A SIMPLE THEORETICAL BASIS FOR DROPLET-INDUCED SURFACE FATIGUE

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ABSTRACT

Surface wetting is a major source of droplet failure and contamination. We propose a simple theoretical treatment to model the effect of droplet wear on surface surfactant coverage, itself a major cause of surface degradation in use. The model showed good concordance with effects predicted by a numerical iterative treatment in MatLab Simbiology.

KEYWORDS: Surfactant distribution, modelling, surface fatigue, wetting

INTRODUCTION

Droplet microfluidics has become a dominant research topic in the field of MicroTAS [1, 2]and enjoyed great success. This area depends upon the successful formation of a stable microemulsion under flow, something that requires a surfactant to adjust interfacial tensions within the system to the optimal region.[3, 4] The preferred system for most applications has become a fluorous continuous phase stabilized by a perfluoropolyether/polyethyleneglycol block copolymer surfactant.[5, 6] Surface wetting has an enormous impact on the long term stability of droplets and on the usable lifetime of a particular device. When no wetting of the dispersed phase occurs transport from the droplet to the chip is minimal and the droplets stable. When wetting occurs the stability of droplets begins to degrade and many wetting induced droplet failure modes begin to manifest as shown in Figure 1 a)-c). It is notable that most of these modes become more prevalent over time in usage.
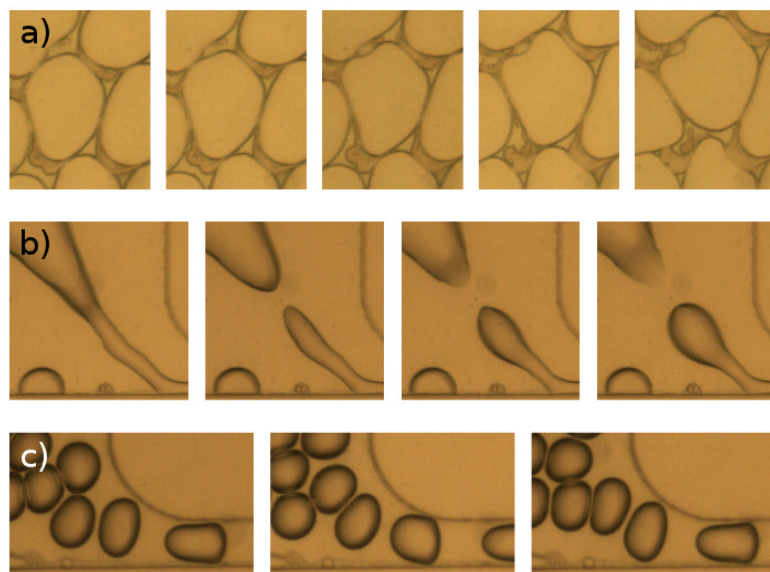

Figure 1: Wetting induced droplet failure: a) Substrate-driven droplet deformation b) Wetting c) Generalised surface-driven droplet deformation in channels only

Many techniques for pre-usage surface modification have been developed [7] but these tend to ignore the fact that the surfactant coats not only the droplet but also the chip wall. It is almost certain that the primary barrier to surface wetting is the wall surfactant monolayer and so maintenance of this monolayer is a key concern for extending chip and droplet lifetimes.

THEORY

   Complex predictors for surfactant kinetics are available[8, 9] but in essence the flow field within the microdevice simplifies matters. As the flow field is ordered, and droplet flow periodic and predictable in most droplet devices, it is reasonable to assume that the equilibrial systems within the chip will behave as an approximate continuum. In other words instead of treating the droplets within the system as individual units, it should be safe to treat them as a quorum surface. Most such models use a modified Langmuir system to achieve results and this we have emulated to produce a predictive system for surfactant distribution based on a few key constants. Firstly a model of the equilibrial system was constructed using MatLab's Simbiology package and droplet flow simulated within it. The effect of droplet flow on surfactant wall coverage can be seen in Figure 2. The validity of an assumed equilibrial position can be clearly seen.
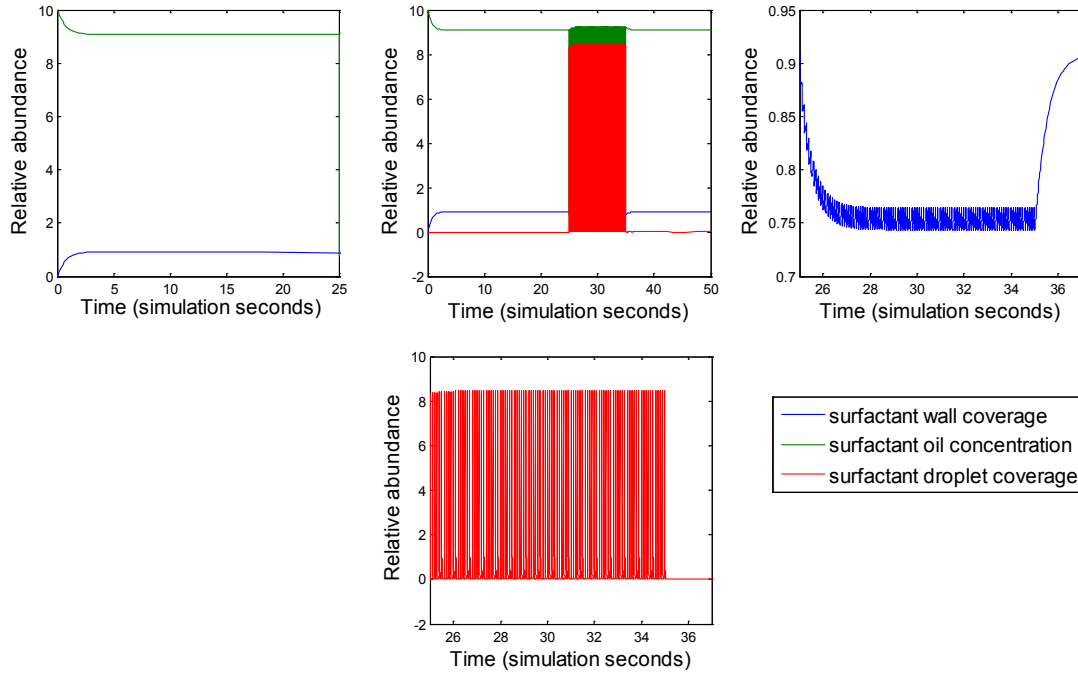

Figure 2: Surfactant distribution within a numerical iterative simulation of droplet flow

   Our model uses a notional constructed membrane instead of the periodic droplet flow. We can thus dispense with iterative modelling and proceed straight to the equilibrial position.

RESULTS AND DISCUSSION

   Put simply, the system assumes a surfactant delivered in the oil phase which is distributed between the chip surface and the droplet according to the ratio K_d/K_w where K signifies the distribution coefficient for the system. (Subscript w throughout indicates wall, d indicates droplet). The oil phase is assumed to be at equilibrium. It can be easily shown that the amount of coverage of the chip wall N_w varies strongly according to the oil fraction θ, and the ratio of distribution constants, as well as with the initial surfactant concentration in oil, C.

$$N_{tot} = N_w + N_d + N_o \tag{1}$$

$$C\theta V = \frac{k_w A_w K_w C_1}{1 + K_w C_1} + \frac{k_d A_d K_d C_1}{1 + K_d C_1} + C_1 \theta V \tag{2}$$

Where C = initial oil surfactant concentration, C_1 = equilibrium oil surfactant concentration, θ = oil fraction of developed flow, N_{tot} = total surfactant burden of the system, N_w = wall monolayer burden, N_d =the droplet monolayer burden, N_o = oil burden, k_w =surface adjusted distribution coefficient for the wall, k_d = surface adjusted distribution coefficient for the droplet, V= chip volume, A_w= wall surface area and A_d = droplet surface area.

This system allows predictive calculations of the equilibrial endpoint to be undertaken in a simple spreadsheet. The k and A terms used are proxies for concentration and the A term scales linearly with droplet channel population. The droplets are treated as though they are a boundless membrane with a set area, A_d, situated within the diffusive timecone of the chip wall so that a high (>5) value of the Fourier number is maintained. This assumption is valid for most droplet scenarios but has limitations: where the droplet is considerably smaller than the channel diameter, and the channel length is large this system will begin to lose validity. We term this notional quorum a Synthetic Quorum Membrane (SQM), and we believe this treatment has wider application in understanding droplet mass transfer kinetics *inter* alia. Given the simple nature of the model the necessary constants can be inferred simply from experiment and this work is underway. The system allows the predictions that increased chip lifetimes will occur if the wall affinity for surfactant is increased, the oil fraction increased or droplet surface area decreased. We are extending this model to take account of the advective surfactant transport within flowing systems and experiments are underway to quantify this.

CONCLUSION

A simple model for droplet surface fatigue is proposed using simple equilibrial mathematics to predict the wear endpoint of the fluctuating droplet system.

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