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The Nature of Glass Remains Anything but Clear

By KENNETH CHANG

Correction Appended

It is well known that panes of stained glass in old European churches are thicker at the bottom because glass is a slow-moving liquid that flows downward over centuries.

Well known, but wrong. Medieval stained glass makers were simply unable to make perfectly flat panes, and the windows were just as unevenly thick when new.

The tale contains a grain of truth about glass resembling a liquid, however. The arrangement of atoms and molecules in glass is indistinguishable from that of a liquid. But how can a liquid be as strikingly hard as glass?

“They’re the thickest and gooiest of liquids and the most disordered and structureless of rigid solids,” said Peter Harrowell, a professor of chemistry at the University of Sydney in Australia, speaking of glasses, which can be formed from different raw materials. “They sit right at this really profound sort of puzzle.”

Philip W. Anderson, a Nobel Prize-winning physicist at Princeton, wrote in 1995: “The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition.”

He added, “This could be the next breakthrough in the coming decade.”

Thirteen years later, scientists still disagree, with some vehemence, about the nature of glass.

Peter G. Wolynes, a professor of chemistry at the University of California, San Diego, thinks he essentially solved the glass problem two decades ago based on ideas of what glass would look like if cooled infinitely slowly. “I think we have a very good constructive theory of that these days,” Dr. Wolynes said. “Many people tell me this is very contentious. I disagree violently with them.”

Others, like Juan P. Garrahan, professor of physics at the University of Nottingham in England, and David Chandler, professor of chemistry at the University of California, Berkeley, have taken a different approach and are as certain that they are on the right track.

“It surprises most people that we still don’t understand this,” said David R. Reichman, a professor of chemistry at Columbia, who takes yet another approach to the glass problem. “We don’t understand why glass should be a solid and how it forms.”

Dr. Reichman said of Dr. Wolynes’s theory, “I think a lot of the elements in it are correct,” but he said it was not a complete picture. Theorists are drawn to the problem, Dr. Reichman said, “because we think it’s not solved yet — except for Peter maybe.”

Scientists are slowly accumulating more clues. A few years ago, experiments and computer simulations revealed something unexpected: as molten glass cools, the molecules do not slow down uniformly. Some areas jam rigid first while in other regions the molecules continue to skitter around in a liquid-like fashion. More strangely, the fast-moving regions look no different from the slow-moving ones.

Meanwhile, computer simulations have become sophisticated and large enough to provide additional insights, and yet more theories have been proffered to explain glasses.

David A. Weitz, a physics professor at Harvard, joked, “There are more theories of the glass transition than there are theorists who propose them.” Dr. Weitz performs experiments using tiny particles suspended in liquids to mimic the behavior of glass, and he ducks out of the theoretical battles. “It just can get so controversial and so many loud arguments, and I don’t want to get involved with that myself.”

For scientists, glass is not just the glass of windows and jars, made of silica, sodium carbonate and calcium oxide. Rather, a glass is any solid in which the molecules are jumbled randomly. Many plastics like polycarbonate are glasses, as are many ceramics.

Understanding glass would not just solve a longstanding fundamental (and arguably Nobel-worthy) problem and perhaps lead to better glasses. That knowledge might benefit drug makers, for instance. Certain drugs, if they could be made in a stable glass structure instead of a crystalline form, would dissolve more quickly, allowing them to be taken orally instead of being injected. The tools and techniques applied to glass might also provide headway on other problems, in material science, biology and other fields, that look at general properties that arise out of many disordered interactions.

“A glass is an example, probably the simplest example, of the truly complex,” Dr. Harrowell, the University of Sydney professor, said. In liquids, molecules jiggle around along random, jumbled paths. When cooled, a liquid either freezes, as water does into ice, or it does not freeze and forms a glass instead.

In freezing to a conventional solid, a liquid undergoes a so-called phase transition; the molecules line up next to and on top of one another in a simple, neat crystal pattern. When a liquid solidifies into a glass, this organized stacking is nowhere to be found. Instead, the molecules just move slower and slower and slower, until they are effectively not moving at all, trapped in a strange state between liquid and solid.

The glass transition differs from a usual phase transition in several other key ways. Energy, what is called latent heat, is released when water molecules line up into ice. There is no latent heat in the formation of glass.

The glass transition does not occur at a single, well-defined temperature; the slower the cooling, the lower the transition temperature. Even the definition of glass is arbitrary — basically a rate of flow so slow that it is too boring and time-consuming to watch. The final structure of the glass also depends on how slowly it has been cooled.

By contrast, water, cooled quickly or cooled slowly, consistently crystallizes to the same ice structure at 32 degrees Fahrenheit.

To develop his theory, Dr. Wolynes zeroed in on an observation made decades ago, that the viscosity of a glass was related to the amount of entropy, a measure of disorder, in the glass. Further, if a glass could be formed by cooling at an infinitely slow rate, the entropy would vanish at a temperature well above absolute zero, violating the third law of thermodynamics, which states that entropy vanishes at absolute zero.

Dr. Wolynes and his collaborators came up with a mathematical model to describe this hypothetical, impossible glass, calling it an “ideal glass.” Based on this ideal glass, they said the properties of real glasses could be deduced, although exact calculations were too hard to perform. That was in the 1980s. “I thought in 1990 the problem was solved,” Dr. Wolynes said, and he moved on to other work.

Not everyone found the theory satisfying. Dr. Wolynes and his collaborators so insisted they were right that "you had the impression they were trying to sell you an old car," said Jean-Philippe Bouchaud of the Atomic Energy Commission in France. "I think Peter is not the best advocate of his own ideas. He tends to oversell his own theory."

Around that time, the first hints of the dichotomy of fast-moving and slow-moving regions in a solidifying glass were seen in experiments, and computer simulations predicted that this pattern, called dynamical heterogeneity, should exist.

Dr. Weitz of Harvard had been working for a couple of decades with colloids, or suspensions of plastic spheres in liquids, and he thought he could use them to study the glass transition. As the liquid is squeezed out, the colloid particles undergo the same change as a cooling glass. With the colloids, Dr. Weitz could photograph the movements of each particle in a colloidal glass and show that some chunks of particles moved quickly while most hardly moved.

"You can see them," Dr. Weitz said. "You can see them so clearly."

The new findings did not faze Dr. Wolynes. Around 2000, he returned to the glass problem, convinced that with techniques he had used in solving protein folding problems, he could fill in some of the computational gaps in his glass theory. Among the calculations, he found that dynamical heterogeneity was a natural consequence of the theory.

Dr. Bouchaud and a colleague, Giulio Biroli, revisited Dr. Wolynes's theory, translating it into terms they could more easily understand and coming up with predictions that could be compared with experiments. "For a long time, I didn't really believe in the whole story, but with time I became more and more convinced there is something very deep in the theory," Dr. Bouchaud said. "I think these people had fantastic intuition about how the whole problem should be attacked."

For Dr. Garrahan, the University of Nottingham scientist, and Dr. Chandler, the Berkeley scientist, the contrast between fast- and slow-moving regions was so striking compared with the other changes near the transition, they focused on these dynamics. They said that the fundamental process in the glass transition was a phase transition in the trajectories, from flowing to jammed, rather than a change in structure seen in most phase transitions. "You don't see anything interesting in the structure of these glass formers, unless you look at space and time," Dr. Garrahan said.

They ignore the more subtle effects related to the impossible-to-reach ideal glass state. "If I can never get there, these are metaphysical temperatures," Dr. Chandler said.

Dr. Chandler and Dr. Garrahan have devised and solved mathematical models, but, like Dr. Wolynes, they have not yet convinced everyone of how the model is related to real glasses. The theory does not try to explain the presumed connection between entropy and viscosity, and some scientists said they found it hard to believe that the connection was just coincidence and unrelated to the glass transition.

Dr. Harrowell said that in the proposed theories so far, the theorists have had to guess about elementary atomic properties of glass not yet observed, and he wondered whether one theory could cover all glasses, since glasses are defined not by a common characteristic they possess, but rather a common characteristic they lack: order. And there could be many reasons that order is thwarted. "If I showed you a room without an elephant in the room, the question 'why is there not an elephant in the room?' is not a well-posed question," Dr. Harrowell said.

New experiments and computer simulations may offer better explanations about glass. Simulations by Dr. Harrowell and his co-workers have been able to predict, based on the pattern of vibration frequencies, which areas were likely to be jammed and which were likely to continue moving. The softer places, which vibrate at lower frequencies, moved more freely.

Mark D. Ediger, a professor of chemistry at the University of Wisconsin, Madison, has found a way to make thin films of glass with the more stable structure of a glass that has been "aged" for at least 10,000 years. He hopes the films will help test Dr. Wolynes's theory and point to what really happens as glass approaches its ideal state, since no one expects the third law of thermodynamics to fall away.

Dr. Weitz of Harvard continues to squeeze colloids, except now the particles are made of compressible gels, enabling the colloidal glasses to exhibit a wider range of glassy behavior.

"When we can say what structure is present in glasses, that will be a real bit of progress," Dr. Harrowell said. "And hopefully something that will have broader implications than just the glass field."

This article has been revised to reflect the following correction:

Correction: July 31, 2008
An article on Tuesday about the nature of glass described incorrectly the phase transition from water to ice. When water molecules are lined up into ice, energy (called latent heat) is released. The phase transition does not require energy to line up the molecules. (In the phase transition for glass, there is no latent heat.)