Soft spheres settle in somewhat surprising structure

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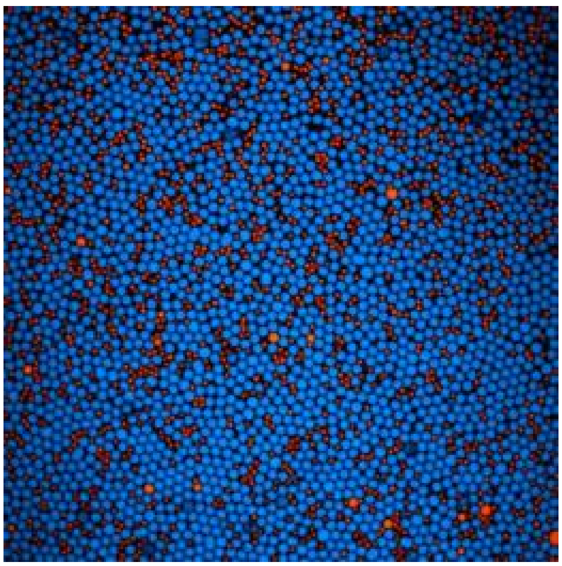

Blue and orange balls of different sizes as seen through a confocal microscope. The smaller orange spheres fill in the spaces between the larger blue spheres. Credit: Joseph McDermott, Penn State

Latex paints and drug suspensions such as insulin or amoxicillin that do not need to be shaken or stirred may be possible thanks to a new understanding of how particles separate in liquids, according to Penn State chemical engineers, who have developed a method for predicting the way colloidal components separate based on energy.

"The ongoing assumption was that if you have a mixture of different sized particles in a liquid, the faster-settling particles will end up on the bottom," said Darrell Velegol, professor of chemical engineering. "We found that in many cases it doesn't matter how fast they settle. The particles keep jostling until they reach the low-energy state."

Another known mechanism for settling is the Brazil nut effect, where dry particles eventually sort themselves out with the larger particles on the top -- the way the Brazil nuts are always found on the top of the can of mixed nuts. This mechanism, however, does not apply to particles in liquids.

Velegol, working with César González Serrano, former graduate student, and Joseph J. McDermott, graduate student, found that settling speeds were not the determining characteristics of settling mixtures, but that the particles on the bottom are the ones in the lowest energy state. They reported their results in today's (July 24) online issue of *Nature Materials.*

"Sedimentation is an old field, and it's taken us a long time to figure it out," said Velegol.

Velegol explains that small colloidal particles -- roughly 1 micrometer, about 1 percent as thick as a human hair -- in weakly ionic liquids like water are soft, surrounded by an electrostatic field that allows them to feel other particles before they actually touch. Because of the electrostatic charge, repel the other particles, allowing the particles and the liquid to keep in constant motion.

In higher-ionic-strength liquids like seawater, spheres are hard, unable to sense other spheres until they actually touch. They create glassy mixtures where the particles become locked in place before they find their lowest energy state.

"Soft particles, because they have forces between, avoid becoming glassy," said Velegol. "All things try to go to the lowest energy state, but most of the time particles can't get to that state. The Brazil nut effect is not a minimal energy state. The nuts are frozen in a non-equilibrium state, not where they really want to be in the end."

The road to understanding this separation process was initially accidental. González Serrano, working on another project was having difficulty seeing the two kinds of colloidal particles he was using, so he decided to use two different colors of material. He left the extra mixture in a beaker overnight and found two distinct color layers in the morning. The researchers repeated the experiment and consistently found the same result, but were initially unable to explain why it happened.

"We found that dense particles went to the bottom, even if they were very small and settled slowly," said Velegol.

The researchers found that the particles settled in the order of their density. Particles of silica and gold, for example, will always settle with the gold on the bottom and the silica on top because gold is denser than silica. This occurs even when they used gold nanoparticles, which settle extremely slowly.

When it comes to particles of the same material, the process becomes more difficult to explain. Using differently sized and colored particles of the same substance, the researchers found what appeared to be a layer of large particles below a layer of smaller particles. On closer inspection, while the top layer was completely small particles, the bottom layer was actually a layer of the large particles with a small amount of small particles.

The separation of particles occurs because of packing densities. Normally uniform spheres filling a space can occupy only 64 percent of the space. However, if one material is smaller, the packing density can increase.

"The unusual thing is that this mixture of spheres in water behaves as a single substance with a higher density than one type of sphere in water," says Velegol. "We can predict the percentage of the bottom layer that will be composed of each size particle because we can calculate the energy of the entire system."

Some of the separations even create a uniform layer on the top and bottom with a mixed layer in between.

"We ran one mixture after calculating the minimum energy and predicted three phases," said Velegol. "Sure enough, we had three phases when we did the experiment. The lower phase was a mixture of polystyrene and poly(methyl methacrylate), the middle was pure PMMA and the top layer was pure polystyrene. No one would have predicted that before."

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