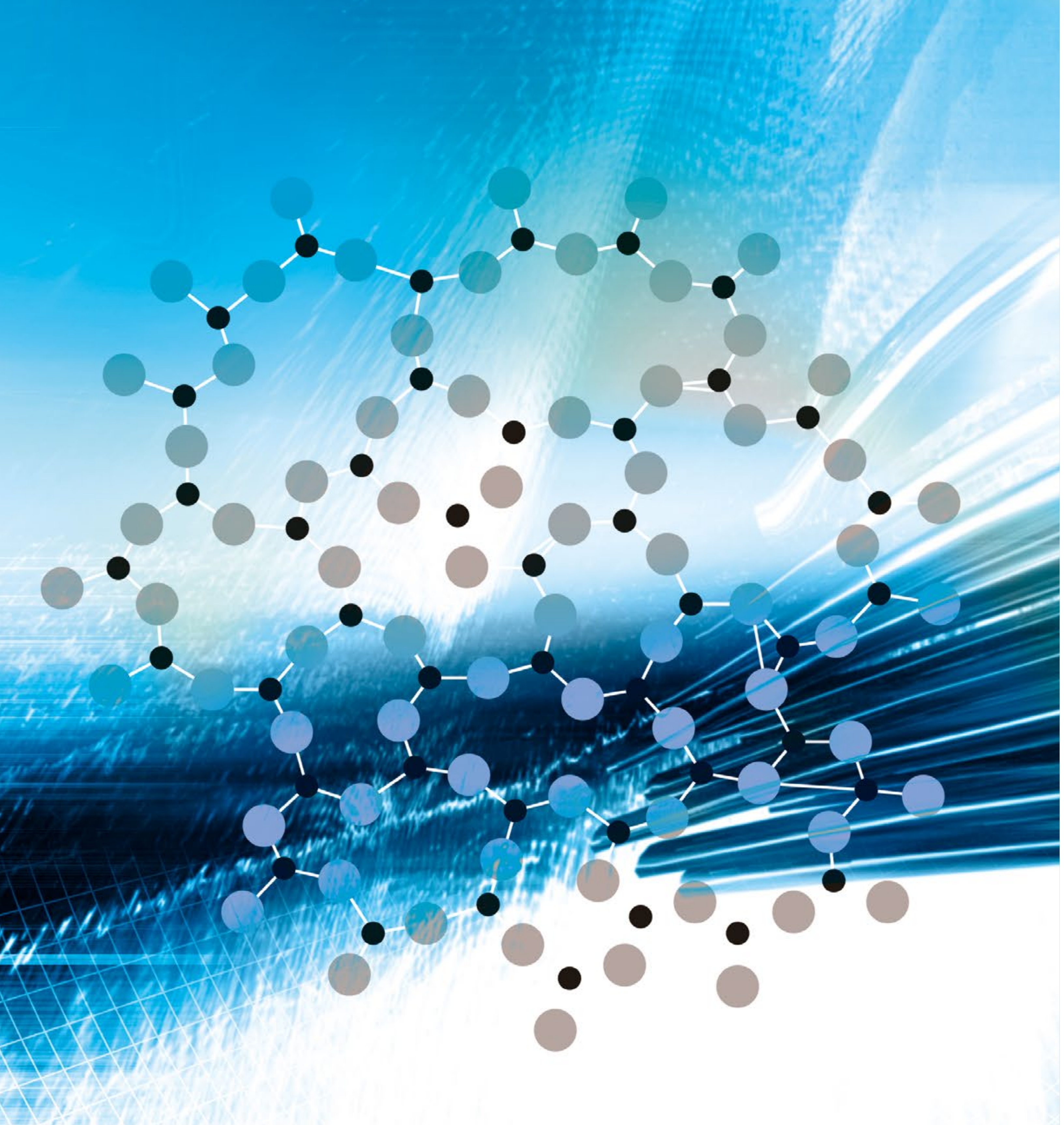
Understanding glassy dynamics



Dr Nussinov and **Dr Kelton** are professors at Washington University in Saint Louis. **Dr Weingarter** recently completed his PhD studies in Dr Nussinov's group. A shared passion of these three researchers concerns the nature of one of the most common states of matter – glass. A deeper theoretical understanding of glasses may, in turn, lead to numerous applications. Apart from improving age-old studied silicate glasses (such as those used in windows), an understanding of the structure and dynamics of glasses might also have profound ramifications to the many varied and far more recently discovered glass formers currently appearing across diverse arenas. These applications include those of bioactive materials, new drug design (organic glasses are more soluble than crystals), and various industries.

One of the most interesting, yet challenging issues in physics is the enigmatic behaviour of glasses. These complex systems can be contrasted with the far better understood ordered crystals. Glasses are rigid. However, unlike crystals, glasses are not neatly ordered.

The periodic, ordered structures of crystals have long captivated scientists. In the 17th century, long before the discovery of the atom, prominent scientists such as Robert Hooke (an astronomer, physicist and first biologist to coin the term "cell"), Christiaan Huygens (a mathematician, physicist, and inventor of the first reliable pendulum clock) and their contemporaries proposed that the sharp facets of single crystals resulted from recurrent fundamental unit cell configurations. Indeed, as we now know, in simple crystals, the structure of extremely small atomic unit cells is replicated to span the entire system. In essence, this replication endows large crystals with quantum mechanical behaviours.

Traditionally, quantum mechanics describes very small spatial scales (e.g., single atoms and molecules). However, thanks to the periodic locations of atoms in a crystal, quantum mechanics comes to life on the very large spatial scale of the entire crystal; the well known quantum energy levels of electrons in single atoms lead to an analogous "band structure" in crystals. Indeed, the invention of solar cells and the transistor was made possible by the understanding of these precise band structures.

Inspired by these and other well known successes, Dr Nussinov initially proposed that (like crystals) the behaviours of glass formers might also be more readily understood within a quantum mechanical framework and provided a prediction for their viscosity. An intense pursuit followed in which the combined theory-experiment team of the three researchers and their collaborators examined the viscosities of all known glass formers and, to their delight, found that these conform to the theory's predictions. Additional aspects and new related ideas were introduced and critically studied by the team (many of which are detailed at length in Dr Weingarter's recent PhD thesis).

WHAT, PRECISELY, ARE SUPERCOOLED LIQUIDS AND GLASSES?

In principle, and provided that they are sufficiently rapidly cooled (so-called

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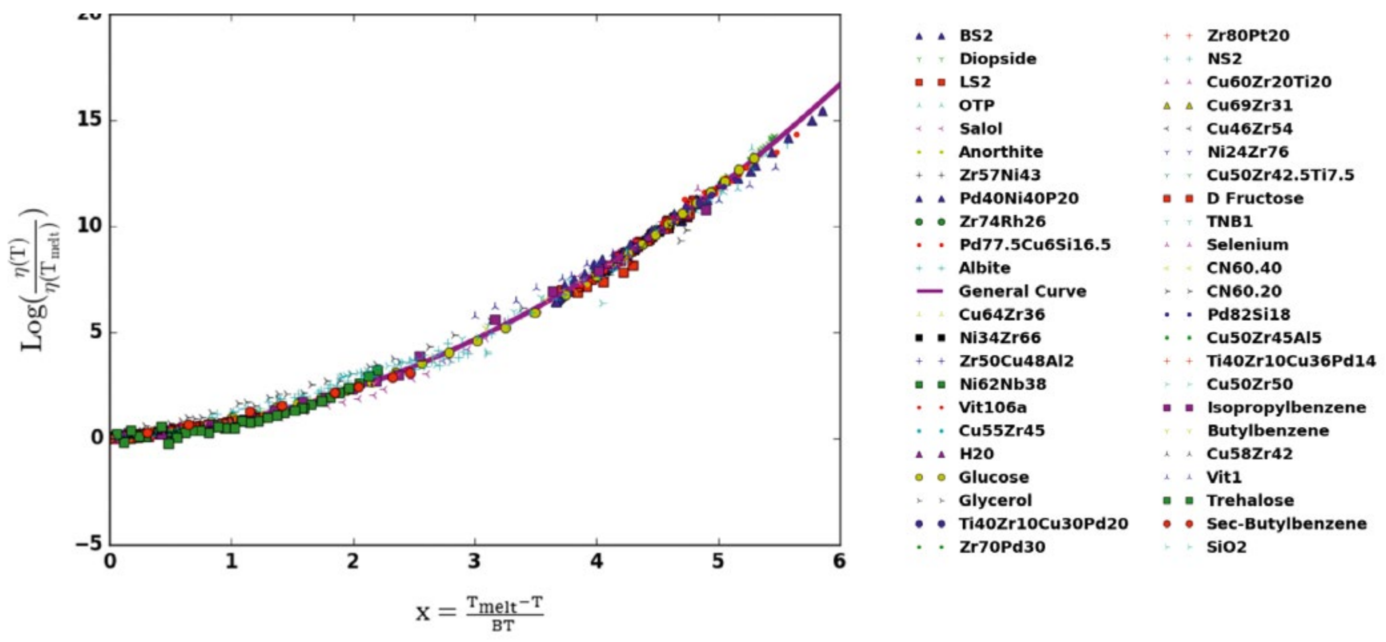

"supercooled") below their melting point (temperature), all liquids in nature will form glasses owing to the fact that there is insufficient time for them to crystallise, and thus they will not form an ordered solid. Pure bottled water may also be supercooled in household freezers, allowing for interesting stunts (such as crystallisation into a column of ice upon tapping or pouring onto a hard surface). The viscosity of some supercooled liquids (i.e., their resistance to flow) can increase by fifteen orders of magnitude for just a modest temperature drop. Once a supercooled liquid has become sufficiently viscous at low enough temperatures, flow ceases and it behaves as an amorphous rigid solid – a "glass".

UNIVERSAL GLASSY DYNAMICS

Understanding the nature of glassy dynamics is one of the few remaining unsolved and challenging issues in condensed matter physics, thus demonstrating the importance of the team's research. In fact, to highlight the emphasis put on this subject by the scientific community, Philip Anderson, who was awarded a Nobel Prize in Physics (1977), described glassy dynamics and glass transition as "the deepest and most interesting unsolved problem in solid state theory".

Over the decades, there have been numerous attempts to rationalise the behaviours of glasses. Usually these approaches appeal to various special parameters and putative temperatures. It has been a long held belief that (apart from their appearance in "reduced glass temperature" ratios) the standard equilibrium melting transition temperatures play no direct role in the formation of glasses.

The theory studied by the three researchers and their collaborators questions this belief. Unlike other approaches, the new theory does not assume that special exotic states, radically different from those in equilibrium systems, are needed in order to characterise glasses. The core guiding principle of the theory is that the same complete set of many body atomic states (quantum mechanical "eigenstates" or classical "microstates") is sufficient to describe both (1) the supercooled liquids and (2) the equilibrium systems. A logical corollary of this principle enabled the prediction of all observable properties of glasses in terms of those of equilibrium systems. Consequently, the equilibrium melting temperature is of paramount importance.

The figure above demonstrates the collapse of all measured viscosities of known supercooled liquids onto a universal curve. The solid "General Curve" is the prediction of the theory; all other points are given by experiments. The logarithmic scale of the vertical axis corresponds to the ratio of the viscosity η of each supercooled liquid at a temperature T divided by the viscosity of that supercooled fluid at its equilibrium melting temperature T_{melt}; note that this ratio varies by a factor of ~ 10^{16} (i.e., ten million billion or ten quadrillion) over the entire range – the viscosity of the glass can be far larger than of the supercooled fluid at its equilibrium melting temperature. The dimensionless constant B ~ 0.1 does not vary significantly from fluid to fluid. Similar behaviour appears for the relaxation times measured for other fluids.

In particular, according to this new theory, the viscosity of all glassformers should collapse onto a universal curve with the only important temperature scale indeed being that of equilibrium melting. As demonstrated by the team, the viscosity and relaxation data of 66 different liquids precisely collapse onto such a single scaling curve, thus suggesting a universal dynamic behaviour of supercooled liquids. Regardless of the theory that led to it, the collapse found by the team points to a previously overlooked link between equilibrium physics and glassy dynamics. Earlier studies of the team and their collaborators unveiled how solid-like rigid structures appear and grow as the temperature of the supercooled liquid drops.

The work of the researchers intends to provide distinct answers and a valid theoretical framework to one of the most puzzling topics in condensed matter physics. Providing a clear understanding of the true nature of glassy systems will revolutionise the way we look at and use glasses and might offer a plethora of underlying industrial applications.

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Q&A

On which sectors of industry or research will this new knowledge of glassy dynamics have a profound impact?

Glassy dynamics are ubiquitous. Due to their importance and universal prevalence, glasses are studied by physicists, chemists, materials scientists, and geologists. Industries rely on glasses for numerous applications. Concepts from glass and "spin-glass" physics have also led to potent algorithms for combinatorial optimisation and other computer science problems. Apart from structural glasses, similar dynamics appear in various electronic and magnetic systems. In principle, all liquids in nature can become glassy on supercooling. Our ideas and found universal collapse of the relaxation time are general, simple, and may apply for all liquids and glasses studied in industry and academia.

What are the current limitations in research that have not allowed for a better understanding of glassy dynamics?

Numerical simulations are hampered by long convergence time (indeed a quintessential feature of glassy systems is their sluggish motion). Earlier theories studied dynamics in high dimensional "energy landscapes" and hydrodynamics with memory effects. The difficulty underlying such approaches is that glasses involve many atoms. Direct calculations are impossible so various models and approximations were advanced. We aim to bypass these problems by using nature's own solutions. That is, the equilibrium characteristics of the very same many-atom systems are known empirically. This information is then used to predict characteristics of supercooled liquids and glasses as averages of their equilibrium values.

How can we have the capacity to manufacture new structural materials based on the knowledge of glassy dynamics?

The current research suggests a link between equilibrium and glassy dynamics in all glassformers. Beyond the research discussed here, machine learning techniques used by ourselves and many others may suggest which new materials could be most suitable for manufacturing purposes. Additionally, viscosity plays a critically important role in glass formation through the dynamics of the crystal nucleation and growth (see next question). The ability to predict the temperature dependence of the viscosity from sparse data (which is possible from our results) may enable better control of nucleation and growth during cooling.

What are the basic principles of supercooling a liquid to form a glass?

To form a glass, one needs to supercool a liquid rapidly enough that crystallisation is bypassed and ultimately, at sufficiently low temperatures, the viscosity exceeds a critical threshold; the system then becomes rigid on typical observations scales. This rigid amorphous state is called the "glass". How fast one needs to cool in order to achieve a glass depends on the system. For some materials such as silicates (that form window glasses), a relatively modest cooling rate suffices while for other systems (such as metallic liquids) far more rapid cooling may be necessary.

What more is needed so that you and your team can have solid evidence for introducing this theory about the true nature of glassy systems?

Our theory enables the calculation of any property of the glass as an appropriately weighted average of the equilibrium property. If various data become available on a specific supercooled liquid system, then one will be able to test whether the same weighted average may account in unison for all measured properties of the liquid. Thus far, we have largely tested dynamical data.

Detail

RESEARCH OBJECTIVES

Dr Nussinov, Dr Weingartner and Dr Kelton's collaborative work has focused on the structure of glasses.

FUNDING

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COLLABORATORS

Dr Flavio Nogueira; Dr Christopher Pubelo

BIO

Zohar Nussinov received his BSc from Tel-Aviv University and his PhD from UCLA. He has held postdoctoral positions at the Lorentz Institute and at Los Alamos National Laboratory. Since 2005, he has been a member of the physics department at Washington University, St Louis (where he is currently an Associate Professor).

Kenneth F Kelton received his PhD from Harvard University in 1983. He is Professor of Physics and the Arthur Holly Compton Professor in Arts & Sciences at Washington University in St Louis, and is a Fellow of the American Physical Society.

Nicholas Weingartner received his BSc from Saint Louis University in 2012, and his PhD from Washington University in 2017. He currently holds a position as a Modeling Analyst in the Underwriting, Research, and Control department of the GEICO home office.

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