Gazing into Crystal Balls

Colloids help scientists understand how materials melt

By CORINNA WU

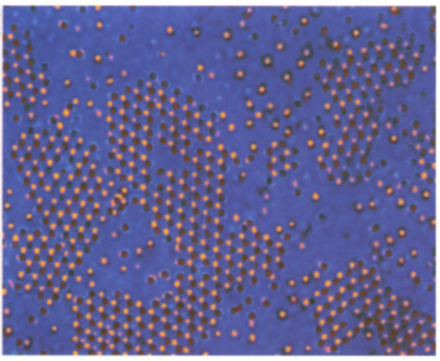
Liquids freeze into solids; solids melt into liquids. These commonplace phase transitions, in which one state of matter transforms into another, nevertheless retain an aura of mystery. No one fully understands what happens at the interface between two phases—an uncharted borderland where atoms rearrange themselves out of one structure and into another.

Tracking atoms as they make these rearrangements isn't easy. Although scientists can use electron microscopes to image individual atoms as fuzzy blobs, that's not a practical way to study an interface between two phases. Atoms move in and out of the boundary region quickly and unpredictably, making it hard to know which atoms to look at.

One way around these observational hurdles is to study a model system instead of real atoms. Many scientists are turning to colloids, suspensions of small particles dispersed in a liquid. Under the right conditions, colloidal particles can organize to form crystals—three-dimensional arrangements with a specific structure—which can then melt like conventional materials. Colloidal crystals provide scientists with a way to test how atoms interact and what they do during phase transitions. Recent experiments have revealed some surprising things about the nature of these interactions, standing accepted theory on its head.

Far from being exotic laboratory concoctions, colloidal suspensions are found widely in nature. A person sipping a glass of milk is ingesting a colloidal suspension of proteins dispersed in water. Gemstone opals get their fiery colors from crystallized silica colloids that are just the right size for scattering light.

Colloidal systems have many industrial uses as well. For example, paint consists of pigment particles suspended in a liquid binder. When colloidal particles bump, they clump—creating that gooey glob of pigment that lurks at the bottom of an unstirred paint can. The paint industry doesn't like precipitation, but "in the dairy industry, that's known as cheese," says David G. Grier, a physicist at the University of Chicago. "Many of the industrial applications involve controlling the interaction between particles."



These polystyrene spheres stick together in crystals even after 10 minutes of melting. The facets on the crystals suggest that the negatively charged spheres can attract each other over a large distance.

Learning about colloidal interactions could prove useful not only for understanding existing materials but for making entirely new ones. Materials consisting of linked colloids could have interesting properties. For example, researchers are discussing making photonic crystals, materials that act as semiconductors for light, out of colloids. To do so, they must arrange colloidal particles of a particular size to filter light in a prescribed way.

Accordingly, Grier and other researchers around the world have focused their attention on the physics of colloidal crystals. Some groups use gold or silica clusters for their work. Others, including Grier, choose tiny, commercially available polystyrene beads, "beautifully spherical" particles less than a micrometer in diameter. The beads are so uniform, says Cherry A. Murray, head of the semiconductor physics research department at Lucent Technologies in Murray Hill, N.J., that scientists use them to calibrate the magnification of electron microscopes.

In addition to uniform size, other properties make the beads attractive to colloid researchers. The beads are manufactured with a surface coating of thousands of sulfate salt groups, which dissociate into ions when the beads are placed in water. The positively charged ions float away, leaving a host of negative charges on the beads. Squeezing the fluid against a glass wall concentrates the negatively charged spheres so that they coalesce into an orderly array—a colloidal crystal—but as soon as the pressure is released, the crystals fall apart. In other words, they melt.

Even though the spheres are small, they are big enough to be seen under a light microscope, making them easier to study than other types of colloidal particles. Murray, who has worked with colloidal crystals for more than 15 years, pioneered a method of videotaping the crystals as they form and disintegrate. She digitizes the video images so a computer can trace the particles' patterns of movement.

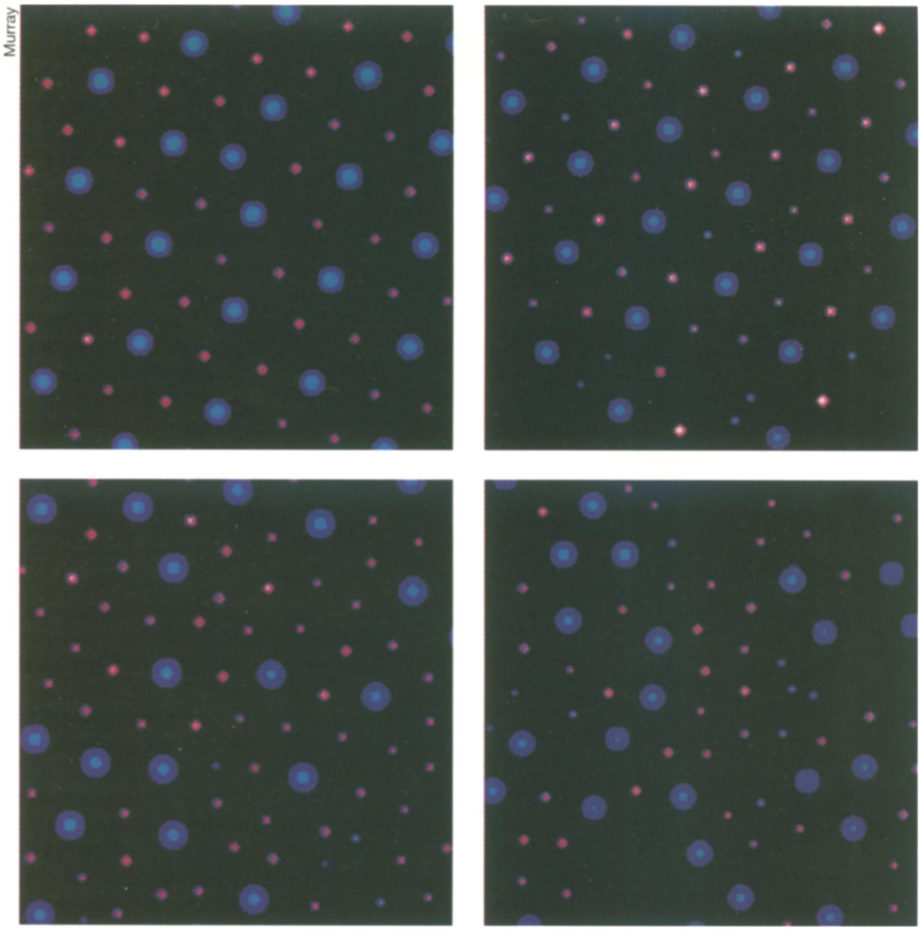
"I like to call it analog molecular dynamics simulation," Murray says. "The observer can see each sphere move individually and follow it in time."

She uses the word "analog" to distinguish the method from molecular dynamics simulations performed wholly on the computer. Such simulations calculate behavior of crystals existing only as mathematical constructs. Videotaping and digitizing an image of a real colloidal crystal, Murray says, overcomes the limitations of even supercomputer simulations.

For example, a computer has only so much memory, which limits the size of the crystal that can be simulated. A real crystal could, in principle, contain as many beads as the researcher wants. Also, that crystal could be left to equilibrate in the lab for as long as necessary. Time on a supercomputer is too precious to design lengthy experiments.

Grier, who worked with Murray several years ago, also captures colloidal crystals on video. One day, he and his colleague Amy E. Larsen, now at St. Olaf College in Northfield, Minn., ran what they expected would be a routine experiment: compressing layers of spheres against the walls of a glass container, releasing the pressure, and watching the crystal melt. Instead, what they saw challenged a basic tenet of the currently accepted theory of colloidal interactions.

That theory says that a group of particles with the same charge should repel each other, and indeed, they usually do. If negatively charged polystyrene spheres had only repulsive interactions, they



Murray

These frames from a video of two different-size polystyrene beads show that they can arrange themselves to form an ordered crystal (top) or a disordered glass (bottom). The large (bright blue) and small (pink) spheres are 0.6 and 0.3 micrometer in diameter, respectively.

should push away from each other in a matter of seconds. Surprisingly, some of the crystals made by Grier and Larsen refused to melt. Instead, they stayed together for nearly an hour. "It's exactly like slush, or a frozen margarita," Grier says. "You have chunks of crystal floating around in a very dilute fluid."

What keeps the colloidal slush from melting? Grier and Larsen concluded that the colloidal particles must possess some sort of long-range attraction, even though their individual charges should repel each other. Two Japanese scientists first proposed this idea more than a decade ago, developing what became known as the Sogami-Ise theory. Experiments supported the idea of long-range attractions in colloids, but other calculations eventually exposed flaws in the theory's details, says Grier.

The currently accepted theory of how particles interact balances the repulsive forces and the weak attractions caused by shifting electric charges in the spheres. Grier and Larsen's results suggest that the theory does not account adequately for the strong attractive part of the interaction.

The shape of the crystals, which show facets, or flat edges, provides additional evidence to support this idea, he says. Faceted crystals need more energy to hold themselves together than amorphous blobs do.

To elucidate the nature of this long-range attraction, the scientists tested the influence of the glass plates against which they squeezed the crystals. Previous studies had shown that glass promotes attractive interactions between the spheres. They measured the interaction between two polystyrene beads near a glass wall. At a distance of about 2.5 micrometers from the wall, the two beads attracted each other, within a certain range of separations, but at about 9.5 micrometers from the wall, they always repelled each other.

The crystals in the slush were too big and too far from the glass for the effect of the walls to explain their stability, however. "The wall-induced attraction could be holding together the first layer, but then what's holding together the second, third, fourth, fifth, sixth layers?" asks Grier. He and Larsen described their findings in the Jan. 16 Nature.

Since two spheres repel each other but many spheres attract, Grier describes this anomaly as a many-body effect, a catchall phrase for this kind of phenomenon. In a colloid, each negatively charged sphere tends to attract a cloud of positive ions around it. Grier suggests that the overlapping of these positive ion clouds might hold a collection of spheres together. A similar thing happens in metals, whose electrons spread out in a sea over all of the atoms in the material. Grier's suggestion may also explain how a glass wall causes nearby spheres to attract. "The glass turns out to be [negatively] charged in water also," Grier says, so the positive ion cloud associated with it could act as a mediator between the spheres.

The origin and nature of the long-range attractions that Grier and Larsen see in their colloidal crystals remain mysterious. In particular, molecular dynamics simulations performed on a computer show no such phenomenon under the conditions of the experiment, says Mark J. Stevens of Sandia National Laboratories in Albuquerque, N.M.

Beyond understanding how colloids themselves interact, researchers want to see how well these crystals can simulate other materials. The way polystyrene spheres pack together to form colloidal crystals offers a useful simulation of the close packing of atoms in a typical metal, Murray says, but colloids are not good mimics of other elements. For example, she explains, "silicon wants to bond with four nearest neighbors in a tetrahedral arrangement" that the tiny spheres don't reproduce.

The resemblance to metals becomes even more pronounced in systems that consist of two kinds of colloids. By mixing two types of polystyrene spheres with different sizes or electric properties, Murray can create colloidal crystals that behave like metal alloys. One system she's found closely resembles the structure of a calcium-copper mixture.

Murray is also using these binary mixtures to study the kind of phase transition certain crystals make when they transform from tight arrays into glasses, whose particles are less ordered. "You can get very complicated phases," she says.

Despite the evident similarities, extrapolating from the micrometer-size beads to atoms one ten-thousandth their size is tricky, Stevens cautions. The beads are classical systems, but on the scale of true atomic systems, quantum mechanics takes over. That difference in the physics governing each system limits how far the analogy between colloidal and atomic crystals extends.

The next challenge, Grier says, will be to place the new experimental results in a theoretical framework.

"The understanding of phase transitions is, in my opinion, one of the most important problems in condensed-matter physics today," he says. Perhaps as theory, experiment, and computer simulations gradually come together, scientists' understanding of colloids and materials will crystallize too. ☐