

COLLOIDS

A useful boundary

Soft solids consisting of two bicontinuous, immiscible solvents separated by a tortuous membrane of small solid particles have been predicted as novel reaction media. Experimental demonstration of these materials is possible by careful treatment of the particles' surfaces.

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An interface between two immiscible fluids (such as the surface of a water droplet or an air bubble in oil) offers an ideal platform for making useful membranes composed of small particles that will preferentially assemble there. These particles can then be crosslinked^{1–3} and the resulting layer transferred to another solvent, leaving 'armoured' air bubbles^{4,5} or semipermeable membranes that could encapsulate and release cellular or macromolecular cargo in a controlled fashion. On page 966 of this issue, Herzig *et al.* show that this approach can lead to membranes composed of tiny particles arranged in an altogether different topology⁶. Their materials contain two distinct and immiscible fluid phases that are separated by a solid, permeable membrane — and yet, unlike standard emulsions, both fluids are continuous throughout the sample (Fig. 1). In this remarkable material, the oil and water phases could each flow from one edge of the sample to another, in any direction, and share an enormous area of exposure to one another.

A simple experiment with droplets (for example by shaking a simple vinaigrette) readily shows that creating a bicontinuous shape with an enormous interfacial area requires some trickery. Here is the elegant method used by Herzig and colleagues: building on earlier computer simulations^{7,8}, they developed a system in which this bicontinuous membrane appeared spontaneously, without shear or other energy input. To see how this arises, consider first a vial of water with a small quantity of oil: after shaking, one finds small oil droplets suspended in the water; shortly thereafter the droplets coalesce. Similarly, shaking a vial full of oil with a small quantity of water leads — briefly — to water droplets. What happens with comparable amounts of

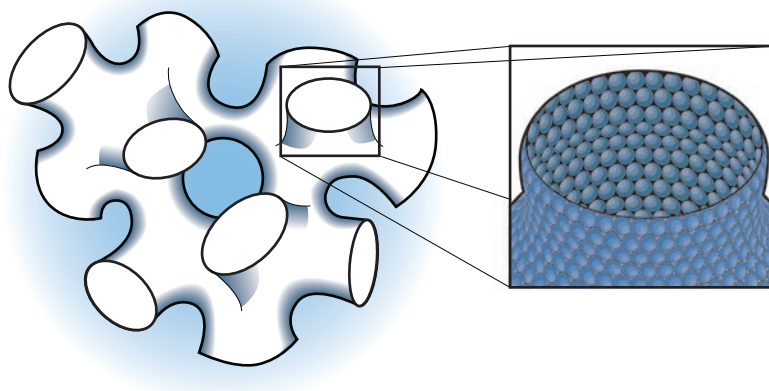


Figure 1 Illustration of a bicontinuous structure. This remarkable sponge-like structure allows each of the two separate fluids to flow in a continuously connected volume of space. This interface costs energy, however, and normally shrinks away rapidly. In the work described here^{6,7}, the interface is spontaneously coated with a single layer of small spheres, which jam into a solid membrane as the interface shrinks. At this stage, reactants could be flowed into the two phases and allowed to interact at the surface, or the solvents could be exchanged with miscible ones to allow the diffusion of small objects through interstices in the membrane.

the two fluids? For a range of temperatures and compositions, phase separation can proceed not by droplets of one phase appearing inside the other, but rather by the rapid appearance of an amorphous, convoluted interface separating the two phases. This process, known as spinodal decomposition, typically requires a very rapid change of temperature but is more accessible near the critical point, where the two phases have the same composition (Fig. 2). Over time, the interfacial tension forces the interfacial area to shrink and become flat, and the two phases macroscopically separate from one another.

Now the challenge shifts to freezing the convoluted interface structure before it ages and the tortuous boundary is lost. The solution is to add a small concentration of suitably prepared particles to the starting liquid. These particles tend to assemble at the interface as it is created during the initial stage of spinodal decomposition. As the interfacial area decreases with ageing, this layer of particles is compressed. Once

the particles pack the entire interface, they jam and form a rigid membrane — no crosslinking is needed. Herzig *et al.* showed that the jammed layer remains stable, provided that the particles have nearly equal preference for residing in either fluid; if they prefer one solvent, then a preferred curvature can lead to insufficient coverage or perhaps to droplets. The authors achieve suitable modification of the particles' surfaces, halting further evolution of the structure by the jammed layer for at least several months. Assuming that no particles remain in free suspension, the area of this membrane is on the order of 4,000 cm² per cm³ of sample; this is equivalent to the area of a tablecloth squeezed into the volume of a teaspoon. Clearly the interfacial self-assembly toolkit has been expanded to include the formation of structures that appear spontaneously but are then trapped on demand in an unstable state far from equilibrium.

Future work could take these results in several directions. The experiments described

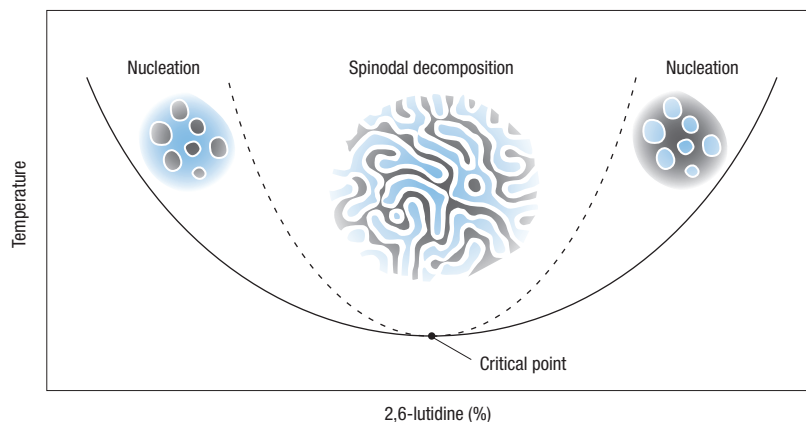


Figure 2 Schematic phase diagram for a mixture of two fluids. On heating a mixture of water and 2,6-lutidine, two phases with different concentrations appear, separated by a distinct interface. Blue: water-rich phase; grey: 2,6-lutidine-rich phase. The pathway of this process is typically one of two types. Either droplets of one phase grow in the other phase, which is continuous throughout the sample, or spinodal decomposition occurs, in which both phases form symmetric structures and both are continuous throughout the sample. In both pathways, ageing occurs as the interfacial area is reduced — unless particles are trapped at the interface and are then jammed together.

by Herzig *et al.* use 0.58- μm -diameter spheres of silica, but a key advantage of interfacial assembly is that only the surface properties of the particles matter. Herein lies a key distinction from bicontinuous phases that form in equilibrium mixtures of liquid with a molecular surfactant: in the latter case the separating membrane is fluid and its properties cannot readily be altered. When using particles as the interfacial agent, however, only their surface chemistry matters and the cores can be composed of (for instance) metal,

semiconductor or polymer; they could have a catalytic function or they might respond to magnetic fields, temperature or chemical changes. The particles could perhaps be nanometre-sized⁹ or micrometre-sized, allowing precise tuning of the size of the interstitial pores between the assembled particles. Moreover, polymers could be used¹⁰ instead of simple liquids, and added nanoparticles might stabilize a bicontinuous structure that could be solidified and selectively etched. In contrast, if the two fluids were replaced with miscible

ones², then the membrane might serve as a size-selective filter with enormous area. Miscible fluids have no interfacial tension, so this step would first require that the particles become permanently attached to one another, either covalently³ or by means of surprisingly strong van der Waals interactions between ligands¹¹. Finally, on the basis of their computer simulations, Stratford *et al.*⁷ proposed that the bicontinuous material might be ideal for micro-reactors that expose oil-soluble and water-soluble reactants to one another over a large area while allowing reactants and products to flow in and out.

Mixing fluids and suspended particles might seem an uncontrolled approach to a designed structure, but experiments are showing that, with careful attention to interfacial and colloid chemistry, the process can lead to exquisite control of features at small and large scales simultaneously.

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SEMICONDUCTORS

A new class of metamaterials

Conventional metamaterials that show negative refraction suffer from high intrinsic losses and are difficult to fabricate. A novel anisotropic semiconducting metamaterial offers a solution.

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The significant and varied interactions of materials and light enable the construction of technologically relevant devices — from computers to mobile phones, from televisions to MP3

players — which no doubt have shaped the modern world. Although there has been significant progress in harvesting light–matter interactions within the past hundred years or so, scientists were recently surprised to learn that the range of response from natural materials represents only a small fraction of what is theoretically possible, because artificially structured composites can extend material response to create materials with unparalleled

properties. On page 946 of this issue, Anthony Hoffman and colleagues introduce a new material that facilitates further advances in electromagnetism¹. They report the development of a semiconductor-based material, which exhibits all-angle negative refraction, thus adding to available materials for the construction of novel devices.

This work builds on exciting developments in a field — called