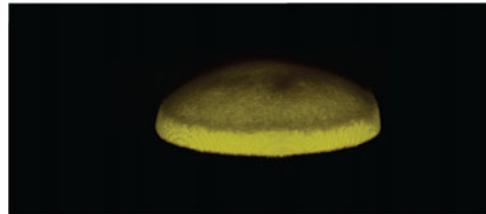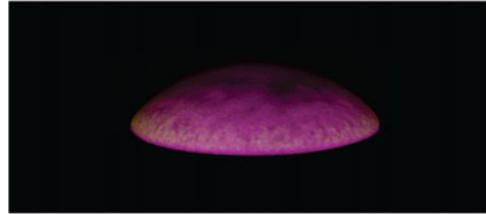# Focus on Fluids

Towards controlled liquid–liquid microextraction

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In a recent paper, Chu & Prosperetti (*J. Fluid Mech.*, vol. 798, 2016, pp. 787–811) calculate the dissolution of a two-component droplet in an immiscible liquid. Here we discuss in what sense their results go much beyond the Epstein–Plesset solution of a dissolving single-component droplet and hitherto used approximations for dissolving multicomponent droplets. We also highlight the relevance of Chu & Prosperetti's result for liquid–liquid extraction processes for chemical analysis.

Key words: drops, emulsions

1. Introduction: the Epstein–Plesset droplet

When a droplet of liquid comes into contact with water, we tend to think only in two categories, 'insoluble' or 'soluble': e.g. an olive oil droplet is seen as insoluble, whereas an ethanol droplet is soluble and in fact perfectly miscible with water. However, the truth lies in the middle: solubility is a matter of time scales, and even heavy oil dissolves in clean water, provided one waits long enough. The dissolution dynamics of an isolated spherical droplet in a bulk liquid at rest was analytically calculated in a classical paper by Epstein & Plesset ([1950](#)), originally formulated for bubbles and later extended to droplets (Duncan & Needham [2006](#); Su & Needham [2013](#)). The result of this exact calculation is that a droplet shrinks with a square-root behaviour in time on a time scale governed by $\tau_{EP} = R_0^2 \rho_d/(D c_s)$. Here, c_s is the solubility of the solute in the solvent, ρ_d the droplet density, D the diffusion constant and R_0 the initial droplet radius. While the density and diffusivity of liquid solutes do not vary too much, their solubility in water can vary by many orders of magnitude, leading to huge lifetime differences between different drops of the same size (table [1](#)). Here we assumed that the surrounding water far away from

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Liquid	c_s (kg m^{-3})	ρ_d (kg m^{-3})	D (10^{-9} m^2 s^{-1})	$\tau_{EP}^{R_0=0.1\,\mathrm{mm}}$ (min)
Decane	5.2×10^{-5}	730	0.75	3.1×10^6
1-Decanol	0.036	830	0.475	8100
1-Heptanol	1.67	822	0.80	92
1-Pentanol	22.0	811	0.89	6.9

TABLE 1. Material properties of various liquids in water at $25\,^{\circ}$C and ambient pressure and the resulting Epstein–Plesset time scale $\tau_{EP} = R_0^2 \rho_d / (D c_s)$ for a $R_0 = 0.1$ mm droplet.

the droplet does not contain any solute. Once the solute concentration c_∞ far away from the drop is non-zero, the dissolution is delayed (by a factor $c_s/(c_s - c_\infty)$) and for positive oversaturation $\zeta = c_\infty/c_s - 1 > 0$ the droplet will even grow.

The Epstein–Plesset problem can be seen as the 'hydrogen atom' of diffusive droplet or bubble dynamics, as it can be solved analytically. But just as an isolated hydrogen atom is rare and hard to realize and the relevant real world consists of larger atoms, molecules and solid-state matter, in real-world fluid dynamics problems we hardly ever have an isolated droplet or bubble in a bulk liquid at rest, but mutually interacting droplets and bubbles, droplets and bubbles at or close to interfaces, in turbulent flow and with surfactants, etc. Moreover, rather than a pure gas or liquid, we often have mixtures of several gases and liquids. Just as atomic, molecular, condensed matter and solid-state physics has had to deal with the 'complications' of the real world, this also holds for the physics of fluids, which has to deal with the above 'complications'.

Here we will focus on the 'complications' arising for droplets of liquid mixtures. While the Epstein–Plesset theory can relatively straightforwardly be extended to bubbles consisting of gas mixtures, this does not hold for multicomponent droplets, not even when they are constituted of miscible liquids. Up to now various approximations have been used: Su & Needham (2013) assumed that the instantaneous droplet–bulk interface composition of spherical droplets can be related to the droplet volumetric composition, i.e. for a two-component droplet with liquids $i = a, b$, they assume $V_a/V_b = A_a/A_b$, where V_i/V and A_i/A are the volume and area fractions of the total droplet volume V and the total droplet interface A. Su & Needham (2013) then calculated the dissolution rate of the individual components based on the total droplet radius, and multiplied this by the surface area fraction A_i/A occupied by the respective component. This approach is equivalent to the use of Raoult's law to determine the partial gas pressures at the bulk side of the interface, in the sense that both approaches assume negligible interaction between the two components a and b, and a homogeneous mixture inside the droplet.

2. Beyond Epstein–Plesset

In a recent paper, Chu & Prosperetti (2016) have now provided a calculation of the dissolution (or growth) problem of a multicomponent droplet, revealing the limitation of the hitherto used approximations. They solve the diffusion equation with concentration boundary conditions at the (moving) droplet interface following from the requirement that the chemical potentials of each of the components have the same value in both phases (Landau & Lifshitz 1986), assuming thermodynamic equilibrium. Remarkably, these concentration boundary conditions lead to time-dependent concentrations at the droplet interface, resulting in a memory term for

the mass flux through the interface, which does not exist for a droplet of a pure liquid. How serious are the deviations from the hitherto used approximations depends strongly on the solubilities and diffusivities of the components. For similar solubilities and diffusivities of the two droplet components, they can be serious, and Chu & Prosperetti (2016) construct a case in which the two-component droplet grows, even though in the solution both constituents of the droplet have a concentration below their saturation concentration, i.e. $\zeta_i < 0$ for both $i = a, b$.

Chu & Prosperetti (2016) performed their calculation for an immersed two-component spherical droplet in a still solvent, but they also sketched how to embody further 'complications' of the real world, namely to an immersed sessile droplet (to which an Epstein–Plesset type approach for the dissolution or growth can also be extended (Lohse & Zhang 2015)) consisting of two components, to two-component droplets in a flow situation, and to droplets consisting of more than two components.

The pioneering calculations by Chu & Prosperetti (2016) stimulated us to perform detailed experiments on dissolving sessile two-component droplets (Dietrich *et al.* 2016). As predicted by Chu & Prosperetti (2016), we indeed find cases in which a segregation of the (miscible!) droplet components at the droplet interface can take place. Two snapshots of such an example are shown as confocal images of a dissolving pentanol/cyclohexane droplet in the figure by the title of this paper. Note that, for sessile droplets, due to the broken spherical symmetry, spatially inhomogeneous dissolution (or evaporation in air) may take place, also leading to segregation of the component in addition to Marangoni flow (Cazabat & Guéna 2010). Obviously, many more experiments should be done to quantitatively study the dissolution and growth of multicomponent droplets and to compare with the theory of Chu & Prosperetti (2016).

3. Relevance

The results of Chu & Prosperetti (2016) have tremendous relevance for various applications in chemical technology and analysis. Here I would like to highlight the process of liquid–liquid extraction. For chemical analysis such as chromatography, ever since the pioneering work of the Nobel Laureate Pregl (1917) on microanalysis, there have been continuous efforts to further miniaturize the extraction process of the analyte and to optimize the extraction recovery and preconcentration factor. In the last two decades so-called single-drop microextraction (see e.g. the review of Jain & Verma (2011)) have become very popular for sample preparation of trace organic and inorganic analysis. The principle of this method is shown in figure 1. Here a solute A dissolved in water accumulates in the droplet of water-immiscible liquid B, due its higher solubility in B as compared to in water. After an equilibrium has been achieved, the droplet, which now consists of a mixture of A and B, is extracted with a syringe, in order to be further analysed by, for example, chromatography. Hitherto it has not been possible to calculate *a priori* the extraction recovery and the preconcentration factor. The work by Chu & Prosperetti (2016) now offers opportunities to do so in the future in order to further optimize the microextraction process. Obviously, one then has to go beyond the case of still liquid and include the effect of turbulent mixing of the flow, which will accelerate the transfer of the analyte to the droplet.

The scale on which single-drop microextraction can be done remains limited, but this limitation is overcome in the modern technique of dispersive liquid–liquid microextraction, invented by Rezaee *et al.* (2006) and Rezaee, Yamini & Faraji (2010). Here, a mixture of two miscible liquids B and C (with low concentration
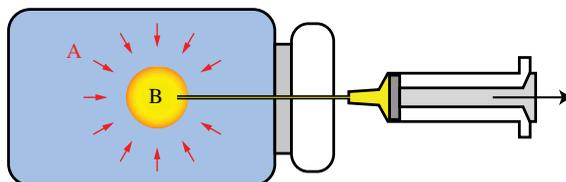
FIGURE 1. Principle of single-drop microextraction: a solute A dissolved in water has higher solubility in the liquid B of the immersed droplet, which has very poor miscibility with water. Once A has accumulated in the drop B, it is extracted with the syringe.

of B) is put into water with the analyte A, with B being immiscible with water, but C being miscible. When poured into water, droplets of B will immediately nucleate. The liquid B is chosen such that the analyte A easily dissolved in it and it is heavier than water and liquid C. The final step is to centrifuge the dispersion and take out the A–B phase. Again, the work by Chu & Prosperetti (2016) offers an approach towards a quantitative understanding of the fluid dynamics of such liquid–liquid microextraction processes, in the spirit of the famous book by Levich (1962).

Acknowledgements

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