

two ferromagnetic layers. In the present case, this is the ferroelectric BaTiO<sub>3</sub> sandwiched between magnetic Fe and La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> layers. Indeed, theoretical calculations<sup>6</sup> have predicted the possibility of significant changes in the interfacial magnetization and spin polarization in a ferromagnet in response to the ferroelectric polarization state across the interface. Thus, the interplay between the non-volatile polarization states of the ferroelectric and its influence on the spin polarization can lead to unusual tunnelling characteristics. This is the focus of the paper by Garcia and co-workers. Using a combination of epitaxial synthesis, scanned probe imaging and high-resolution electron microscopy, they have demonstrated a large tunnelling magnetoresistance that is sensitive to the polarization state of the ferroelectric. The fundamental origin of this large effect arises from the asymmetric screening of the polarization at the two interfaces, albeit at a low temperature of 4.2 K.

So, what are the implications of this approach? It is now becoming increasingly clear that ferromagnetism, and thus spin polarization, can be controlled and manipulated through a coupling

of a magnetic layer to a ferroelectric or a multiferroic. Thus, more than one possible pathway to control magnetism with an electric field exists. Clearly, room-temperature operation is a critical step, although it is probable that that issue will be solved in the near future. However, an aspect that clearly emerges from this work, as well as from previous studies involving the manganites, is the observation that they are not the ideal candidates for room-temperature devices as the transfer of spin polarization at the interface invariably is corrupted. Thus, the discovery of alternative ferromagnets would be a fruitful future research direction to pursue. If using epitaxial oxide heterostructures is a possible pathway, the possibility of using the orbital degree of freedom in oxides as an active component of their interface interactions can also be a fertile area of research. Some initial results in this direction are already available. The robustness of these interactions, particularly with respect to electric-field cycling, long-term stability and speed of operation are all issues that need to be addressed for real-world devices. Finally, by far the most important issue will probably be this: what

are the device structures and applications that will be enabled by these new observations?

In summary, the paper by Garcia and co-workers has demonstrated, in a convincing way, the great potential of oxide electronics, particularly in the framework of controlling and manipulating spin transport in ferromagnets. Their work presents an exciting approach to this problem and complements what has been shown using multiferroics. It is fair to state that this field is poised for some dramatic scientific and technological breakthroughs in the immediate future. So stay tuned. □

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#### References

1. Awschalom, D. D. & Flatté, M. E. *Nature Phys.* **3**, 153–159 (2007).
2. Parkin, S. S. P., Hayashi, M. & Thomas, L. *Science* **320**, 190–194 (2008).
3. Garcia, V. et al. *Science* **327**, 1106–1110 (2010).
4. Chu, Y. H. et al. *Nature Mater.* **7**, 478–482 (2008).
5. Laukhin, V. et al. *Phys. Rev. Lett.* **97**, 227201 (2006).
6. Zhuravlev, M. Y., Sabirianov, R. F., Jaswal, S. S. & Tsymlal, E. Y. *Phys. Rev. Lett.* **94**, 246802 (2005).

## GELATION

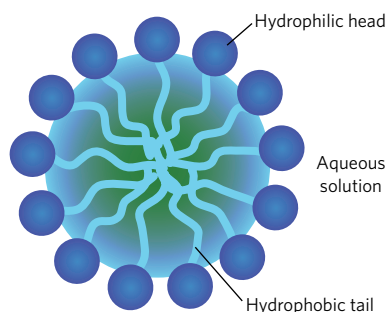
# Grow with the flow

So far, flow-induced transitions and structures formed by the assembly of surfactant micelles have been reversible. Now, a microporous extensional flow process forms a permanent gel, which remains intact even after flow has stopped.

Matteo Pasquali

Soap has been used since the earliest recorded history. However, its active ingredient — surfactant molecules — was not termed as such until the 1950s. Since this time, the science of surfactants has been studied intensely because of fundamental interest and because of their widespread use in high-value applications such as detergents, personal care products, pharmaceuticals and oil recovery. Despite this extensive and productive history, the surfactant molecule still manages to surprise us. Writing in *Nature Materials*, Sureshkumar and co-workers<sup>1</sup> report a new mechanism for the flow-induced formation of irreversible gels in a surfactant system. Their discovery challenges our understanding of the formation and stability of surfactant phases and may have implications in various applications.

Surfactants are molecules composed of water-loving (hydrophilic) and water-hating

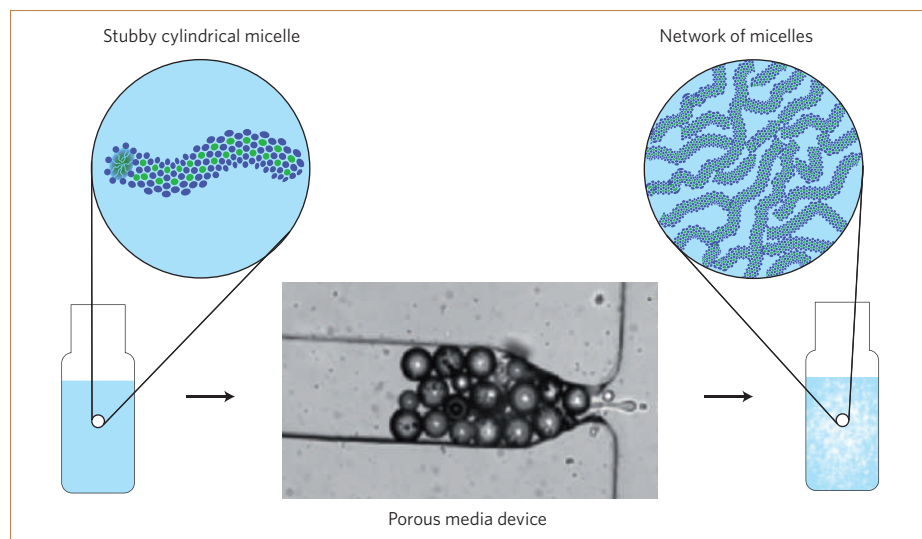


**Figure 1** | A schematic of a spherical micelle of surfactant molecules in aqueous solution. The hydrophobic sections of the surfactant are close to each other and the hydrophilic head groups face outwards into the solution.

(hydrophobic) sections. In water, surfactants aggregate spontaneously to form micelles in which the hydrophobic sections huddle

together (Fig. 1). Micelles are not permanent structures — instead, their constituent molecules are constantly hopping back and forth between the micelles and the surrounding liquid. In water, surfactants exhibit a rich phase behaviour and can arrange into ordered structures forming disordered networks, ordered arrays of cylindrical micelles, lamellar phases, as well as ordered, interconnected networks and bicontinuous phases. These are self-assembled, equilibrium systems, the occurrence of which is controlled by the molecular structure and concentration of the surfactant, as well as temperature and the presence of additives.

It is well established that flow can alter the structure of surfactant phases. The mechanism behind this is partially understood<sup>2</sup> and has been exploited in different applications. For example, rod-like surfactant micelles are effective



**Figure 2** | The formation of a permanent gel, made up of a network of micelles, using a microfluidic porous-medium technique. Left: schematic representation of stubby cylindrical micelles that are present before the flow process. Middle: the formation of a permanent gel in a microfluidic channel filled with microparticles, as observed by light microscopy (image reproduced from ref. 1). Right: schematic representation of a gel network consisting of partially aligned micellar regions.

drag-reducing agents in the pumping of fluids in pipelines<sup>3</sup>. This is because, much like polymers, they reduce the formation of small-scale vortices in turbulent flow<sup>4</sup>. The micelles break under the vigorous flow-induced strain but, unlike polymers, they reform in regions of weaker flow and, therefore, are effective for long operation periods. In this respect, surfactant systems behave like other complex fluids whose dynamic micro- and nanostructure evolves under the action of applied shear. However, until now, all known flow-induced changes in surfactant systems were reversible and lost soon after the cessation of flow — the exception being permanent shear-induced transitions in concentrated liquid-crystalline surfactant systems<sup>5</sup>.

Sureshkumar and co-workers now report the first observation of the flow-induced formation of stable and irreversible gels in a relatively dilute surfactant system (Fig. 2). First, by shearing a dilute surfactant-salt solution in a conventional rheometer (which produces moderately high rates of shearing), Sureshkumar *et al.* observe reversible flow-induced structure formation, in accord with previous reports in the literature<sup>6</sup>. However, when the same surfactant-salt solution flows through a microfluidic channel filled with randomly packed glass beads (Fig. 2, middle), a permanent gel is formed. In each narrow constriction between the glass beads, the solution is strained at rates up to a thousand times higher than those achieved in the rheometer; the straining process is repeated many times as the solution flows

through the porous packed bed before exiting the microfluidic device. It is this sudden and intense straining within the extensional flow system that causes the instantaneous formation of the gel. Even after flow is stopped, the gel remains stable for many months.

Direct imaging by cryo-transmission electron microscopy revealed that the stubby cylindrical micelles present before the flow (Fig. 2, left) had been converted into much longer ones and that these longer micelles had entangled to form a seemingly permanent network (Fig. 2, right); this network moves sluggishly and confers to the fluid high viscosity and elasticity, typical of a gel. Further analysis revealed that the conditions of the experiments closely matched earlier predictions<sup>2</sup> for the critical strain rate needed to fuse rod-like micelles into longer structures.

This report generates an interesting question: is the flow-induced structure a thermodynamic equilibrium state, or is it merely kinetically stable as a consequence of the high viscosity of the gel? Recent studies have shown that the input of energy (in the form of ultraviolet light) in a surfactant system can induce transitions to different equilibrium states by changing the conformation of the surfactant molecules<sup>7</sup>. However, such an effect is improbable in the present system because the transition could be observed in several chemically different surfactant-salt systems.

Strong flow can also induce long-lived non-equilibrium structures. Anyone who

has made vinaigrette knows that it is possible to mix two low-viscosity liquids by mechanical shearing to form a high-viscosity fluid that is stable for hours or months (note that naturally occurring surfactants in mustard or egg yolk are also at work here). This process has been used recently to form highly elastic emulsions of nanoscale droplets<sup>8</sup>. However, in emulsions, elasticity comes from the increased surface area of the small drops that are generated during shearing. In the present study, elasticity comes from larger structures grown during flow. It is surprising that, despite the ongoing exchange of surfactant molecules between the micelles and the surrounding fluid, such structures can survive for many months. Intriguingly, Sureshkumar and colleagues noticed the presence of well-defined interfaces between the gel and solution phases in their microfluidic device. It is not known whether flow-induced concentration changes may have contributed to raising the local surfactant concentration and aided the formation of the micelle network.

This process for making permanent surfactant gels is simple and scalable, making it attractive in the manufacture of nanostructured materials for scaffolds and catalysts, and the delivery of biomolecules into cells. It also raises fundamental questions about the nature of the flow-induced gel state and about the potential synergistic effect of other processes, such as mass transfer or conformational changes in the surfactant molecules.

There is a famous phrase, spoken by British clergyman Bishop Robert Smith (1634–1716), which says wonder is surprise, and surprise stops with experience: this practical and intriguing discovery of an irreversible gel tells us that perhaps this is not true for seemingly simple surfactants. □

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#### References

1. Vasudevan, M. *et al.* *Nature Mater.* **9**, 436–441 (2010).
2. Turner, M. S. & Cates, M. E. *J. Phys. Condens. Matter* **4**, 3719–3741 (1992).
3. Shenoy, A. V. *Colloid Polym. Sci.* **262**, 319–337 (1984).
4. Sureshkumar, R., Beris, A. N. & Handler, R. A. *Phys. Fluids* **9**, 743–755 (1997).
5. Siero, P. & Roux, D. *Phys. Rev. Lett.* **78**, 1496–1499 (1997).
6. Rehage, H., Wunderlich, I. & Hoffman, H. *Prog. Colloid. Polym. Sci.* **72**, 51–59 (1986).
7. Ketner, A. M., Kumar, R., Davies, T. S., Elder, P. W. & Raghavan, S. R. *J. Am. Chem. Soc.* **129**, 1553–1559 (2007).
8. Meleson, K., Graves, S. & Mason, T. G. *Soft Mater.* **2**, 109–123 (2004).