

will end up on either D nucleus with equal probability.

But, according to his calculations, Schiedslag believes the electric field pushed the electron partially into the $1s\sigma_g^+$ state, thereby breaking the wavefunction's symmetry and introducing bias toward one D nucleus over the other. The bias depends on which way the field is pointing and hence on the CEP.

Although the recolliding electron is essential to their experiment, Vrakking and Krausz emphasize that symmetry-breaking CEP dependence can occur without the electron's help. The field itself is what breaks the symmetry, not the first electron, whose presence is a consequence of experimental expedience: It's easier to start with deuterium molecules than with deuterium cations.

Indeed, in a 2004 theory paper, Vladimir Roudnev, Brett Esry, and Itzik Ben-Itzhak of Kansas State University analyzed the dissociation of HD^+ and H_2^+ and found a CEP dependence of comparable magnitude.² Esry would like to see Vrakking and Krausz start directly with HD^+ , H_2^+ or D_2^+ . Those three-body systems (two nuclei, one electron) approach the current limit for solving the time-dependent Schrödinger equation in an intense laser field.

The experimental frontier, as Krausz

sees it, involves improving the ability to shape the pattern of electric field within a pulse. Broadening the frequency range down to the IR and up to the UV (at present it remains all-optical), would bring two benefits. First, at higher energies, the field itself could excite the target molecule. Second, a spectral band spanning several octaves would extend the range over which one can adjust the field's instantaneous amplitude and frequency. The result is stronger CEP dependence and greater freedom to shape the pulse from one subfemtosecond quarter cycle to the next.

Conceivably, as Paul Haljan, Misha Ivanov, and Paul Corkum of Canada's National Research Council proposed ten years ago, a shaped, broadband pulse could excite a molecule from its ground state to one or more excited states.³ A later oscillation in the same pulse could then steer the excited electron inside the chemical bond, changing the atoms it would otherwise connect.

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References

1. M. F. Kling et al., *Science* **312**, 246 (2006).
2. V. Roudnev, B. D. Esry, I. Ben-Itzhak, *Phys. Rev. Lett.* **93**, 163601 (2004).
3. P. Haljan, M. Yu. Ivanov, P. B. Corkum, *Laser Phys.* **7**, 1 (1997).

Colloidal particles crystallize in an increasingly wide range of structures

Two groups working in different size regimes have found similar recipes for making new and potentially useful materials.

A material's properties depend not only on its constituents but also on how the constituents are arranged in space. Diamond, for example, shares the same atomic constituents as graphite and the same tetrahedral structure as silicon, yet it resembles neither black flaky graphite nor gray brittle silicon.

So if you want to make a new material with preternatural properties—a transparent magnet, say, or a chemical-sensing resistor—you may need to choose your construction plan as well as your building blocks. And to avoid having to put each block in its individual place, you'd rather the material assembled itself, like a virus's protein coat or a cell's lipid membrane.

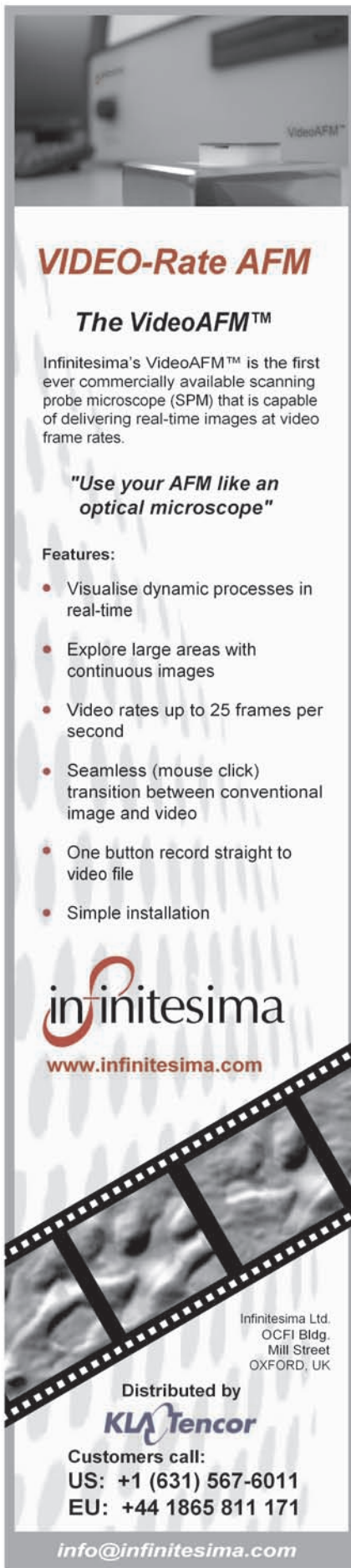
Colloids may provide a path toward that ideal. Their nanometer-to-micrometer particles can be tailored by size and chemistry. And even the simplest colloids—identical hard spheres that neither attract nor repel each other—

will spontaneously crystallize (see Alice Gast and William Russel's *PHYSICS TODAY* article, December 1998, page 24).

But identical hard spheres arrange themselves into the familiar close-packed face-centered cubic structure (fcc). If they come in two sizes, the number of spontaneously forming structures increases to about five. Still, material designers would prefer to select structures à la carte from a long menu of densities and symmetries.

Now, two groups have more than doubled the number of self-assembled colloidal structures—in two different size regimes. Alfons van Blaaderen of the University of Utrecht in the Netherlands and his collaborators are working with micron-sized plastic and glass particles.¹ As of May, they have found 12 new structures.

Dmitri Talapin and Christopher Murray of IBM's T. J. Watson Research Center in Yorktown Heights, New York,



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and their collaborators are working with metallic, semiconducting, magnetic, and dielectric nanoparticles.² As of May, they have found 15 new structures.

Both groups foresee applications.

Paint, ink, and opals

Most colloids are disordered. Indeed, because colloidal particles usually vary in size, they can't crystallize. But in the 1950s, engineers developed techniques to make micron-sized spheres of uniform radius. Because the spheres are big enough to be imaged directly rather than diffractively, physicists began to use them in colloidal suspensions to study the generic features of crystallization.

Convenience isn't the only attraction. In principle, the interparticle forces in colloids can be tuned. Paint, ink, and other colloidal suspensions consist of particles dispersed in a solvent. When some of the solvent molecules break up, one species of charged fragment tends to stick to the particles while its oppositely charged counterpart remains in solution.

The presence of opposite charge in the solvent screens the charge on the particles, yielding an exponential, Yukawa-style potential. Adding a salt to the solution boosts the screening and shrinks the potential's range. Van der Waals and other forces are present, too. They become more significant when the particles' size and separation fall below 10 nm.

The solvent itself also influences the forces. Water dissociates so readily that micron-sized particles in aqueous solution accrete thousands of H^+ or OH^- ions. But in a nonpolar solvent, such as toluene or chloroform, the interparticle forces can become negligible and crystallization resembles the packing of hard spheres.

In that case, raising the particle density leads to the formation of an fcc structure. Nature favors fcc over disorder because the close-packed structure gives the particles more room to jostle in the solvent and therefore more entropy—which is why the colloid crystallizes.

Entropy-driven crystallization was first observed in lab experiments in the 1980s, but natural examples of the end product were already known. Opals consist of spheres of silica dis-

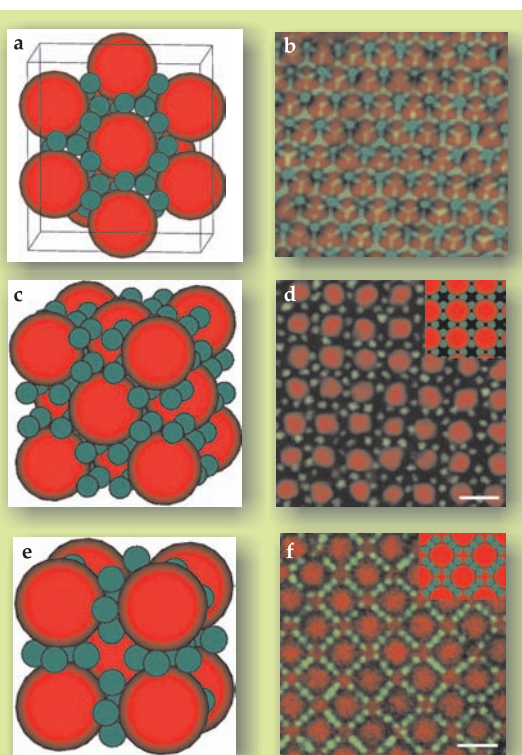


Figure 1. Equilibrium structures that form in the lab also form on the computer. In both cases, the starting point is a colloidal suspension of negatively charged small particles (radius $0.31\ \mu\text{m}$) and positively charged larger particles (radius $1.16\ \mu\text{m}$). Panels a, c, and e show computer-predicted unit cells. The other panels show crystal planes observed in the lab with confocal optical microscopy. The inserts in panels d and f are the corresponding computer predictions. (Adapted from ref. 3.)

persed in a solid solution of hydrated calcium carbonate. The regular arrangement of the spheres, whose size and spacing correspond to optical wavelengths, endows the gems with beguiling iridescence.

Most opals consist of spheres of one size. But in the 1970s, John Veysey Sanders and M. J. Murray discovered Brazilian opals made up of two different sizes of particle. When they determined the opals' structures, they found a surprising variety, including the exotic AB_{13} , whose unit cell contains more than 100 particles arranged with nested tetragonal and icosahedral symmetries.

Sanders and Murray conjectured that for a given size ratio $r_A:r_B$ and a given stoichiometry $N_A:N_B$, the most stable structure is the densest. Observations support the conjecture, but the problem of predicting in advance what structure forms for a given size ratio and stoichiometry remains unsolved.

Interestingly, the AB_{13} structure shows up elsewhere, in the intermetal-

lic compound $NaZn_{13}$. Indeed, several of Sanders and Murray's opal structures have atomic counterparts.

Opposite and modest

Van Blaaderen and his team wanted to create new binary colloidal crystals. One way forward seemed clear: attractive forces. Binary crystals can be thought of as interpenetrating A and B lattices. If the As attract the Bs, their respective lattices can stabilize each other. But if their mutual attraction is too strong, the two species will aggregate before they crystallize.

Attractive forces in colloids are far harder to tune than repulsive forces. The difficulty lies in placing a modest number of opposite charges on different colloidal particles. But in 2002, almost by chance, van Blaaderen discovered that by adding a certain salt, tetrabutylammonium bromide (TBAB), to his nonpolar solvent he could control the charge on his plastic and glass microspheres.

Although the control mechanism isn't clear, it seems the TBAB molecules dissociate, migrate to the surfaces of particles, and compensate whatever charges are already there. Because the particles are two different sizes, the compensation either falls just short or just over, and the two species end up oppositely and modestly charged.

Van Blaaderen and his collaborators soon found their binary colloidal mixtures crystallized into a range of equilibrium structures at different size ratios and stoichiometries.¹ Some, like AB_{13} , were familiar, but others were entirely new.

By using a simple pairwise potential, the Utrecht team could assess the stability of their structures and even identify some new ones in advance of their experiments. Antti-Pekka Hynninen, who is now at Princeton University, and Marjolein Dijkstra developed a Monte Carlo scheme that starts off with big particles, the As, arranged in a simple lattice. As the temperature drops, the small particles, the Bs, are randomly moved until a minimum-energy structure is found.³ Figure 1 shows a selection of predicted and observed structures.

Van Blaaderen and his collaborators are interested in photonic applications. They use transparent, strongly scatter-

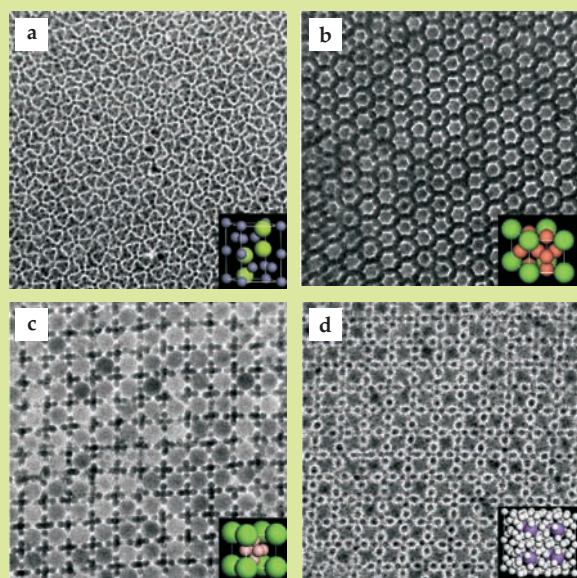


Figure 2. Diverse structures are formed spontaneously by particles of different materials, radii, and stoichiometries. (a) 6.2 nm PbSe, 3.0 nm Pd, 1:2. (b) 7.2 nm PbSe, 5.0 nm Au, 1:5. (c) 5.8 nm PbSe, 3.0 nm Pd, 1:6. (d) 7.2 nm PbSe, 4.2 nm Ag, 1:13. Insets show modeled unit cells. (Adapted from ref. 2.)

ing particles whose sizes are comparable to the wavelength of light. Finding optimum structures is paramount.

Murray, Talapin, and their collaborators are interested in electronic applications. They want to combine two different types of functional nanoparticles into so-called binary nanoparticle superlattices (BNSLs). The goal is a material whose properties arise not only from the two types of constituent but also from how the two types interact.

As a first step, Murray and Talapin's group sought to crystallize BNSLs, though not necessarily functional ones. Their nanoparticles ranged in electrical resistance from metals, through semiconductors, to insulators and in size from 3 to 10 nm.

Like the Utrecht microspheres, IBM nanoparticles acquire opposite and modest charges, thanks to a judicious choice of solvent and additives. And, as figure 2 shows, the nanoparticles also form a variety of familiar and unfamiliar structures, including AB_{13} .

Quantifying the stability of BNSLs is more difficult than for crystals of

micron-sized particles. On length scales of 1–10 nm, the electrostatic, Van der Waals, dipole-dipole, and other interparticle forces all fall within a single order of magnitude.

Even so, the appearance of AB_{13} in BNSLs and natural opals suggests that hard-sphere packing, though not driving the crystallization, could at least provide a set of destina-

tions. The attractive electrostatic forces in the Utrecht and IBM colloids may serve to hasten arrival and avoid detours to unwanted phases.

Goals and applications

A key goal in photonics is the development of efficient and practical bandgap materials that transmit light in a narrow wavelength range through circuits without loss. To work, a photonic bandgap material must be structured on the same scale as the wavelength of light. That scale is easy to achieve with colloidal crystals.

But the right scale isn't enough. The best light-steering performance comes from materials with the most symmetric Brillouin zones, which, in turn come from structures of high point-group symmetry. Close-packed structures have threefold symmetries. But diamond has fourfold symmetry and quasicrystals have five and higher.

High symmetries are tricky to realize. Diamond's structure arises from carbon's directional—that is, nonspherically symmetric—covalent bonds, and

quasicrystals form in a race against the usually more stable normal crystal.

Still, given the tweaking possible—including ternary mixtures and selectively dissolving or sintering one species—van Blaaderen is optimistic. Better photonic bandgap materials, besides improving photonic circuitry, would also boost the efficiency of laser cavities by blocking access to transitions that don't lase.

In the case of BNSLs, the role of structure is to mediate whatever interaction the two species have that underlies the material's function and *raison d'être*. One interaction that could lead to novel materials is spin exchange.

Ferromagnetic materials come in two types: hard magnets, which have low, difficult-to-reorient moments, and soft magnets, which have high, easy-to-reorient moments. Hard magnets, like the rare-earth-based $Nd_2Fe_{14}B$, are used to store data. Soft magnets, like permalloy, are used in electric motors and antennas.

A third type of magnet, one whose moment is high and difficult to reorient, is conceivable. To realize it, one could create a BNSL of magnetically hard and soft nanoparticles. Spin exchange, so the theory goes, would tie the high moment of the softs to the high coercivity of the hards.

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References

1. M. E. Leunissen et al., *Nature* **437**, 235 (2005).
2. E. V. Shevchenko et al., *Nature* **439**, 55 (2006).
3. A.-P. Hynninen et al., *Phys. Rev. Lett.* **96**, 138308 (2006).

Drops of liquid exhibit surprising self-propulsion on ratcheted surfaces

Cooks use the Leidenfrost effect to see when skillets are hot enough. Some day it may serve to keep microprocessor arrays cool.

The self-winding wristwatch provides a familiar example of a ratchet. An internal mechanism that's asymmetric with respect to clockwise and counterclockwise converts the energy imparted by random wrist motion into purpose-

ful winding of the clockwork. More generally, a ratchet is a kind of rectifier—macroscopic or microscopic—that forces the otherwise random thermal or mechanical motion of a system that's out of equilibrium into a specific

direction by means of an asymmetric potential. Microscopic ratchets called Brownian motors are thought to be important for motion in biological systems (see the article by Dean Astumian and Peter Hänggi in *PHYSICS TODAY*,