Physicists shatter stubborn mystery of how glass forms

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Credit: Lynn Greyling/public domain

A physicist at the University of Waterloo is among a team of scientists who have described how glasses form at the molecular level and provided a possible solution to a problem that has stumped scientists for decades.

Their simple theory is expected to open up the study of glasses to non-experts and undergraduates as well as inspire breakthroughs in novel nanomaterials.

The paper published by physicists from the University of Waterloo, McMaster University, ESPCI ParisTech and Université Paris Diderot appeared in the prestigious peer-reviewed journal, *Proceedings of the National Academy of Sciences* (*PNAS*).

Glasses are much more than silicon-based materials in bottles and windows. In fact, any solid without an ordered, crystalline structure—metal, plastic, a polymer—that forms a molten liquid when heated above a certain temperature is a glass. Glasses are an essential material in technology, pharmaceuticals, housing, renewable energy and increasingly nano electronics.

"We were surprised—delighted—that the model turned out to be so simple," said author James Forrest, a University Research Chair and professor in the Faculty of Science. "We were convinced it had already been published."

The theory relies on two basic concepts: molecular crowding and string-like co-operative movement. Molecular crowding describes how molecules within glasses move like people in a crowded room. As the number of people increase, the amount of free volume decreases and the slower people can move through the crowd. Those people next to the door are able to move more freely, just as the surfaces of glasses never actually stop flowing, even at lower temperatures.

The more crowded the room, the more you rely on the co-operative movement with your neighbours to get where you're going. Likewise, individual molecules within a glass aren't able to move totally freely. They move with, yet are confined by, strings of weak molecular bonds

with their neighbours.

Theories of crowding and cooperative movement are decades old. This is the first time scientists combined both theories to describe how a liquid turns into a glass.

"Research on glasses is normally reserved for specialists in condensed matter physics," said Forrest, who is also an associate faculty member at Perimeter Institute for Theoretical Physics and a member of the Waterloo Institute for Nanotechnology. "Now a whole new generation of scientists can study and apply glasses just using first-year calculus."

Their theory successfully predicts everything from bulk behaviour to surface flow to the once-elusive phenomenon of the glass transition itself. Forrest and colleagues worked for 20 years to bring theory in agreement with decades of observation on glassy materials.

An accurate theory becomes particularly important when trying to understand glass dynamics at the nanoscale. This finding has implications for developing and manufacturing new nanomaterials, such as glasses with conductive properties, or even calculating the uptake of glassy forms of pharmaceuticals.

More information: Cooperative strings and glassy interfaces, Thomas Salez, DOI: 10.1073/pnas.1503133112

Abstract
We introduce a minimal theory of glass formation based on the ideas of molecular crowding and resultant string-like cooperative rearrangement, and address the effects of free interfaces. In the bulk case, we obtain a scaling expression for the number of particles taking part in cooperative strings, and we recover the Adam–Gibbs description of glassy dynamics. Then, by including thermal dilatation, the Vogel–Fulcher–Tammann

relation is derived. Moreover, the random and string-like characters of the cooperative rearrangement allow us to predict a temperature-dependent expression for the cooperative length ξ of bulk relaxation. Finally, we explore the influence of sample boundaries when the system size becomes comparable to ξ. The theory is in agreement with measurements of the glass-transition temperature of thin polymer films, and allows quantification of the temperature-dependent thickness hm of the interfacial mobile layer.

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