

poloidal magnetic fields (which are oriented in meridional planes and brought downward by the convection) into gradually intensifying toroidal fields. As a result of the stable density stratification in the tachocline, the toroidal fields can reside in the tachocline for some time before magnetic buoyancy and other instabilities disrupt these flux concentrations and drag them upward until they ultimately emerge as loops at the surface. The weaker poloidal field is thought to be regenerated either in the convection zone through cyclonic turbulence or near the surface through the breakup of twisted active regions. The turbulent convection will pump the poloidal field back into the tachocline to continue the overall process of large-scale field generation.

Recent mean-field dynamo models (10, 11) have shown that an interface dynamo, in which the toroidal and poloidal fields are generated in

separate regions, can produce field strengths similar to those inferred from observations. Advances in massively parallel supercomputing are gradually allowing more realistic three-dimensional simulations of the essential components of the global dynamo. Detailed models are emerging for how turbulent convection in spherical shells redistributes angular momentum to yield a pronounced differential rotation (12), and how magnetic fields can be pumped downward by the strong downflow networks inherent in compressible convection (13).

The continued interplay between helioseismic observations and theoretical modeling will be crucial for gaining a detailed understanding of the Sun's magnetic cycles. The helioseismic discovery of the tachocline has forced profound changes in solar dynamo models. The temporal variations revealed by the new generation of helioseismic instruments are now showing that large-

scale ordered and evolving flows accompany the magnetic changes (1, 6, 7). There are likely to be other surprises as such probing continues throughout a solar cycle.

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PERSPECTIVES: COLLOIDAL SYSTEMS

Playing Tricks with Designer "Atoms"

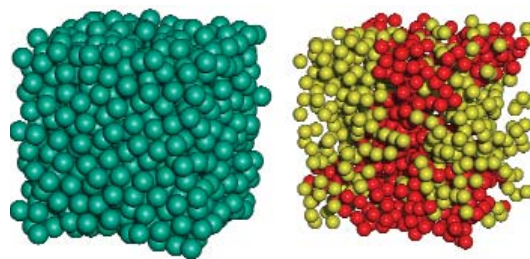
Daan Frenkel

Tailor-made, submicrometer particles will be the building blocks of a new generation of nanostructured materials with unique physical properties. Two articles in this issue on pages 106 and 104 (1, 2) show how the macroscopic physical properties of colloidal suspensions—solutions of particles with diameters ranging from tens of nanometers to micrometers—can be influenced dramatically by tuning the interactions between their building blocks. This work is not only important for materials science. It also allows us to address some longstanding fundamental questions about the nature of liquids, crystals, and glasses.

Just over a century ago, J. H. van't Hoff received the first Nobel prize in Chemistry for his groundbreaking work on osmotic pressure. He had found that the osmotic pressure of dilute solutions depends on the concentration of dissolved molecules, in the same way that the pressure of a gas depends on the concentration of gas molecules. Subsequent theoretical work by Onsager (3, 4) and others showed that the analogy that van't Hoff had noted for dilute solutions is valid at arbitrary densities. This implies that, just as atomic gases may condense at high pressures to form a liquid and eventually a solid, macromolecules in solution may undergo a transi-

tion to a "liquid" or "crystalline" solution state at sufficiently high osmotic pressure.

This phenomenon is often observed in colloidal suspensions. Although colloidal particles are much larger than atoms (a micrometer-sized colloid may contain billions of atoms), they nevertheless exhibit the same phases as, say, argon: vapor, liquid, and crystal. Like simple molecules, the phase behavior of macromolecules in solution is completely determined by the nature of the forces acting between the constituent particles.



Snapshots of computer-generated repulsive and attractive glasses. The repulsive glass (left) was generated by compressing a system of hard spheres to a volume fraction of 59%. The particles can only move in "cages" formed by their neighbors. The attractive glass (right) was generated at a much lower volume fraction (22%) by introducing infinitely short-ranged ("sticky") interactions between the hard colloidal spheres. The particles shown in red all belong to a single percolating cluster and cannot move at all. This extreme example illustrates the fact that, in an attractive glass, the particles are more strongly confined than in a repulsive glass, even though the overall density of the attractive glass may be much lower.

This is where matters become interesting. The forces acting between small, spherical molecules all depend in a qualitatively similar way on intermolecular separation. As a result, all such substances exhibit very similar phase behavior, an observation already quantified in 1880 by Van der Waals in his "Law of Corresponding States." If the forces between macromolecules in solution were similar in shape to those between gas atoms, then all colloidal suspensions would exhibit the same phase diagram as an assembly of argon atoms. However, the forces between macromolecules in solution come in all sorts and shapes. Furthermore, we can "tune" these forces by choosing an appropriate combination of solvent, solute, and additives. Hence, far from being simply a scale model for atomic fluids, colloidal suspensions can form new states of matter, the building blocks of which are large "designer atoms."

With such tailor-made colloids, we can investigate some longstanding questions. For instance, what happens to the freezing transition if all attractions between the colloidal particles are switched off? This question was first addressed systematically in the 1950s by computer simulations (5, 6). The answer—no attraction is needed for freezing—is somewhat counterintuitive because a crystal phase formed by colloids that behave like hard elastic spheres ("hard-core colloids") has a higher entropy than the liquid phase at the same density. Yet it was confirmed in experiments on hard-core colloids (7).

Subsequent experiments (8) showed that mixtures of large (L) and small (S) hard-sphere colloids could form surprisingly complex

crystal lattices (LS₂, LS₁₃) by spontaneous crystallization. Velikov *et al.* (1) go one step further, illustrating how a new class of binary colloidal crystals with interesting optical properties can be made by “steering” the crystallization process. Such colloids can be used to confine, switch, and amplify light in optoelectronic devices. One technique used by Velikov *et al.* is to grow the crystals on patterned templates. A second trick is to use the capillary forces exerted by a drying front to force small colloidal particles into the holes between the larger ones.

With these techniques, the authors obtain very large single crystals of structures, such as the peculiar LS₃ structure, which will not form in bulk colloidal crystallization. This holds especially for the crystals that were obtained by making a binary crystal of two different colloids, one of which can be burned away. What remains is a low-density crystal of the heat-resistant colloid. This crystal could never have formed by spontaneous self-assembly. The report by Velikov *et al.* illustrates that completely novel colloidal materials can be made by combining the use of tailor-made building blocks with novel construction methods.

Pham *et al.* (2) address another long-standing question: What would happen to the phase behavior of spherical particles if we could change the range of attraction? In simple atomic systems, this question cannot be addressed because the range of the attractive

forces depends only on fundamental physical constants, and these cannot be changed. For this reason, Van der Waals's law of corresponding states holds for all simple molecules. However, in 1983 Gast *et al.* (9) showed that the law of corresponding states does not hold for colloids with short-ranged attraction. These suspensions have only two phases: fluid and solid. The colloidal liquid-vapor transition has disappeared.

Pham *et al.* studied the effect of short-ranged attractions on glass formation. In the glassy state, the system is out of equilibrium—the equilibrium state would be a crystal. However, hard-core colloids can be made to bypass crystallization and form a dense glassy state (10). In this glass, the colloids are unable to diffuse because they are confined in the cages formed by their neighbors. Switching on an attraction between colloids in the glassy state makes them stick together. One might think that this would make it even harder for the colloids to move.

Not so, say Pham *et al.* Initially, the effect of attraction is to break up the glassy structure. This is surprising: it is like loosening up a packed bed of glass beads by adding glue. When the attraction is made sufficiently strong, the system again forms a glass. But now the colloids are not confined due to repulsion but rather due to attraction (see the figure). Theoretical work by Dawson *et al.* (11) and by Pham *et al.* suggests that, when the strength of the attraction is increased, there

can be a sharp transition from the repulsive to the attractive glass. In the equilibrium crystal phase, computer simulations have shown that short-ranged attractions can cause a first-order phase transition from a repulsive to an attractive solid (12). But the nature of the transition between nonequilibrium repulsive and attractive glasses is not clear. Future experiments will have to reveal how the colloidal glass behaves in the vicinity of this transition.

Insights into the nature of “attractive” and “repulsive” colloidal glasses should improve our understanding of glasses and gels formed by smaller molecules, such as globular proteins. In particular, it would be interesting to know whether nature employs similar tricks to control the mechanical properties of gels in living organisms.

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PERSPECTIVES: POLYCRYSTALLINE MATERIALS

Grain Boundaries and Dislocations

Helena Van Swygenhoven

In coarse-grained metals, plastic deformation is mainly carried by dislocations—line defects of the regular crystal lattice—within the individual grains. Dislocations can move through the crystal grains and can interact with each other (1). Grain boundaries often hinder their transmission, creating a dislocation pile-up at the boundary and thereby making the material harder to deform.

One of the best known theories based on dislocation pile-up, described by the Hall-Petch equation (2, 3), predicts the hardness of the material to be inversely proportional to the square root of the grain size. However, as grain sizes are reduced to the nanometer scale and the percentage of grain boundary atoms increases correspondingly, this traditional view

of dislocation-driven plasticity in polycrystalline metals needs to be reconsidered. In a sample with grain diameters of 20 nm, 10% of atoms are located at grain boundaries. Dislocation sources and pile-up are hardly expected to exist in such a material and deformation is believed to be carried mostly by the grain boundaries via a particular accommodation mechanism.

Experimental measurements have shown various deviations from the Hall-Petch equation as grain sizes reach the nanometer scale. Some may be attributed to synthesis or measurement artifacts; others indicate intrinsic properties of the nanostructured materials (4, 5). However, atomic level understanding of the grain boundary accommodation mechanism is limited. No direct experimental visualization technique is available that allows nonintrusive investigation of grain boundary structures during defor-

mation. Transmission electron microscopy requires samples to be thinned to a thickness comparable to the grain size, inducing structural relaxations and thus changing the grain boundary structure (6).

Massively parallel supercomputers offer the possibility to shed light on the deformation mechanism in atomistic simulations involving millions of atoms, equivalent to computer samples of three-dimensional networks of up to 15 grains with a 20 nm diameter or 100 grains with a 10 nm diameter (see the figure). When a special replica technique known as periodic boundary conditions is used, the sample can be considered as a small part of an infinitely large bulk nanocrystalline sample.

The computational sample may be “synthesized” in different ways, such as cooling down from the melt, compaction of nanoclusters, and a simple space-filling technique called the Voronoi construction (7–9). These techniques lead to the formation of different grain boundary structures. For example, liquid-like grain boundaries can result from cooling down from the melt, whereas grain boundaries with a high degree of structural order, not fundamentally different from the grain boundaries in

The author is at the Paul Scherrer Institute, Villigen CH-5232, Switzerland. E-mail: helena.vs@psi.ch