

arrangement—or, rather, an ensemble of arrangements—that gives them the highest entropy. This energy-versus-entropy dichotomy exists in the field of quasicrystals, too, but with the difference that some theorists believe that most, if not all, quasicrystals could be stabilized by entropy.

Advocates of both energy and entropy stabilization find evidence in Tsai's discovery to support their cases. Cornell University's Veit Elser of the entropy camp notes that $\text{Cd}_{5.7}\text{Yb}$ is a congruent melter—that is, the solid can be in equilibrium with the liquid, suggesting entropic kinship between the two phases. Says Elser: "When you take the high-temperature liquid cadmium-ytterbium and cool it down, the first thing that forms is the quasicrystal. And to get the approximant, you need a solid-state reaction involving the quasicrystal and the other crystal phase at lower temperature. That, for me, is a key point."

Elser also finds support for the entropy picture in the structure that Tsai proposed for $\text{Cd}_{5.7}\text{Yb}$'s atomic building blocks (see figure 2). At the center of the cluster is a tetrahedron of Cd atoms that breaks the cluster's overall icosahedral symmetry. The energetic view relies on the deterministic packing of identical units, but in the entropic picture the units don't have to be arranged so carefully. "You just don't care how the tetrahedron is oriented. All orientations are just as

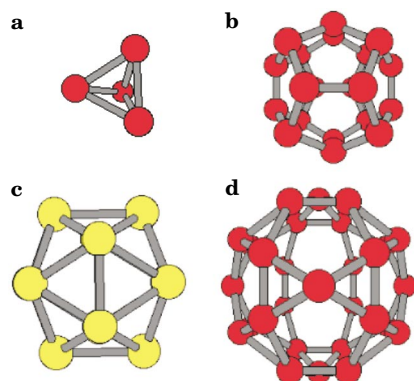


FIGURE 2. A PRELIMINARY STRUCTURE for the atomic cluster that forms the basis of $\text{Cd}_{5.7}\text{Yb}$ quasicrystal. Cadmium atoms are shown in red, ytterbium in yellow. Like a Russian doll, the successively smaller units (c, b, a) fit within the largest unit (d).

likely," says Elser.

In the energy camp, Princeton University's Paul Steinhardt sees the cluster's tetrahedron as providing the asymmetry that energy stabilization needs. In the energy picture, a repeating unit, the quasi-unit cell, finds the lowest energy state by maximizing its density. "The discovery of stable binary quasicrystals," says Steinhardt, "is consistent with a simple relationship with crystals. Energy stabilization, local growth rules, simple repeating units—all these features, which are

found in crystals, are also found in quasicrystals."

The key difference between quasicrystals and regular crystals is that the units in quasicrystals can overlap, making it possible to realize symmetries that are forbidden to regular crystals. Though once rather complicated, the rules for overlapping atomic clusters are now simpler in the latest version of the energy-stabilization theory and don't require the long-range collusion that was a feature of earlier versions.

Despite their differences, both camps agree that more and better structural data are needed on the Cd-Yb and Cd-Ca systems. For one thing, Tsai's atomic cluster model is a first guess based on the Cd_6Yb approximant. Also needed are measurements of the materials' mechanical, thermal, and electrical properties. But don't expect too many applications for $\text{Cd}_{5.7}\text{Yb}$. Cadmium is poisonous. "The allure of these new materials will remain intellectual for the foreseeable future," says Thiel.

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Hydrodynamics May Explain Like-Charge Colloidal Attraction

We are taught from the first lectures in electrostatics that like charges repel each other. That expected behavior breaks down, however, in some colloidal suspensions. There, large colloidal particles (called macroions), typically all with the same charge, are surrounded by smaller, oppositely charged counterions, not to mention a polar fluid, charged surfaces on the walls of the container, and possible additional ions. In such complex fluids, many varied experiments over the past 15 years have produced evidence of attractive interactions between the macro-ions.

In many regards, latex colloidal suspensions, with their spherical particles of nearly identical diameter, are useful models for studying behavior in more complex systems (see, for instance, the article by Alice Gast and William Russel in *PHYSICS TODAY*,

As two like-charged particles are repelled by a nearby charged wall, the resulting fluid flow can make them move toward each other.

December 1998, page 24). Attractions in such systems at short length scales—on the order of a few nanometers—are well established and attributable to correlations among multivalent counterions; such attraction in biological systems is discussed in the article by William Gelbart and coauthors in *PHYSICS TODAY*, September 2000, page 38. But in some systems, attraction has been observed at length scales of several microns, and an understanding of that behavior has been elusive. Recently, Todd Squires of Harvard University and Michael Brenner of MIT have proposed an explanation for some of the

experimental results, incorporating hitherto overlooked effects of hydrodynamics.¹ Their model produces quantitative agreement with measurements, by Amy Larsen and David Grier at the University of Chicago, of the behavior of two colloidal particles near a single wall.²

Hints of attraction

A typical charge-stabilized latex colloidal suspension consists of spheres with diameters on the order of $1\text{ }\mu\text{m}$ or smaller, dispersed in water. Sulfate or other groups on the spheres dissociate in solution, producing a large surface charge density on the spheres. The spheres are surrounded by counterions that are many times more numerous and much smaller than the spheres. As a result, the dynamics of the counterions have a significantly faster time scale than that of the

spheres. Averaging over the counterion dynamics yields a screened, exponentially decreasing electrostatic interaction between the spheres—the Derjaguin-Landau-Verwey-Overbeek (DLVO) model. Adding salt introduces more ions in solution, which decreases the screening length.

The mean-field DLVO theory has been shown to produce purely repulsive interactions between the spheres. It consequently fails to explain the various experimental hints that there is some sort of effective attraction. Many of these hints have come from observations made in bulk colloidal systems. For example, although one would expect repulsive interactions to spread the particles out evenly, Norio Ise and coworkers at Kyoto University have seen empty regions in deionized suspensions (characterized by large screening lengths). And analyzing the equilibrium distribution of particles in suspension, Seth Fraden at Brandeis University and Mauricio Carbajal-Tinoco (now at Mexico's National Polytechnic Institute) and colleagues independently derived attractive pair potentials for the particles.

Instead of looking at bulk systems, Grier's group at Chicago has looked at pairs of particles, positioning them with optical tweezers and then releasing them and observing their motion. Those experiments showed that whereas the behavior of two isolated spheres is well described by standard DLVO theory, when confined between two walls—or even just near one wall—the spheres behave as though they experience an effective attractive interaction.

Going with the flow

The evidence for long-range attraction when screening lengths are long and when two spheres are confined, but not when isolated, has led many researchers to look toward many-body effects, nonlinear interactions, and other factors for possible statistical mechanical explanations. Recognizing that some of the experimental systems were not in equilibrium, Squires and Brenner have introduced a new effect for consideration: hydrodynamics. They have examined the case of two charged spheres near a single wall as investigated in Grier's

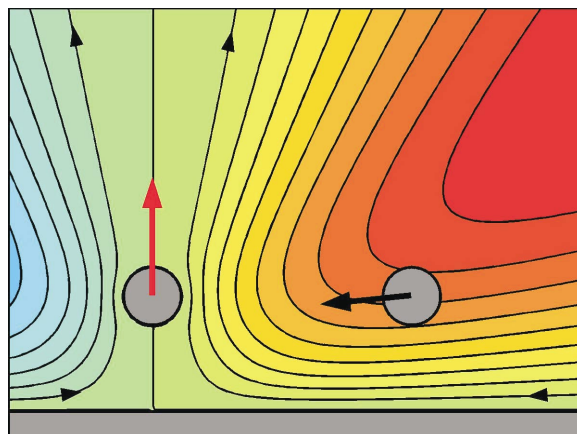


FIGURE 1. HYDRODYNAMIC FLOWS can draw colloidal particles toward each other, even when they have like charges. Here, the left sphere is moving away from the wall at the bottom, dragging nearby fluid with it as indicated by the black lines. As the surrounding fluid flows in behind the sphere, it pulls the nearby right sphere along, toward the other. Similar motion toward each other occurs when both spheres are moving away from the wall. (Courtesy of T. Squires.)

experiments. Figure 1 illustrates the effect: As one sphere moves away from a similarly charged glass wall due to electrostatic repulsion, it entrains the nearby fluid to follow along. Fluid moving in behind the sphere can drag a second nearby sphere toward the first. Thus the observed motion of the spheres toward each other may be

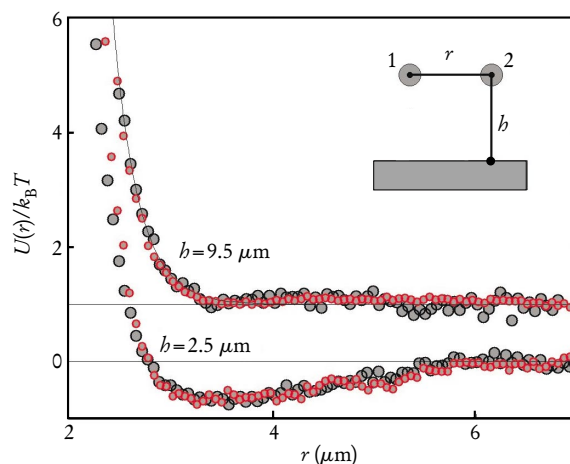


FIGURE 2. WITH HYDRODYNAMIC effects incorporated, simulations of the motion of two charged spheres $0.65\ \mu\text{m}$ in diameter near a similarly charged wall quantitatively account for the observed motion. Here, the simulated¹ (red) and the observed² (gray) motions have been analyzed as if they were due to forces given by the gradients of an effective potential U that depends on the interparticle separation r , for two values of the distance h from the wall (offset for clarity). (Courtesy of T. Squires.)

attributable to hydrodynamic flows that arise from the proximity of the two spheres to the wall, rather than arising from an attractive interaction between the spheres themselves.

Squires and Brenner have been able to quantify the effects of their hydrodynamic considerations by using standard hydrodynamic theory coupled to the DLVO screened Coulombic interaction between the spheres and between each sphere and the wall. They came up with an analytic expression for the hydrodynamic effects, which they then combined with diffusive Brownian motion in simulations.

The theory has only one free parameter, the surface charge density on the wall. With a judicious choice for its value, Squires and Brenner can quantitatively account for the experimental observations of the relative motion of the spheres.² Figure 2 shows the results of the model calculations along with the experimental observations, when both are cast as being due to forces that are the gradient of an “effective potential.” (The actual interparticle forces are strictly repulsive in this model, however.) The model correctly accounts for the depth of the effective potential as well as its long range: The observed maximum effect occurs for an interparticle spacing that is several times larger than the particle diameter or the screening length, but on the order of the distance to the wall. “This is in fact one of the major clues that tipped us off to the hydrodynamic effect,” notes Brenner.

The wall's charge density in the earlier one-wall measurements isn't known, and so the charge density used in the model hydrodynamic calculations can't be verified without further experiments. Still, says Grier, the value is reasonable: “It's right in the sweet spot.”

A kinematic effect

The hydrodynamic interactions between the spheres arise only in non-equilibrium situations in which the spheres are moving. “If you could pin the two spheres and measure the force between them, you'd find pure repulsion,” says Squires.

The case of two spheres near one wall is the only case Squires and

Brenner have examined quantitatively, although they do make a qualitative extension to the case of two spheres between two parallel confining walls. For two spheres that are precisely in the midplane between the walls, the hydrodynamic effects from each wall will cancel by symmetry. But Squires and Brenner argue that if the spheres are slightly off center, which is almost inevitable experimentally, the hydrodynamic effects won't exactly cancel and could produce an apparent attraction of the magnitude observed in earlier measurements by Grier with John Crocker.

Because the hydrodynamic theory

is applicable only to nonequilibrium measurements, there is no direct implication for the bulk equilibrium measurements that have also shown evidence for attractions between colloidal particles. To the extent that Squires and Brenner's model does indeed account for the observed two-sphere behavior near a single wall, it indirectly sets limits on the influence of electrostatic or other effects that could also be playing a role, both in that system and in the bulk. Meanwhile, a consensus is emerging that many-body effects originating in counterion correlations are at the heart of the observed attraction in the bulk.

The jury is still out on the value of wall charge density, which will determine the extent to which hydrodynamic effects account for the observed behavior of two charged spheres near a wall. Grier is working closely with Squires and Brenner to reevaluate his old experiments and perform new ones aimed at settling this issue, for both one-wall and two-wall systems.

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New Printing Technologies Raise Hopes for Cheap Plastic Electronics

Semiconducting polymers might not compete with silicon for speed and durability in electronic circuits but they are candidates for applications in which low cost and flexibility are paramount—such as large-format displays or bar codes that can be remotely interrogated. In quest of cheap polymer electronics, researchers over the last five years have progressed from making fairly rudimentary single all-polymer transistors,¹ to turning out high-performance integrated circuits made all,² or nearly all,³ from plastics (see PHYSICS TODAY, November 2000, page 9). The large-scale circuits were patterned by relatively expensive techniques such as photolithography.

Two groups have now demonstrated alternative, cheaper printing methods—stamping and inkjet printing—done outside a clean room. John Rogers and his coworkers from Bell Labs, Lucent Technologies, have used a rubber-like stamp to pattern an active matrix of 256 polymer transistors on the backplane of a flexible optical display,⁴ as they reported at the Materials Research Society meeting in Boston in late November. In addition, Richard Friend and his colleagues from the University of Cambridge have used high-resolution inkjet printing to produce thin-film transistor circuits, with fewer transistors but with electrical interconnections between layers.⁵ Other teams are working on similar printing methods. The new methods are not ready for commercial debut, but the progress is encouraging.

George Whitesides of Harvard University, whose lab has developed microcontact printing (stamping),⁶ asserts

▶ Inkjets and rubber stamps just might replace expensive photolithography steps in the printing of polymer circuits. If so, we may one day read our newspapers off reloadable, flexible plastic sheets.

that plastic printing methods are potentially “real technology dislocators.” He adds, “polymers are increasingly looking as if they can do things that inorganics just can't do.”

The lure of solution chemistry

Researchers have aspired to make electronic circuits with organic materials ever since they learned to turn polymers into conductors and semiconductors (see PHYSICS TODAY, December 2000, page 19). The lure is the ease of processing polymeric thin films with solution chemistry. Another attraction is the flexibility of plastic substrates, which should allow large-area circuits to be printed in a continuous manner on sheets that are rolled onto and off of large reels.

A key building block of electronic circuits is the transistor. The semiconducting layer in a field-effect transistor (see figure 1) might be made of one polymer and the source, drain, and gate electrodes of another, conducting, polymer. A thin film of the semiconducting polymer can be easily applied to the device. The electrodes, however, require patterning and, for inorganics such as metals, that step has traditionally been done with lithographic and etching techniques. For low-cost plastics, however, photolithography is not a good choice because it is relatively expensive, incompati-

ble with some polymers, difficult to apply on uneven substrates such as flexible plastics, and not appropriate for reel-to-reel processing. These drawbacks have motivated the search for alternative printing methods.

At Philips Research Laboratories in Eindhoven, the Netherlands, a team led by Dago de Leeuw has developed a version of photolithography called photochemical patterning. In the place of a resist, the experimenters expose a light-sensitive polymer to ultraviolet light through a mask. The regions exposed to the UV light change from conducting to nonconducting, defining the desired pattern. According to Philips researcher Bart-Hendrik Huisman, their technique is cheap due to the high throughput, does not require a vacuum, and can be used on flexible substrates, as they have shown with their all-plastic integrated circuit.²

Nevertheless, other researchers want to pursue possibly cheaper methods that are capable of printing on a larger variety of polymers. These alternatives must be able to pattern sufficiently small feature sizes. The critical dimension is the distance that the field-induced charges must traverse—the distance between the source and drain. For the polymers typically used, that distance must be on the order of 10 μm to give acceptably high drive current and switching speeds.

Microcontact printing with elastomeric, or rubber-like, stamps, does have the required resolution. The Bell Labs group has used it to pattern organic transistors;⁷ the new work extends their capability to a much larger scale (15 cm $\times$ 15 cm). To date,