that is been submitted to the EPSRC by a consortium of companies. The experimental data obtained from the OFC and liquid jet is used by mathematicians to validate their mathematical models [4,5].

We have described earlier how an improved understanding of interfacial effects on the fluid dynamics of surfactant-containing systems has very wide applicability. The jet provides a more general platform also for measuring the adsorption kinetics of surfactants on short timescales under well-defined hydrodynamic conditions. This knowledge is of importance in many other problems, including milling, emulsification and penetration into porous media.

6. Dissemination

Two long papers describe the primary work carried out in the project [1,2]. Supporting studies to assist interpretation of the experimental data have resulted in two further papers [7,8] (not listed on IGR since they were co-funded by GR/M83797). Oral presentations were made at the following conferences: (2001) AIChE Annual Meeting, Reno; (2002) IChemE Fluid Separation Process Research Event, London; 14th Surfactants in Solution (SIS) Symposium, Barcelona; EuroFoam 4, Manchester; CHISA, Prague; Foams and Minimial Surfaces, Isaac Newton Institute, Cambridge; (2003) 225th ACS National Meeting, New Orleans; 4th European Congress of Chemical Engineering, Granada. The work has been described in numerous research presentations by CDB and RCD in the UK, New Zealand, Australia, Germany and Sweden. Three Advisory Meetings were held with a panel of academics and industrialists during the course of the project. Regular meetings are held with applied mathematicians at Oxford, who have published several papers based on experimental data and insight from the OFC and jet projects [4-6]. The results have been discussed with interested companies, such as Kodak, ICI and Domino.

7. Further Work

Having developed a reliable experimental platform and a theoretical framework, we intend to extend the range of surfactant systems and attack the important question of the role of micellar processes. As part of the ink jet project referred to earlier, we will extend the technical capability to smaller length scales and shorter timescales. The application of our acquired understanding to the mathematical modelling of complex flows will be continued in collaboration with the Oxford Centre for Industrial and Applied Mathematics.

8. References

[1] "Surfactant Adsorption and Marangoni Flow in Liquid Jets: I. Experiments" Battal, T.; Bain, C. D.; Weiss, M.; Darton, R. C. *J. Coll. Interface Sci.*, **2003**, *263*, 250.

[2] "Surfactant Adsorption and Marangoni Flow in Liquid Jets: II. Modelling" Weiss, M.; Darton, R. C.; Battal, T.; Bain, C. D. submitted for publication in *Chem. Eng. Sci.*

[3] "Adsorption of Ionic Surfactants at an Expanding Air–Water Interface" Valkovska, D. S.; Shearman, G.; Bain, C. D.; Darton, R. C.; Eastoe, J. submitted for publication in *Langmuir*.

[4] "Straining Flow of a Micellar Surfactant Solution" Breward, C. J. W.; Howell, P. D. submitted for publication in *Euro. J. Appl. Math.*

[5] "Mathematical Modelling of the Overflowing Cylinder Experiment" Howell, P. D.; Breward, C. J. W. *J. Fluid Mech.* **2003**, *474*, 275.

[6] "The Drainage of Foam Lamella" " Breward, C. J. W.; Howell, P. D. *J. Fluid Mech.* **2002**, *458*, 379.

[7] "Determination of the Dynamic Surface Excess of a Homologous Series of Cationic Surfactants by Ellipsometry " Battal, T.; Shearman, G.; Valkovska, D.; Bain, C. D.; Darton, R. C.; Eastoe, J. *Langmuir*, **2003**, *19*, 1244.

[8] "Surface Equation of State and Adsorption Isotherms for Efficient Surfactants" Taylor, C. D.; Valkovska, D. S.; Bain, C. D. *Phys. Chem. Chem. Phys.*, **2003**, *5*, 4885–4891.