NANOSCALE SCIENCE

Complex rules for soft systems

The nanometre scale is a brave new world for scientists — mixing materials at such small dimensions can cause all sorts of surprising effects. New studies of experimental systems on the nanoscale further our understanding of these complex phenomena.

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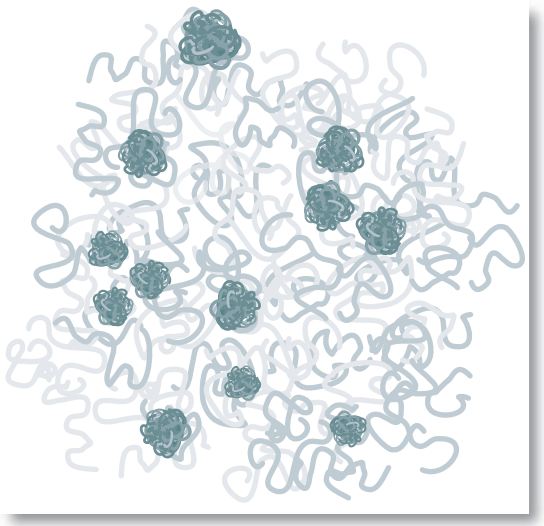

Figure 1 **Nanometre-sized particles can 'fluidize' a melt comprised of similar-sized polymer molecules. The addition of these particles reduces the melts' viscosity and T_g, contrary to what typically occurs for much larger particles.**

Nature is full of surprises when we look at the behaviour of materials whose characteristic size and interactions are on the scale of nanometres. At these length scales (slightly larger than the size of molecules), standard physical principles, which have worked well for so long to predict the behaviour of traditional materials, can fail miserably, sometimes predicting precisely the opposite of what is observed.

On page 762 of this issue, Mackay and co-workers[1] provide a remarkable example of the breakdown of a classic theory of bulk fluid behaviour due, apparently, to nanoscale effects. Early in the last century, Einstein predicted that a fluid's viscosity should increase with the addition of hard particles undergoing Brownian, or random, motion in the fluid[2]. Indeed, this famous prediction from 1906 has been borne out time and again in experiments on particles in the micrometer size range and above, even in fluids as complex as polymer melts. In this size regime, particles 'see' an essentially homogeneous continuum, and the main effect of the molecules comprising the surrounding medium is to bombard the suspended particles randomly from all sides, resulting in Brownian diffusion. But, when the particles are so small as to be similar in size to the molecules making up the surrounding medium all bets are off, because many of the basic assumptions underlying Einstein's theory no longer hold.

To test this effect, Mackay and colleagues synthesized nanoscopic polystyrene particles by crosslinking linear polystyrene chains into spheres. They mixed these particles into a polymer melt (Fig. 1) comprised of the same linear polystyrene molecules with a 'diameter' (radius of gyration) just slightly larger (7–15 nm) than the nanoparticles themselves. The addition of these particles lowers both the viscosity and the glass-transition temperature T_g of the mixture, opposite to what is observed with larger particles, and contrary to Einstein's prediction. This occurs for dilute systems where the volume fraction of nanoparticles is small, as well as for systems with a concentration of nanoparticles so high that the average interparticle distance is only one nanometre, a distance sufficiently short to cause great distortions in the individual molecules of the surrounding polymer. Through a series of experiments, the authors rule out density inhomogeneities within the matrix, nanoparticle clumping and other possible reasons for the observed behaviour. They conclude that the small size of the nanoparticles, and the small spacing between nanoparticles (in the concentrated case), relative to the size of the surrounding polymers, is solely responsible for the observed viscosity and T_g decrease.

A full theoretical understanding of the mechanism causing the viscosity and T_g decrease is not yet in hand. The findings of Mackay *et al.* agree with earlier predictions by computer simulations, which showed that nanoparticles dispersed dilutely in a polymer matrix with which they interact only weakly can reduce the relaxation time and T_g of the matrix by speeding up the chain dynamics in the immediate vicinity of the nanoparticle surface[3]. This is consistent with an increase in free volume available to the chains[4], as rationalized by Mackay and co-workers[1]. Mackay's results are also consistent with previous observations of T_g reductions in ultrathin polymer films. When confined to thicknesses below 100 nm, relaxation times and T_gs in polymer films can decrease substantially, a challenging and important problem whose solution is still hotly debated[5]. Mobility fluctuations in bulk polymers occurring on the scale of 3–10 nm near T_g even in the absence of nanoscale density fluctuations[6–9], are known to contribute to the breakdown of classical relations between diffusion and viscosity of probe molecules[9].

This phenomenon may also play a role in the system studied by Mackay's group. Recently, breakdown of classical transport relations has also been observed in colloidal suspensions with particles larger than 100 nm, much larger than the polymers in the surrounding matrix, and it is thought to be due to matrix inhomogeneities[10].

These studies demonstrate the interesting phenomena that can arise at the nanoscale as a result of the confluence of molecular and macroscale physics. In the study by Mackay *et al.*, for example, because the nanoparticles and matrix have the same chemical composition, the only difference between them is entropic, arising from the reduced number of conformations available to the crosslinked polymers in the particles, compared with the conformational freedom of the matrix. Moreover, the polymer and particle are roughly the same size. This size similarity is very different from so-called plasticizers — molecules considerably smaller than the polymer molecules, which intersperse within the matrix on molecular scales to lower its T_g. At the opposite end of the spectrum are traditional composites and particulate suspensions, in which the particles are large and components mix only on micrometre and larger scales, and where viscosity generally increases on addition of particles. The experimental system of Mackay and co-workers has made it possible to work somewhere in between these two extremes, due to the similar size of particle and polymer.

The work by Mackay and colleagues is but one of many to highlight the fascinating science that can occur in soft materials and complex fluids in the nanometre realm. The new-found ability of scientists and engineers to manipulate matter on the nanoscale also creates opportunities for fabricating structures and novel materials with no counterpart on macroscopic scales. Novel structures are possible because of a delicate interplay between thermodynamic immiscibility, geometric and topological constraints, and highly specific interactions only possible at nanometre scales[11]. In these cases, like in the work of Mackay *et al.*, the ways in which the laws of nature conspire to produce new science and new technological opportunities present exciting challenges to experimentalists and theoreticians alike.

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MATERIAL WITNESS

Freedom to build

In what style should we build? Now that architecture claims to have broken free of rule books, this question is more urgent than ever. Architects such as Charles Jencks, Frank Gehry and Daniel Libeskind have found one answer in a startling asymmetry, which Jencks justifies with reference to the physics of phase transitions and symmetry breaking.

It is popular to explain the liberty that architects now enjoy by invoking cultural trends, particularly the post-modernist determination to avoid prescriptive dogmas. But the dramatic, sometimes unearthly edifices that have appeared in the past decade, such as Gehry's Guggenheim Museum in Bilbao and Libeskind's Jewish Museum in Berlin, are made possible largely by technological advances.

Thanks to these changes, just about anything seems possible. No longer do walls have to be flat, rectilinear or assembled from identical small units. Buildings may have not doors and windows but simply 'orifices'. Rather than being most substantial at their base, towers can balloon outwards as they rise up, like the inverted bell figures of marine tunicates. Such freedom might seem a gift to architects, but it can also be artistically paralysing: invention is rendered motherless.

Computerization of the design and the manufacturing processes has been responsible for much of the expansion in architectural possibilities. But equally significant is the advent of new materials and methods of processing them. Lightweight plastic film can clad buildings in a skin lighter than the air they contain. Self-cleaning glass enables vast or inaccessible areas to be glazed without worrying about maintenance.

Not all of this new architecture is rootless, however. The plastic domes of the Eden Project, an ecology centre and botanical park in Cornwall, England, throw a nod towards two great pioneers of radical architectural design: Buckminster Fuller and Frei Otto. Otto based many of his designs on the shapes of soap films and bubbles, and his tent-like plexiglass roof for the Munich Olympic stadium in 1972 established a curved, airy, 'organic' architectural language that has been reworked on countless occasions — notably in Norman Foster's roof for the Great Court of the British Museum.

Otto's work, and the influence of new materials, lurk in the background of an exhibition entitled Zoomorphic at London's V&A Museum, which explores the use of animal motifs in architecture. The title is interpreted loosely, encompassing anything from Gehry's explicitly fish-shaped Fishdance restaurant in Kobe, Japan, to buildings based on 'animal architecture' such as nests (a topic explored by ethologist and Nobel laureate Karl von Frisch) or ones that simply display suggestive, 'organic' curves.

One such is the Weald and Downland Museum's Jerwood Gridshell in West Sussex, England. This is basically a wooden barn, acting as a storehouse and conservation workshop. But the undulating body evokes a living form, and its fabric shows the versatility of some traditional materials: the skeleton is a lattice of local oak beams, shaped and moulded while still 'green'. In other words, not all eye-catching new architecture has to be post-modernist or use fancy new materials.

Philip Ball