Unstable Interfaces

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Reaction-Driven Mixing and Dispersion

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The efficiency of mixing between miscible fluids is controlled by the area of the fluid/fluid interface through which molecular diffusion takes place.[1] Usually, this interfacial area can be greatly enhanced by mechanical blending and/or turbulence, which create "swirling" flows on multiple length scales. When, however, these effects are absent—as in static, "layered" fluids or in microfluidic devices—mixing can become problematic.[2] Recent research[3] by De Wit and co-workers at the Université Libre in Brussels suggests that in such cases, chemical reactions can create hydrodynamic instabilities that deform the interface and can ultimately facilitate mixing through the increased interfacial area.

The Brussels team studied a simple arrangement in which liquid A is layered on top of a miscible liquid B. If the liquid densities and diffusion coefficients are the same ($\rho_A = \rho_B$, $D_A = D_B$), the initially planar liquid/liquid interface remains stable, and the only mixing that occurs is through slow diffusion. This situation, however, is predicted to change dramatically if the liquids engage in a chemical reaction that yields a product C whose physical properties differ from those of either A or B. For example, if C is heavier than the reactants, its production at the AB interface is predicted to give rise to long, narrow "fingers" of C that fall downwards from the reaction zone into lighter B, while convection pushes the reaction front upwards (Figure 1 a). The interface can also become unstable as a result of differences in the diffusivities (i.e., $D_C \neq D_{A,B}$). In such cases (Figure 1 b), "fingers" are expected to form both downwards (between B and C) and upwards (between A and C). The authors back up these theoretical predictions with experiments in which instabilities and fingering patterns are induced by a neutralization reaction between layered aqueous solutions of HCl and NaOH.

Why and how does the initially flat interface break into irregular "fingers"? The answer lies in the ability of certain nonlinear systems to amplify small-scale instabilities into large-scale disturbances. In our particular example, the instabilities are of the Rayleigh–Taylor type[4] and arise from an interplay between the production of C and the convection-driven fluid flows. Specifically, as a result of inherent concentration fluctuations, the initially flat interface has regions in which more C is produced than at other locations. In the case when ρ_C is greater than ρ_B, the initially produced, heavier C forms a small "dimple" into the lighter B; in doing so, it displaces the lighter B and initiates its convective flow upwards. Importantly, this process increases the area of the deformed interface such that even more A and B can come into contact and react to produce C and further strengthen dimple formation and convection. As the cycle repeats, the initial, small-scale instability, instead of dying out, amplifies and grows into a large fingering pattern that ultimately facilitates mixing of the stratified fluids.

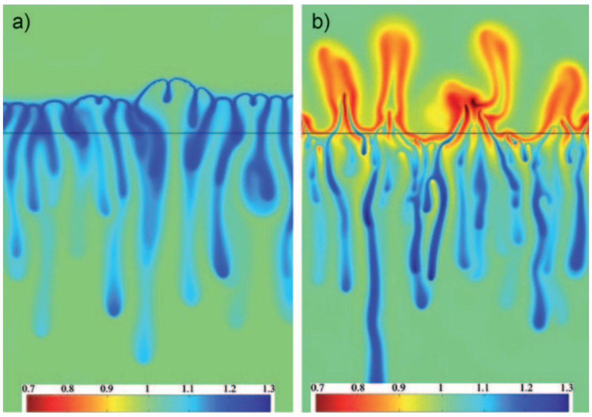

Figure 1. Theoretical two-dimensional density fields of two miscible reactive fluids. Initially, the fluids are neatly layered, and the interface between them is flat (black horizontal lines). When, however, a chemical reaction A + B → C takes place, the interface becomes unstable: a) the "fingers" of C fall into lighter B, or b) when the diffusivities differ, the fingers propagate into both A and B. In both cases, the reaction increases the interfacial area and facilitates mixing. Reproduced from Ref. [3], copyright 2010 American Physical Society.

The drawback of the layered-liquid system is that the instabilities require the presence of gravity to drive convective flows. This requirement makes the mechanism described by the De Wit group not applicable to the mixing in, for example, microfluidic devices, in which inertial and gravitational effects are negligible. Fortunately, other types of reaction-induced instabilities can be construed that are capable of increasing interfacial area and accelerating the mixing, or at least dispersion, of one fluid phase into another.

In this context, biphasic systems, in which an interfacial reaction changes the surface tension, are particularly inter-

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esting (Figure 2).[5] As an example, let us consider a macroscopic droplet of an organic solvent containing an ionizable surfactant (e.g., a long-chain carboxylic acid) and immersed in an immiscible (or poorly miscible) fluid under basic conditions (Figure 2a). In their protonated state, the surfactant molecules prefer to remain buried in the organic phase; when, however, surrounded by an alkaline solution, they migrate onto the droplet surface, where the head groups are deprotonated and face the aqueous phase. Initially, the interface can accommodate all candidates for deprotonation. It does so by deforming the droplet into an oblong "blob" with a larger surface. This stretching, however, cannot continue indefinitely. The elongated droplet becomes unstable, and its tendency to minimize surface area finally prevails. Instead of deforming further, the drop experiences so-called Plateau–Rayleigh instability and divides. The "race for the interface" then starts all over again in the smaller drops, which then divide into even smaller progenies. Within several cycles of these divisions, the macroscopic drop divides all the way into a microscopic emulsion. Similar to the formation of the fingering patterns, droplet division is driven by the chemical reaction at the interface. If the reaction is absent, no instabilities will form, and an organic phase will never spontaneously divide. Long live interfacial reactions!

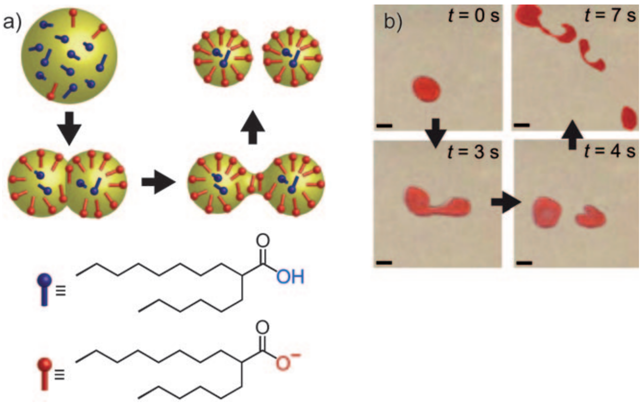

Figure 2. a) Schematic illustration of an example of self-dividing droplets. b) Self-dividing droplets of CH_2Cl_2 containing 2-hexyldecanoic acid and immersed in an aqueous solution of KOH at pH 12 (scale bars: 2.5 mm). Calco Oil Red dye was used for visualization.[6]

Of course, interfacial instabilities are not without their limitations. In the context of mixing, the relevant questions are how rapidly and to how small a length scale the instabilities can mix or disperse the fluids. In the system described by De Wit and co-workers, the characteristic length scale on which the "fingers" form is millimeters. This length scale is probably too large for industrial applications, for which "turbulent" mixing for high Reynolds number flows and chaotic mixing[1] at low Reynolds numbers would induce better homogeneity. In the case of dividing droplets, the ultimate length scale can be much smaller. Here, the final droplet size is dictated by the competition between the favorable free energy of presenting as many charged/deprotonated head groups towards the aqueous phase and the unfavorable energies associated with 1) the electrostatic repulsions between the head groups and 2) interface curvature (increasingly important as the droplets become smaller). While the smaller droplets reported to date[5] are in the micrometer-size regime, our recent experiments[6a] and calculations[6b] indicate that the division process could be favorable until droplets reach diameters of tens of nanometers.

Although these results are promising, the ultimate mixing challenge is to design systems in which chemical reactions could facilitate mixing at even smaller, molecular scales, at which the continuum fluid approximation breaks down. There exist some experimental examples of such mixing in polymer blends,[7] in which reactions between individual chains control the domain size and translate into desired bulk-material properties. Another approach relies on the use of classical methods of chaotic advection to organize initially large components of polymer melts into nanoscale structures, the molecular interactions of which can induce further transitions.[8]

On scales approaching molecular, polymers and, more generally, viscoelastic (non-Newtonian) fluids containing flexible fibers appear more prone to form instabilities than simple Newtonian fluids, since stretched or bent fibers can store large amounts of conformational energy (in comparison to the amount stored by small molecules). Indeed, it has recently been shown that buckling instabilities of fiber suspensions can modulate molecular transport.[9] In these experiments, stretch–coil instabilities/transitions associated with the straining of a polymer suspension near stagnation points (i.e., points where the fluid velocity is zero) buckle the initially elongated filaments and build up elastic stresses, which are then released as the polymer fibers move away from the stagnation loci. Stagnation points that exist in more complex, background (non-Newtonian) flows can produce attractive singular-stress distributions and promote strong small-scale mixing.[9b] Similarly, the so-called orientational instabilities in active suspensions (i.e., suspensions whose microstructure changes shape or exerts stresses on the surrounding fluid as a result of internal forces) were shown to generate strongly mixing, random flows.[10]

Our understanding of these fascinating microscale phenomena remains rather fragmentary, and there is a need for more experimental work as well as detailed, atomistic-level simulations. Given the complexity of the nonlinear phenomena involved, it is likely that further progress in this area will require chemists to collaborate with physicists and fluid mechanicians. Such cross-disciplinary research could pay handsome dividends in the form of new, apparently effortless and "clean" (i.e., without the production of reaction byproducts) mixing modalities, whereby fluids would mix rapidly and thoroughly without the need for mechanical agitation but by the power of chemical reactions alone. How about "reactive sugar" that would mix your afternoon tea by itself?

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