Stöber system. These primary particles are essentially the result of polymerization to form cross-linked silica gel particles. The 0.5-μm spheres are the result of aggregation of the primary particles rather than growth by molecular addition. Zukoski et al. produce a model that predicts narrow particle size distributions as a result of this aggregation.

Although electron microscopy does show primary particles, there is the possibility of these being artefacts of the drying process. Cryoelectron microscopy shows that the primary particles in the Stöber
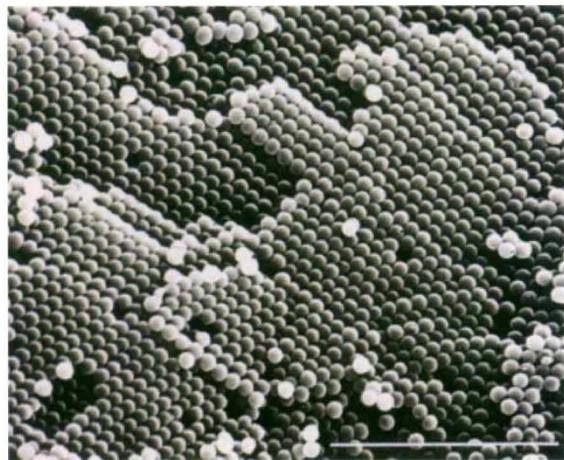
Submicrometre silica spheres formed by the Stöber process. Scale bar, 10 μm. (Courtesy of M. Jiang, Fudan University.)

system are not dense but loose polymeric structures[5]. A similar titania-forming system does however show small dense particles.

In support of aggregation, electron microscopy also shows a fine-scale substructure within many of the varied types of particles. For instance, rod-shaped particles can be seen to be made up of little rods. Zukoski et al. point out that this ordering of nanometre-sized particles is similar to the crystallization of globular proteins. Also disturbing, from the viewpoint of the LaMer model, is Matijevic's remark that spherical particles can be found with strong crystalline X-ray patterns, although this could be explained by crystallization subsequent to the particle formation. He also observes that nucleation can continue after the initial stages of the reaction, which is contrary to LaMer's model.

van Baaderen, van Geest and Vrij from the University of Utrecht[6] disagree. They measured the growth of Stöber silica on seed particles with a bimodal size distribution, derived from two separate precipitations. By following the change in the ratio of the two radii, they showed that the radial growth rate is independent of radius; this, they argue, is consistent with growth being limited by the rate of hydrolysis of tetraethoxysilane and not with aggregation. An induction time for precipitation is observed because time is needed to build up a sufficient concentra-

tion of hydrolysed species before condensation occurs on the surface of the seed. Also, addition of dissolved electrolytes would be expected to enhance an aggregation process by reducing the range of coulombic repulsions between charged particles, but no such effect is seen.

A new paper swings the pendulum back to aggregation. Briois et al.[7] have used small-angle X-ray scattering and EXAFS (extended X-ray absorption fine structure) to study the precipitation of cerium oxysulphate from heated cerium sulphate solutions, a system that others have used to make monodisperse particles. During the heating stage, they see particles form and stabilize as 1.8-nm monodisperse spheres. Several hours later, this suspension starts to precipitate larger particles. The fact that a monodisperse colloid forms, stabilizes and then starts to grow again, suggests that the governing process is one of aggregation rather than reaction. As the paper describing this second stage is in preparation, we must wait for the other shoe to drop.

The charm of the LaMer model is that the source of the narrow size distribution is quite clear. In the aggregation models there is no such simple clarity in the source of monodispersity. The other standard system that produces monodisperse particles is emulsion polymerization, which is the source of the latex particles that are used to calibrate electron microscopes. A burst of free radicals initiates polymer chains which grow until all the monomer is consumed. As each chain grows within a surfactant micelle, they are kept separate and each particle should be a single polymer chain. There have been attempts to draw parallels with Stöber silica, but they are not yet convincing.

Different systems seem to show quite different behaviour. There should be a single explanation for why monodisperse particles are formed but there is evidence against each available model. For the moment this is a case of the more you know, the less you understand. □

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---DAEDALUS---

Flowing free

SHIPS ploughing through the ocean, hydraulic pumps, oil-lubricated bearings — all have to overcome boundary-layer friction. The liquid next to a solid surface sticks on that surface; liquid further away can only move by viscous shear against this boundary layer. Daedalus now has a way out.

He points out that the spherical C_{60} molecules of buckminsterfullerene rotate freely in their crystal lattice. It was once thought that the resulting molecular ball-bearing surface should be utterly frictionless. Not so: solid surfaces are far too rough for such tiny ball bearings to run on them. But a liquid surface is much more hopeful. Imagine, for example, a ship coated with buckminsterfullerene. The freely rotating molecules will be spun up by the drag of the water flowing past them. They cannot quite spin freely, for their rotation is quantized. But their range of accessible rotation rates includes peripheral velocities of the order of a few metres per second: just right for marine transport. So a fullerene-coated ship should slip through the water on molecular ball bearings. It would forge frictionlessly ahead, while its micro-spinning solid surface would in effect remain stationary with respect to the water. Viscous drag would vanish.

This elegant idea is annoyingly sabotaged by the slow oxidation of fullerenes in air. Daedalus argues that partially hydrogenated or fluorinated derivatives should be more stable, and would still show free rotation. Indeed, chemically modified fullerenes suggest an even more cunning scheme. Suppose a spherical fulleroid molecule was mounted on some sort of 'axle', so that it could spin only in one plane. The ideal molecule would be a linear poly-fullerene whose spherical moieties were joined together like free-spinning beads on a string. Such a long-chain polymer could easily be molecularly aligned by spreading it over a flat surface. The coated surface would then have a unique 'easy direction' for fluid flow — the free-spinning direction of the fullerene moieties. The coating would enforce linear streamline flow in one defined direction. Flow in any other direction, including random turbulence, would be damped by viscous drag.

In paint form, the new polymer will gladden the hearts of ship designers, chemical engineers and everyone else concerned with fluid flow. Properly applied, it will eliminate the twin curses of viscous drag and turbulence from pumps, pipes, ships and bearings. Vast amounts of energy, now wasted uselessly in stirring and shearing liquids, will be saved.   David Jones