Soft matter in the real world

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tent with a loose network of necklace- or string-like structures. However, micelles could still exist as a very dense tangled mess like a ball of rubber bands, which could not be distinguished in the microscope images.

The gel is thought to be rich in surfactant because it does not have the characteristic pattern left by sublimating water. To transform the solution from dilute to surfactant-rich, the equilibrium structure has been extensively rearranged, which helps to explain the very long relaxation times. Since the gel structure appeared to contain high concentrations of surfactant, Keller and colleagues tried to make new equilibrium structures from concentrated unsheared solutions, but without success. The researchers therefore concluded that flow is a critical factor in gel formation.

These observations raise many questions. Why do dilute systems form gels, whereas the more concentrated systems are shear-thinning? How can such small flow rates induce a gel from a liquid that is mostly water? The exact structure and the interactions that hold the gel together are not yet known.

Electric charge may hold the key to the problem. Both the dramatic increase in micellar length at a certain concentration and the formation of gels only occur in micelles that carry an electric charge, even if it is small. Keller and colleagues estimate that there is one electron per 9–10 surfactant molecules in the solutions they studied. An increase in surfactant concentration also destroys the effect, as does the addition of extra salt, presumably because the excess ions screen the small charge on the micelles.

Niels Grønbech-Jensen and co-workers at University of California at Los Angeles recently showed that the distribution of counter-ions in the solution can actually cause like-charged objects to attract and these calculations are consistent with experiments on solutions of charged rigid polymers. Could a similar mechanism, initiated by the flow, cause the surfactants to assemble into a gel? This confluence of ideas from charged polymer systems, self-assembly and fluid flow has been virtually untouched, and promises to yield exciting new science.

Soft matter in the real world

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As all experimentalists know, man-made materials rarely consist of identical molecules or particles. This variability is nowhere more apparent than in the world of "soft" matter, which includes materials from our everyday life such as colloids, surfactants, liquid crystals, polymers and membranes. Unlike atoms, which are always the same size, the particles in a colloid are all subtly different in size. This is an example of polydispersity, a phenomenon often found in soft matter but never in the more common hard materials, such as metals and semiconductors.

Physicists have recently started to use statistical mechanics to help understand and predict the properties of these exotic "soft" materials. But the complex nature of polydispersity has caused fundamental problems. Now, however, Peter Sollich and Mike Cates at Edinburgh University and Patrick Warren at the Unilever Research Port Sunlight Laboratory in the UK have shown how statistical mechanics can be applied to polydisperse systems (*Phys. Rev. Lett.* 1998 **80** 1365; 1369). Their very general techniques promise to provide fascinating new insights into the whole field of soft matter.

Polydispersity is important because it occurs in a tremendous variety of practical situations. Almost all biological fluids are colloidal suspensions, as are many foodstuffs and commonplace materials such as paints. Surfactants are key constituents of detergents and cosmetics, while polymers have an incredibly rich range of structural, optical and electronic applications.

These materials have been studied for most of this century to help improve industrial processes and products. Their usefulness depends on knowing and manipulating the different phases that can exist. To take a rather mundane example, shampoo consists of a fine dispersion of oil droplets suspended in a concentrated solution of a surfactant. If the concentration of surfactant is increased, the oil droplets will separate from the surfactant. For a shampoo to be acceptable this must not happen – no-one will pay for a separated mixture of oil and water.

Temperature and density are standard variables that influence the formation of different phases. In a polydisperse system, the phases also have a certain size distribution, which must be treated as another variable. To calculate the stability of the various phases in a polydisperse system, physicists turn to statistical mechanics – a method for determining the macroscopic behaviour of a system by applying statistical laws to the behaviour of the component particles. The most obvious way to look at a polydisperse material is to treat each size of particle as a separate species. It is then relatively straightforward to calculate the phase equilibria.

In the conventional description of a polydisperse system the phase behaviour depends on the density of the component particles. The standard method for finding phase equilibria is to represent the Gibb's free energy of the system as a surface in a multi-dimensional space, with one dimension for each species. When two phases coexist, the particles are distributed among the phases so that the total free energy of the system is minimized. This condition can be determined by constructing a plane that is tangential to the free-energy surface at more than one point.

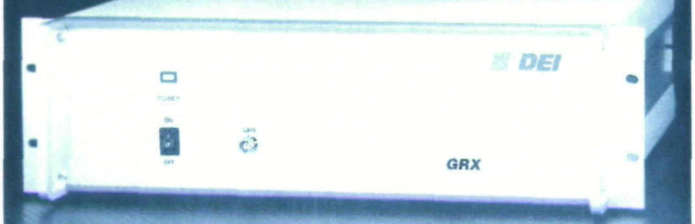
Although the principle is simple, the sheer number of components in a polydisperse system creates difficulties. Micellar solutions contain 10^2 or so different-sized components, but the number reaches 10^5 in polymer solutions, and for colloids the number of components is infinite. Faced with such numbers the standard method is at best cumbersome and is usually totally unmanageable. It is not surprising, therefore, that polydispersity has frequently been ignored.

Sollich, Cates and Warren realized that the problem could be reformulated in a much simpler way that makes it possible to ignore certain combinations of the density variables, and hence reduce the number of variables in the problem. They did this by splitting the free energy of the polydisperse system into a term based on the free energy of an ideal gas and a term for the excess free energy. The excess free energy can be obtained from a suitable statistical model, such as mean-field theory. For polydisperse hard spheres, for example, the excess free energy should depend only on the first four "moments", which are linear combinations of the density variables. Hence the excess free energy no longer depends explicitly on the polydisperse distribution.

The researchers argue that the variables should be the small set of moments that appear in the excess free energy, rather than a large or infinite number of densities. There is still a difficulty with the ideal-gas term, however, as this does depend explicitly on the polydisperse distribution, and prevents the calculation from being transformed into moment variables.

However, the ideal-gas term can be transformed by selecting only the contributions that depend on a selected set of moments. To do this, a shape for the distribution must be chosen. But there are an infinite number of possible distributions that have the same values for the selected set of moments. Sollich, Cates and Warren suggest that the natural choice is the distribution that maximizes the ideal-gas entropy, considerably reducing the complexity of the problem.

The power of this approach is that the accuracy of the calculated phase diagram can be improved systematically by including a greater number of moment variables in the calculation. This will allow many properties of interest to be calculated for a range of polydisperse systems and promises to offer new insights into this important group of materials. The hope is that the new technique will bridge the gap between the simple robust models of soft condensed matter and the real world.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