

GLASSES

Heirs of liquid treasures

The temperature dependence of the viscosity of most glass-forming liquids is known to depart significantly from the classical Arrhenius behaviour of simple fluids. The discovery of an unexpected correlation between the extent of this departure and the Poisson ratio of the resulting glass could lead to new understanding of glass ageing and viscous liquid dynamics.

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A glass is a non-crystalline solid that is formed through the cooling of a highly viscous liquid. As such a liquid cools through its glass transition, its molecules lose their mobility and freeze into place to form the disordered structure of the resulting glass¹. Obviously, the liquid molecular arrangement at the transition temperature has a determining influence on the properties of the solid such as density and short-range order; this indeed is manifest in glassy systems like window glass, polymers, sugars and metallic glasses. In a recent report in *Nature*, however, Vladimir Novikov and Alexei Sokolov demonstrate a much more unexpected and subtle inheritance in the properties of glasses². They find that the Poisson ratio of a glassy material is determined by the viscous character of the liquid phase that precedes glass formation.

When a cylinder of a material such as rubber is compressed along its axis, common experience says that it should expand radially from this axis. This everyday phenomenon is embodied by the material's Poisson ratio, which is defined as the relative transverse expansion divided by the relative compression in the direction of an applied force. Most materials have a positive Poisson ratio of between 0, for which no lateral expansion occurs, and 0.5, for which the expansion acts to keep the total volume of the solid constant. Cork has a Poisson ratio of close to 0, most steels are around 0.3, and rubber is close to 0.5. For glassy materials, Novikov and Sokolov now demonstrate a surprising correlation between Poisson's ratio and deviations in the behaviour of the viscosity of a material's molten phase from an Arrhenius-like temperature dependence.

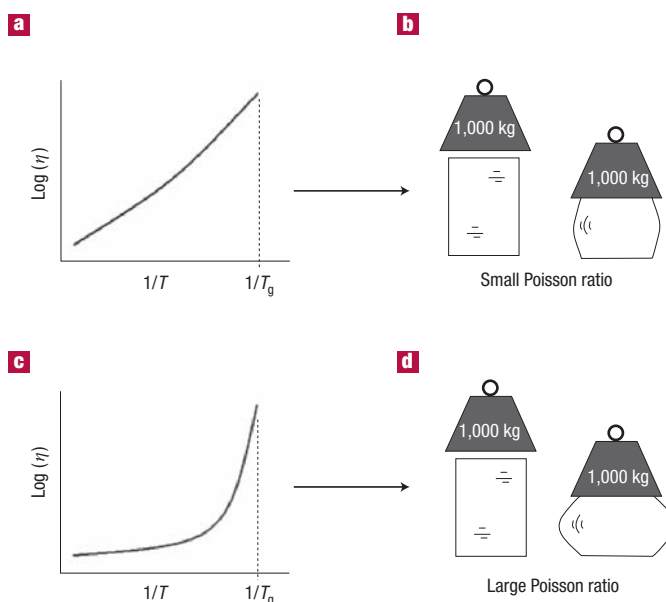


Figure 1 Correlation between the temperature (T) dependence of the shear viscosity (η) of a glass-forming liquid and Poisson's ratio of the resulting glass. **a**, The temperature dependence of a 'strong' glass-forming liquid follows an almost straight line (Arrhenius behaviour) on a plot of $\log(\eta)$ versus $1/T$. **b**, The resulting glass possesses a small Poisson ratio. **c**, In contrast, the $\log(\eta)$ versus $1/T$ behaviour of a 'fragile' glass-forming liquid exhibits a superlinear (non-Arrhenius) behaviour that increases steeply near the glass transition point (T_g). **d**, The resulting glass possesses a large Poisson ratio.

Classical models of fluid behaviour suggest that the viscosity of a fluid, η , varies exponentially with the inverse temperature, $1/T$. A plot of $\log(\eta)$ versus $1/T$ should yield a perfectly straight line according to the famous Arrhenius law. For typical glass-forming liquids, however, the $\log(\eta)$ versus $1/T$ dependence

risers sharply as the glass transition is approached — in some cases exhibiting a tenfold increase in viscosity for a temperature decrease of just 1%. This almost universal deviation from the Arrhenius law — a behaviour that is referred to as a liquid's 'fragility' — constitutes perhaps the single most puzzling feature of glass-forming liquids. We now learn that this treasured liquid property leaves an unexpected 'fingerprint' frozen into the glass. The few glasses like pure silica, which almost obey the Arrhenius law in the liquid phase, have low Poisson ratios. In contrast, glasses formed by cooling organic liquids like salol (phenyl salicylate), which deviate strongly from the Arrhenius law, have large Poisson ratios. In general terms, Poisson's ratio is larger the more non-Arrhenius the liquid is (see Fig. 1).

A correlation is not necessarily a cause–effect relationship, and it is not clear whether the relationship between a glass's non-Arrhenius viscosity and its Poisson ratio is indeed a causal one. Of course, because glass is made from a liquid, it is tempting to conclude that large glass Poisson ratios are somehow caused by strongly non-Arrhenius viscosities. This argument is not compelling, however, because of the following: The structure and properties of a glass are essentially those of a 'frozen' liquid, thus for experiments performed on a liquid over timescales that are much shorter than the liquid's relaxation time the resulting behaviour will be that of the solid state of the glass. In other words, the Novikov–Sokolov correlation implies that the degree of non-Arrhenius viscosity correlates with the short-time mechanical properties of the liquid state.

This does not remove the mystery of the observed correlation, because the relevant short and long timescale behaviours of glass-forming liquids differ enormously. Indeed, the characteristic timescales over which processes in these two regimes occur can easily differ by more than 12 orders of magnitude, with short-timescale processes lasting less than one nanosecond and long-timescale processes occurring over seconds, minutes, hours and longer. Consequently, the task of predicting viscosity from short-time liquid properties is akin to trying to predict the rate of global climate variations over millions of years from observations of the world's weather collected over a single minute.

The suggestion that liquid viscosity is determined by its short-timescale elastic properties, which has been raised a few times in the literature over the past 60 years^{3–5}, seems to be at odds with the prevailing paradigm of glass science, which is embodied in the Adam–Gibbs entropy model⁶. According to this model, viscosity is controlled by the number of different ways the molecules of a liquid may be packed (known as the configurational entropy). In the very brief time over which short-timescale phenomena occur, a liquid could explore any but a few of these configurations and thus hardly 'know' the configurational entropy. Nevertheless, the possibility of short-timescale properties determining the viscosity^{7,8} is gaining increasing support from results from recent inelastic X-ray scattering⁹ and computer modelling¹⁰ studies. The discovery of the Novikov–Sokolov correlation is therefore timely and likely to provide fresh impetus to this idea.

The quest to determine the mechanism that controls liquid viscosity is a fundamental concern of glass science. As this mechanism also governs how glassy materials age, this question is of considerable practical importance, too. A genuine understanding of the dynamics involved should make it possible to optimize properties of glasses and polymers by giving a sound scientific basis for calculating the best temperature schemes to be applied during production. It is too early to tell which theory for liquid viscosity will prevail. But, if the determining influence of short-timescale properties on viscosity is confirmed, the ability to monitor such phenomena (by techniques such as ultrasonic spectroscopy) and thus be able to better control the bulk physical properties of the resulting glass, would have immediate applications.

References

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