

## From Quonset huts to ballerinas: Scientists solve a nanotech mystery

Princeton Engineering researchers have untangled the mystery behind a puzzling phenomenon first observed more than a decade ago in the ultra-small world of nanotechnology.

Why is it, researchers wondered, that tiny aggregates of soap molecules, known as surfactant micelles, congregate as long, low arches resembling Quonset huts once they are placed on a graphite surface?

To fellow scientists and engineers, this question and the researchers' answer is tantalizing since the discovery gives insight into "guided self-assembly," an important technique in nanotechnology where molecules arrange themselves spontaneously into certain structures. It may also one day lead to valuable technological applications such as the creation of anti-corrosion coatings for metals and bio-medical applications involving plaque formation with proteins.

In a paper appearing in the Jan. 13 issue of *Physical Review Letters*, a premier physics journal, Dudley Saville, Ilhan Aksay, Roberto Car and their colleagues explain how they unraveled the mystery.

The scientists discovered they and others had been operating on the flawed assumption that - in response to the texture of the graphite beneath them - surfactant molecules assembled themselves into static 'Quonset Hut' shapes that stayed put.

Because of new atomic force microscope imaging done by research associate Hannes Schniepp, the Princeton scientists were able to see that the micelle structures were not static but, rather, constantly on the move, building and rebuilding themselves over and over again into the same structures.

To understand what the researchers discovered, it is helpful to switch metaphors. Now, rather than envisioning the molecular assemblies as static Quonset huts, think of them as ensembles of ballerinas in constant motion.

"We spent a year trying to describe why these rods orient themselves on the graphite surface," Saville said. "But it turns out that we had imaged the dancers in freeze-frame. What we did not take into account in our original thinking was that micelles on the surface are in constant rotary motion."

Under most conditions, small particles make tiny random movements known as Brownian motion. Powered by Brownian motion, a single surfactant can be thought of as a dancer spinning about on her own; it is impossible to predict the precise pattern of movement

What the researchers discovered was that, when molecules assembled into a micelle and the micellar dancer moved on the graphite "stage," it did so in a choreographed fashion.

Something was overriding the rotary Brownian motion. What was it?

"Saville and his coauthors combined theory at the surfactant and micellar scales with a series of careful experiments to resolve the dilemma," said William Russel, the Arthur W. Marks '19 professor of chemical engineering and dean of the graduate school at Princeton. "Long-range van der Waals forces, which are orientation-dependent, exert a torque on the entire micelle that is strong enough to overcome the randomizing tendency of Brownian motion."

Metaphorical translation: "When micelles appear on the graphite stage, they begin dancing to the music of a van der Waals orchestra," Saville said. The van der Waals interactions - weak links between the electron clouds of the micelles and the graphite below - make the micelles orient in specific directions. Basic work by research associates Je-Luen Li and Jaehun Chun provided a description of the angular variation of the van der Waals interaction and this enabled the group to close the loop.

The scientists said their work opens new horizons to explore. They still have not figured out, for example, how micelles interact with one another on the surface to form large patterned arrays. Or how the micelles disintegrate and reform in the same patterns.

"You need a critical number of dancers for this to happen but we have no idea how many," Aksay said. Moreover, he noted, the researchers can now move on to other interesting questions now that they know that the micelles are dynamic and understand the time frame in which they move. "This opens up the prospect for even more rigorous thinking."

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