

Molecular hopping in solid-like liquids

Understanding the self-diffusion and viscosity of liquid molecules

To fully understand how liquids flow, it is crucial for researchers to build models which can accurately recreate their behaviours on molecular scales – yet since the time of Newton, the complexities involved have presented numerous challenges. In their research, Prof Russ Keanini, Prof Peter Tkacik and Prof Jerry Dahlberg at the University of North Carolina, Charlotte, present new ways to understand the physical mechanisms which take place as liquid molecules ‘hop’ between confining ‘cages’ of surrounding molecules. Through their novel ‘self-diffusion’ model, these findings could soon lead to new advances in fields ranging from chemistry and cellular biology to cosmology and high-energy physics.

Of the three states of matter that surround and compose us, liquids are undoubtedly the most unusual. In solids, atomic and molecular building blocks are tightly packed together and can only move through limited vibrations called phonons. Meanwhile, the building blocks of gases are separated by comparatively large distances and are free to move in any direction. As Prof Russ Keanini, at the University of North Carolina, explains, liquids can exhibit elements of both of these properties – allowing them to move around freely, but with certain mechanisms restricting their movements.

‘While liquid-state molecules are tightly packed together, they are not tightly bound like molecules in solids’, he says. ‘Loose packing gives rise to one of the characteristic properties of liquids: ubiquitous and perpetual hopping of individual molecules from loosely bound cages of surrounding molecules.’ This mechanism has been widely studied for decades, but even now, many of the key characteristics of cage-hopping motions remain a mystery. In their research, Prof Keanini and his colleagues Prof Peter Tkacik and Prof Jerry Dahlberg aim to explore these intriguing mechanisms in detail.

HOPPING BETWEEN CAGES

Ultimately, the tendency of a molecule to hop between cages – a behaviour called ‘self-diffusion’ – is sensitive to several physical features. Among these are the molecule’s mass, the electrostatic and quantum forces exerted by surrounding molecules, and the temperature of the overall liquid. To study liquids in detail, it would be

incredibly useful for researchers to recreate their behaviours in robust physical models. So far, however, their efforts have been hindered by the immense complexity involved in capturing such vast quantities of inter-molecular interactions – making accurate simulations extremely difficult.

Through their research, Prof Keanini’s team have discovered new ways to describe the cage-hopping process physically, without the need to account for all interactions individually. ‘Over any given time span, and over any volume of liquid, the random motion of molecules within the volume can be pictured as the summed motion of an infinite set of wave-like phonons, traveling through the volume’, Prof Keanini describes. Using this picture, the researchers have now gleaned important new insights into how liquids behave on molecular scales and identified the precise mechanisms required for them to hop between cages.

MODELS FOR SELF-DIFFUSION

In their latest study, the researchers have expressed the phonon wave motions in a manner similar to the way Einstein pictured phonon waves in solids. However, ‘in liquids, this solid-like motion produces short-lived molecular cages in which soon-to-hop individual molecules become trapped’, Prof Keanini illustrates. ‘Hopping takes place when the trapped molecule impacts one of its cage molecules.’ When this happens, the trapped molecule will impart some of its kinetic energy, displacing the position of the cage molecule it collides with. Therefore, if its kinetic energy is large enough, the

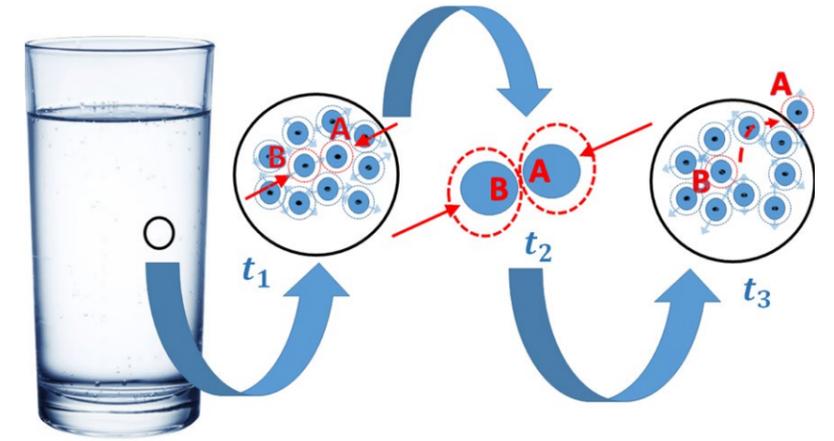
molecule can escape from its cage and hop into another, surrounded by a different group of molecules. Yet, while all of this takes place on imperceptibly fast timescales, the characteristics of the cage-hopping process are far from uniform across all liquids.

Within their models, the collective motions of uncountable numbers of cage-hopping molecules can be approximated to a high degree of accuracy. To fine-tune their predictions, the team incorporated an expansive set of results from both experiments and theoretical studies, carried out over the past 50 years. Through further analysis, they discovered that the molecular motions within their models could be directly compared with those of the more restricted molecules found within solids.

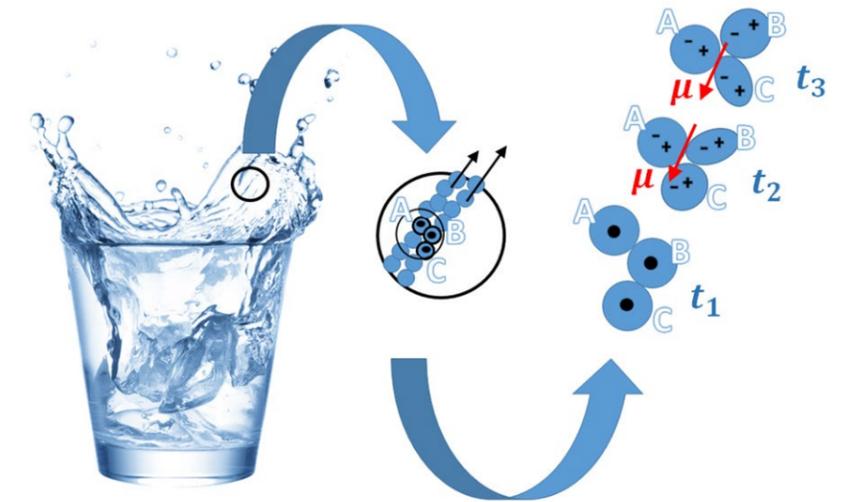
ORIGINS OF VISCOSITY

In the wider field of fluid dynamics, one particularly long-standing mystery surrounding the behaviour of liquids stems from the physical origins of viscosity. Essentially, this quantity is a measure of the ‘stickiness’ of a liquid or, in more scientific terms, of how resistant it is to deformation at a given rate over time. At first, it seems logical to assume that we can gain a fairly accurate picture of a liquid’s viscosity by simply touching it with our fingertips and feeling how readily it deforms as we swirl it around. However, a debate remains over whether the viscosity we feel actually corresponds to the viscosity experienced by individual molecules as they interact with surrounding molecules via electrostatic and quantum forces.

Only adding to the mystery is the fact that the viscosity of a liquid varies widely with the temperature of its surrounding environment. At warmer temperatures, molecules possess more kinetic energy, allowing them to hop between cages more readily – complicating the situation further. ‘While experiments and mathematical models continue to be developed, a deep understanding of the molecular-scale, electrostatic and quantum mechanical origins of viscosity have remained elusive’, Prof Keanini explains. In addition to their new



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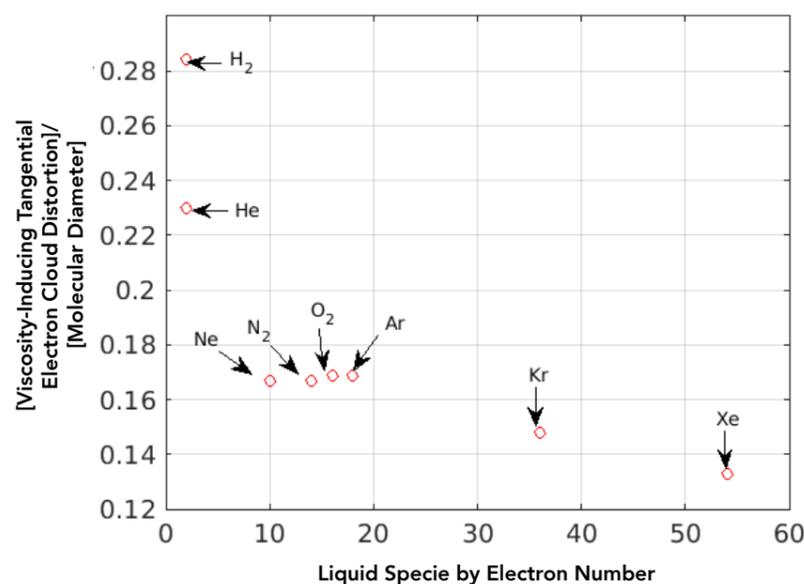
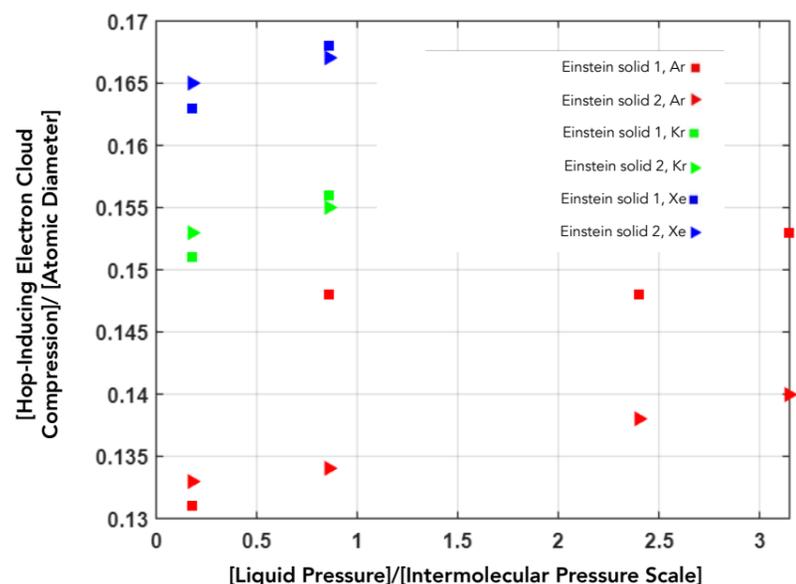
models of self-diffusion, Prof Keanini and his colleagues have also now shed new light onto how the viscosity we experience on large scales emerges on molecular scales.

CONNECTIONS TO NEWTON’S LAWS

To answer this question, we must consider how the frictional forces experienced by individual molecules are connected to the viscosity

surrounding them. If a dust grain were dropped inside an air-filled room, the speed at which the grain sinks could be calculated according to Newton’s laws of motion – which account for the friction imparted by mechanical collisions between air molecules and the grain. In their study, Prof Keanini’s team showed how these rules are tied to the electrostatic and quantum forces acting on individual molecules, despite molecules being orders of magnitude

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smaller than dust grains. Physically, the team showed that friction experienced by individual molecules emerges during collision with other molecules, due to stretching of the molecule's electron cloud.

By applying their new models of molecular self-diffusion and viscosity generation, the researchers can finally draw clear links between cage-hopping behaviours and the Newtonian mechanics we observe on far larger

scales. 'Our particle-based model corresponds to a more comprehensive version of Newton's law, applied to a single molecule', Prof Keanini explains. Likewise, 'our field-based model captures the average motion of a virtual molecule, subject to known thermodynamic laws, as well as the laws of mass, momentum, and energy conservation.' These results reveal for the first time that the viscosity we feel with our fingertips is indeed slightly different than that experienced by single molecules. In particular, the team drew the first clear links between this large-scale stickiness and the frictional forces experienced by single molecules in liquids.

SOLVING DIVERSE PROBLEMS

Prof Keanini and his colleagues now hope that the answers provided by their self-diffusion and viscosity models will be just the first step towards a potentially expansive range of applications: exploring both the fundamental properties of liquids and their application in cutting-edge research. 'Gaining a deep understanding of the forces producing random, self-diffusive hops, as well as the viscous frictional forces retarding molecular motion bears centrally on an array of scientifically and technologically important problems', Prof Keanini concludes.

In one area, the self-diffusion and viscosity models could help chemists better understand the roles of liquid reactants and products involved in chemical reactions. Elsewhere, these may enable biologists to study how liquids flow through microscopic channels within cells – a key feature of many living organisms. For physicists, the team's results could lead to designs for better liquid-based detectors for picking up cosmological radiation and theoretical dark matter particles, as well as the products of high-energy collisions within particle accelerators. Even further, they could help geologists and astronomers to study the corrosion and weathering of geological features – including the surfaces of distant planets and moons. Such a diverse array of potential applications clearly demonstrates how useful a more advanced understanding of cage hopping and viscous friction could be.

Behind the Research



Dr Russ Keanini

E: rkeanini@uncc.edu

T: +1 704-687-8336

W: <https://coefs.uncc.edu/rkeanini/>



Dr Peter Tkacik

E: ptkacik@uncc.edu

T: +1 704-687-8114

W: <https://coefs.uncc.edu/ptkacik/>



Dr Jerry Dahlberg

E: jdahlbe2@uncc.edu

T: +1 704-687-1394

W: <https://coefs.uncc.edu/jdahlbe2/>

Detail

Russ Keanini
Department of Mechanical Engineering and Engineering Science
University of North Carolina at Charlotte
9201 University City Blvd.
Charlotte, NC 28223-0001
USA

Bio

Russ Keanini is a Professor in the Department of Mechanical Engineering and Engineering Science at UNC Charlotte. He received his PhD in Mechanical Engineering from the University of California, Berkeley, and was a 2020 recipient of the Geological Society of America's Kirk Bryan Award in Geomorphology. His current research focuses on single molecule dynamics in liquids, subcritical fracture in rock, and the non-equilibrium statistical mechanics of vibration-driven grain beds.

Peter Tkacik is Professor of Mechanical Engineering and Engineering Science at the University of North Carolina at Charlotte, where he was a recent recipient of the Bonnie E. Cone Early-Career Professorship in Teaching. He also holds an appointment in the Department of Biomedical Engineering at the Wake Forest School of Medicine, and prior to joining UNC Charlotte he was Vice President of Engineering for Carastar Industries.

Jerry Dahlberg is an Assistant Teaching Professor in the William States Lee College of Engineering at the University of North Carolina at Charlotte. Prior to joining UNC Charlotte, he served for 21 years in the U. S. Army. He currently serves as the Senior Design Committee Chair and conducts research in experimental fluid dynamics.

Funding

- Office of Naval Research, grant N00014-18-1-2754
- National Science Foundation and the US-Israel Binational Science Foundation, grant 1839148

Collaborators

- Missy Eppes (UNC Charlotte)
- Kenneth Ortega (University of Colorado at Denver)
- Susan Trammel (UNC Charlotte)

Research Objectives

Profs Keanini, Tkacik and Dahlberg study the behaviour of liquids at the molecular level.

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Personal Response

Could the new self-diffusion help researchers to design new liquids for advanced applications?

// A great question! Yes, I think with the powerful tools available in computational chemistry, new liquids could be designed, for example having low viscosity and enhanced self-diffusivity – both advantageous in molecule- and cell-scale drug delivery. //

