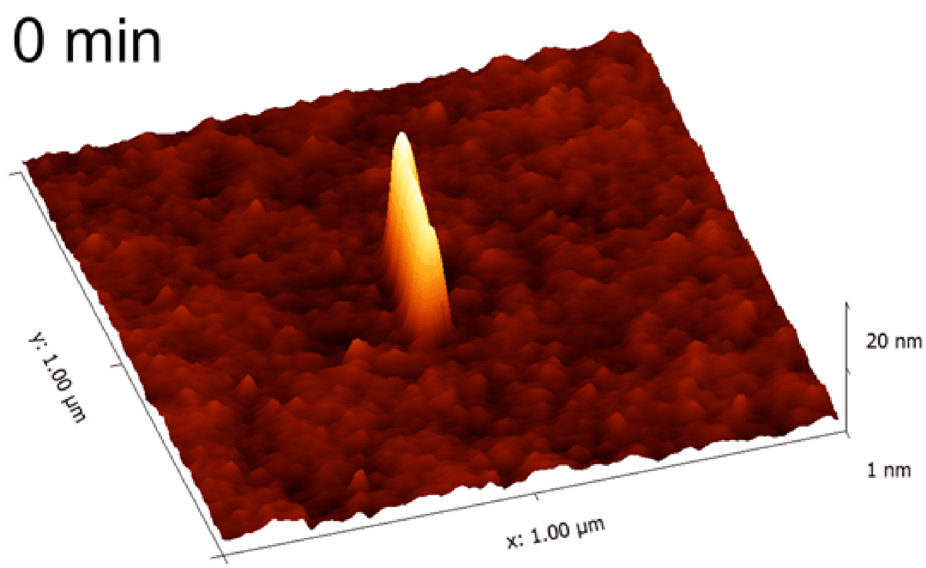
PHYS ORG

# Researchers discover a surprising property of glass surfaces

April 10 2017




A 3D image of the virus on the glass surface. Credit: University of Pennsylvania

Researchers at the University of Pennsylvania have developed a new technique to study the surface of different types of glass. Using this technique, they discovered a surprising property of the top layer of glasses, which could pave the way to developing better glass materials.

The research was led by Yue Zhang, a graduate student in the Department of Chemistry in Penn's School of Arts & Sciences, and

Zahra Fakhraai, assistant professor of chemistry. Zhang received an APS Padden Award for the research, which recognizes excellence in polymer physics research.

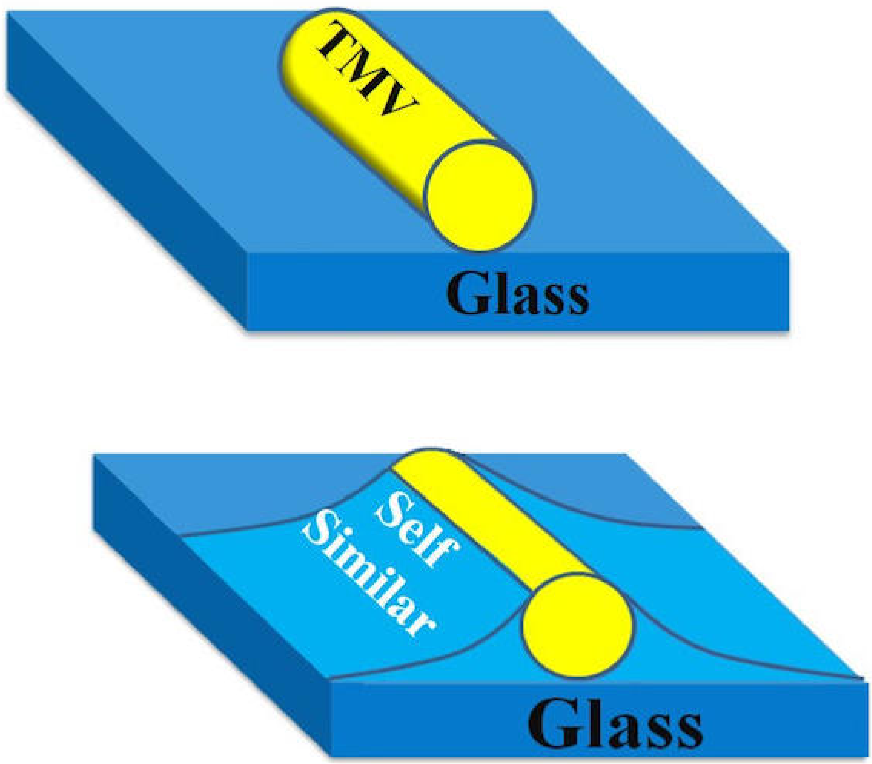
The distinction between crystals and liquids is that, while crystals are ordered and solid, liquids are disordered and can move around to fill whatever container they are in. But if one were to cool a liquid sufficiently, it would remain disordered while the motion of its molecules would slow down so much that it would seem solid. This is how amorphous materials such as glasses form.

Honey, for instance, is a liquid, but when it is refrigerated its properties become more like that of a solid.

The Penn researchers were investigating how interfaces or surfaces, the boundaries between two phases of matter, would affect the properties of glasses. According to Fakhraai, when a free surface is introduced to the material, the motion speeds up again, which propagates into the film.

Even though the honey would seem solid, the molecules in the top 5 or 10 nanometers would remain liquid and moving. If a needle were put on the surface of the honey, it would dip and form a meniscus, allowing the molecules to move around, whereas the same needle would have no effect on a solid.

In a previous paper published in *Soft Matter*, the researchers shrunk this technique down to nanometer length scales using a virus as a needle and watched the surface molecules come in and slowly try to form a meniscus around the virus. While the molecules in the center of the material may take millions of years to move, for the molecules at the top it would be more like a few hundred seconds.




A sketch showing the process of the glass forming a meniscus around the virus. Credit: University of Pennsylvania

"The technique that we developed is really exciting because in the field there are not many techniques to directly probe the surface motions," Zhang said. "Our technique is very efficient and mathematically simple, and we can easily extend it to other systems."

One of the most challenging aspects of developing the technique, Fakhraai said, was figuring out that they could use viruses to probe the materials.

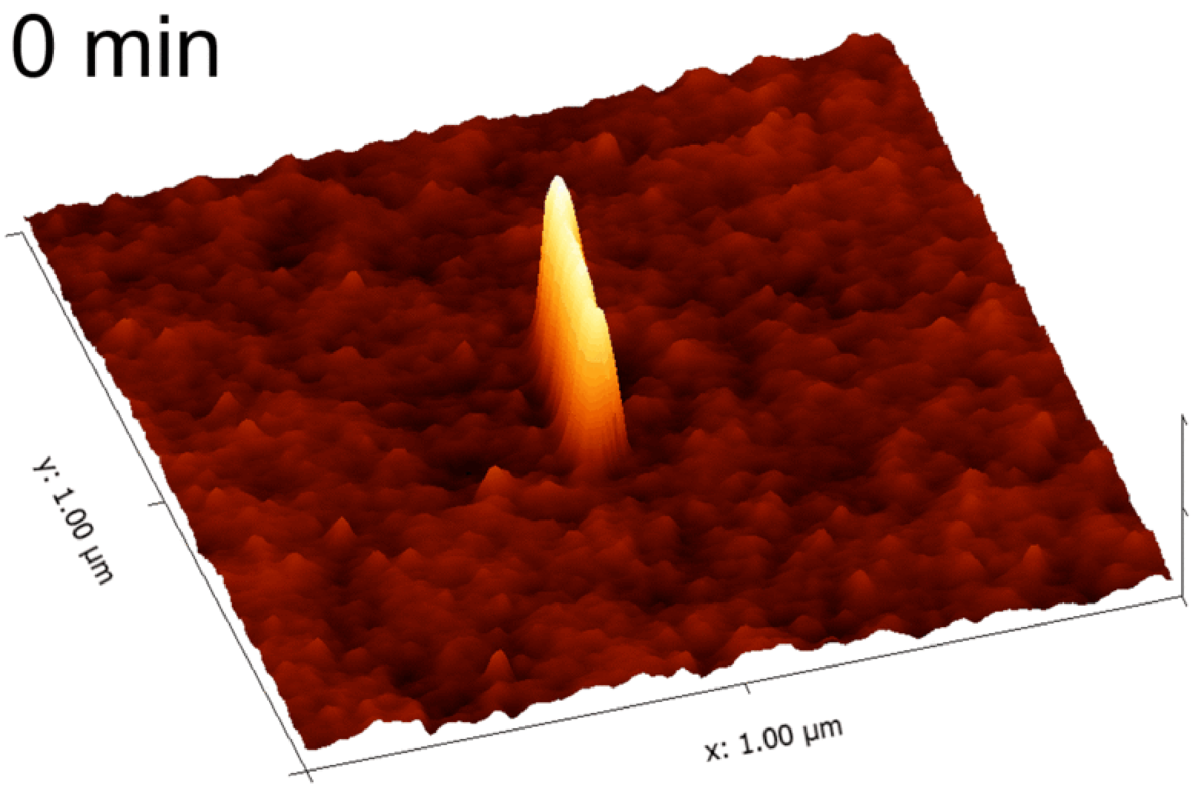
"For a few years we tried to synthesize nanorods that looked like needles and were long and uniform enough," she said. "Viruses are perfect because they have these crystalline structures that are exactly the right dimensions that we need. Thinking about the virus as a nanoparticle really helped us move forward."

Using this technique, the researchers wanted to determine how the motion of the molecules on the free surface is coupled with the motion below. In particular, they wanted to see if the molecules on the surface would be affected if the motion of the molecules beneath them was sped up or slowed down.

In another previous paper published in *Physical Review Letters*, the researchers used different deposition techniques to better pack the molecules and form stable glasses. This made everything extremely slow to the point that it would take longer than the age of the universe for molecules at the center to move.

In their most recent paper, published in the *Proceedings of the National Academy of Sciences*, they sped everything up by making thinner films, which would have more of a free surface.

"Based on many different theories, we would have expected that the motions at the center and the free surface would be coupled together," Fakhraai said. "The example I like to make is if you're say at the front of the parade and you're moving faster, things should follow you. But it doesn't happen that way. The immediate top layer doesn't really couple: Those molecules can move around without affecting whatever's happening behind them."




Meniscus growth on unstable glass. Credit: University of Pennsylvania

These results, she said, were surprising. While there were many different ideas of whether this correlation exists, no one had really measured it before. They found that, no matter what type of motion, the molecules at the top and the molecules at the center have no effect on each other.

The researchers hope to be able to probe the second and third layers, which may be important in the densification process of the materials during deposition, which is the basis of making stable glasses and is of technological importance. Since the molecules at the first layer aren't affected by the motion of the molecules beneath them, the motion of the underlying layers become crucial in the process.

"We think that it's really the molecules at the second layer and third layer that are participating in this densification process, and the molecules at the free surface are just like a sea of free objects that can provide that mobility but don't necessarily participate in the process," Fakhraai said.

They also hope to better understand the transition from the fast moving particles at the surface to the extremely slow moving molecules at the center. People standing at the front of a parade are free to move around, Fakhraai explained, but the deeper you go into the parade, motion becomes more constrained.

"The question is how deep the effect is and how that process comes about," Fakhraai said. "How do I change from something that takes 100 seconds to move to something that takes billions of years? I think that's the next big challenge in the field: to understand that gradient."

According to Fakhraai, investigating this process will allow researchers to not only better understand theories but to improve coatings on materials and design better amorphous materials.

"We understand what sets the clock in the middle of the film, but we don't know what sets the clock for those surface molecules," Fakhraai said. "I think that's something to understand more in the future."

**More information:** Yue Zhang et al. Invariant Fast Diffusion on the Surfaces of Ultrastable and Aged Molecular Glasses, *Physical Review Letters* (2017). DOI: 10.1103/PhysRevLett.118.066101

Yue Zhang et al. Using tobacco mosaic virus to probe enhanced surface diffusion of molecular glasses, *Soft Matter* (2016). DOI:

PHYS.ORG

10.1039/C6SM01566B

Yue Zhang et al. Decoupling of surface diffusion and relaxation dynamics of molecular glasses, *Proceedings of the National Academy of Sciences* (2017). DOI: 10.1073/pnas.1701400114

Provided by University of Pennsylvania