# Is glass liquid or solid?

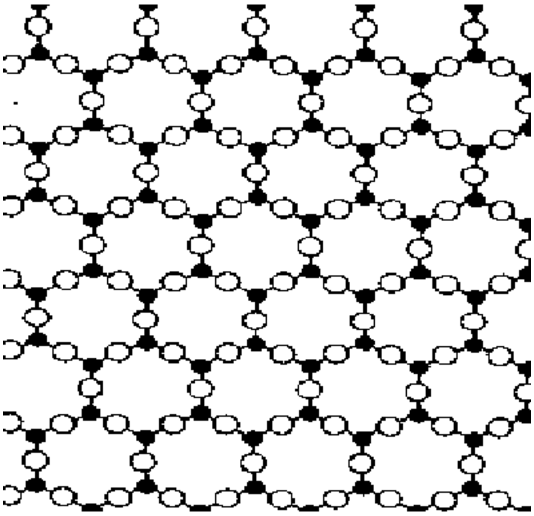
## By Philip Gibbs

**Abstract**: It is sometimes said that glass in very old churches is thicker at the bottom than at the top because glass is a liquid, and so over several centuries it has flowed towards the bottom. This is not true. In Mediaeval times panes of glass were often made by the Crown glass process. A lump of molten glass was rolled, blown, expanded, flattened and finally spun into a disc before being cut into panes. The sheets were thicker towards the edge of the disc and were usually installed with the heavier side at the bottom. Other techniques of forming glass panes have been used but it is only the relatively recent float glass processes which have produced good quality flat sheets of glass. Nevertheless, the frequently asked question "Is glass liquid or solid?" is not so straightforward to answer. To do so we have to understand its thermodynamic and material properties.

**Thermodynamics of glass**

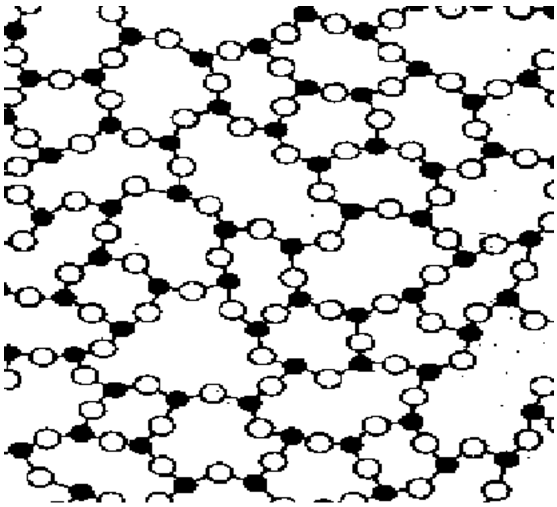
There is still much about the molecular physics and thermodynamics of glass that is not well understood, but we can give a general account of what is thought to be the case.

Many solids have a crystalline structure on microscopic scales. The molecules are arranged in a regular lattice. As the solid is heated the molecules vibrate about their position in the lattice until, at the melting point, the crystal breaks down and the molecules start to flow. There is a sharp distinction between the solid and the liquid state, that is separated by a *first order phase transition*, i.e. a discontinuous change in the properties of the material such as density. Freezing is marked by a release of heat known as *the heat of fusion*.



***molecular arrangement in a crystal***

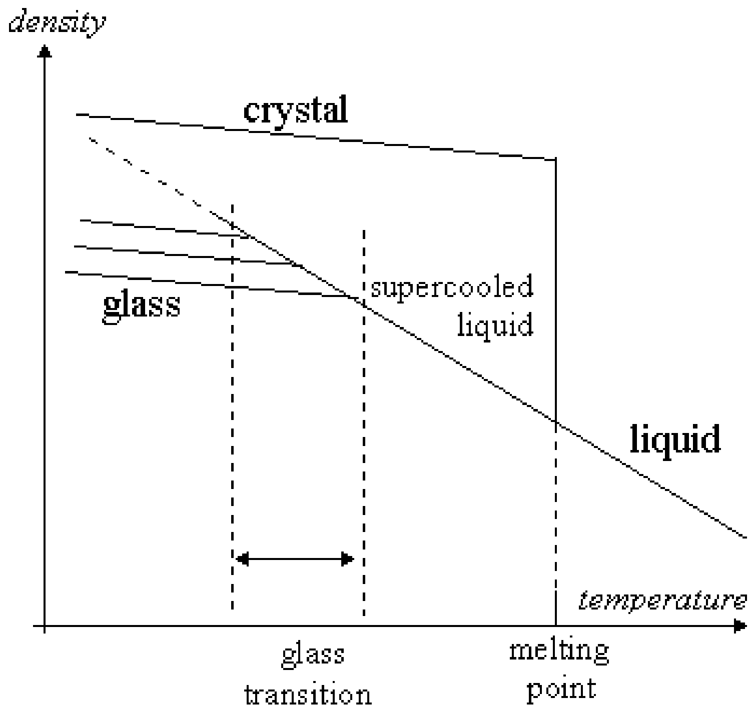
A liquid has *viscosity*, a measure of its resistance to flow. The viscosity of water at room temperature is about 0.01 poises. A thick oil might have a viscosity of about 1.0 poise. As a liquid is cooled its viscosity normally increases, but viscosity also has a tendency to prevent crystallisation. Usually when a liquid is cooled to below its melting point, crystals form and it solidifies; but sometimes it can become *supercooled* and remain liquid below its melting point because there are no nucleation sites to initiate the crystallisation. If the viscosity rises enough as it is cooled further, it may never crystallise. The viscosity rises rapidly and continuously, forming a thick syrup and eventually an amorphous solid. The molecules then have a disordered arrangement, but sufficient cohesion to maintain some rigidity. In this state it is often called an amorphous solid or glass.



***molecular arrangement in a glass***

Some people claim that glass is actually a supercooled liquid because there is no first order phase transition as it cools. In fact, there is a *second order transition* between the supercooled liquid state and the glass state, so a distinction can still be drawn. The transition is not as dramatic as the phase change that takes you from liquid to crystalline solids.  There is no discontinuous change of density and no latent heat of fusion.  The transition can be detected as a marked change in the thermal expansivity and heat capacity of the material.

The temperature at which the glass transition takes place can vary according to how slowly the material cools.  If it cools slowly it has longer to relax, the transition occurs at a lower temperature and the glass formed is more dense.  If it cools very slowly it will crystallise, so there is a minimum limit to the glass transition temperature.




***Density as a function of temperature in the phases of glassy materials***

A liquid to crystal transition is a thermodynamic one; i.e. the crystal is energetically more favourable than the liquid when below the melting point.  The glass transition is purely kinetic: i.e. the disordered glassy state does not have enough kinetic energy to overcome the potential energy barriers required for movement of the molecules past one another.  The molecules of the glass take on a fixed but disordered arrangement.  Glasses and supercooled liquids are both metastable phases rather than true thermodynamic phases like crystalline solids.  In principle, a glass could undergo a spontaneous transition to a crystalline solid at any time.  Sometimes old glass devitrifies in this way if it has impurities.

The situation at the level of molecular physics can be summarised by saying that there are three main types of molecular arrangement:

**crystalline solids**: molecules are ordered in a regular lattice
**fluids**: molecules are disordered and are not rigidly bound.
**glasses**: molecules are disordered but are rigidly bound.

[Just to illustrate that no such classification could ever be complete, recently scientists have succeeded in making *quasi-crystals* that are quasi-periodic. They do not fit into the above scheme and are sometimes described as being halfway between crystals and glass.]

It would be convenient if we could conclude that glassy materials changed from being a supercooled liquid to an amorphous solid at the glass transition, but this is very difficult to justify. Polymerised materials such as rubber show a clear glass transition at low temperatures but are normally considered to be solid in both the glass and rubber conditions.

It is sometimes said that glass is therefore neither a liquid nor a solid. It has a distinctly different structure with properties of both liquids and solids. Not everyone agrees with this terminology.

## Material properties of glasses

Usually when people talk about solids and liquids, they are referring to macroscopic material properties rather than the arrangement of molecules. After all, glass as a material was known about long before its molecular physics was understood. Macroscopically, materials exhibit a very wide range of behaviours. Solids, liquids and gases are ideal behaviours characterised by properties such as compressibility, viscosity, elasticity, strength and hardness. But materials don't always behave according to such ideals. For example, it's possible to take water from being a liquid to a gas at high pressure without its passing through a phase transition; so at some stage it must be between an ideal liquid and an ideal gas.

For crystalline substances the distinction between the solid and liquid states is very clear, but what about glasses? Indeed, where do polymers, gels, foams, liquid crystals, powders and colloids fit into this picture? Some people say that there is no clear distinction between a solid and a liquid in general. A solid, they claim, should just be defined as a liquid with a very high viscosity. They set an arbitrary limit of $10^{13}$ poises above which they say it's a solid and below which it's a liquid.

According to another point of view, this ignores a distinction between viscosity of liquids and plasticity of solids. An ideal Newtonian liquid deforms at a rate which is proportional to stresses applied and its viscosity. For arbitrarily small stresses a viscous liquid will flow. Molasses, pine pitch and Silly Putty are examples of liquids with very high viscosity that flow very slowly under only the force of their own weight. On the other hand, plastics can be very soft but are still considered solid because they have rigidity and do not flow.

Solids are elastic when small stresses are applied. They deform but return to their original shape when the stress is removed. When higher stresses are applied some solids break while others exhibit plasticity. Plasticity means that they deform and don't return to their original shape when the stress is removed. Many substances including metals such as copper have plasticity. The resistance to flow under plastic deformation is called its viscoplasticity. This is like viscosity, except that there's a minimum stress known as the elastic limit below which there is no plasticity. Materials with plasticity do not flow, but they may creep, meaning they deform slowly but only when held under constant stress.

So an arbitrary measure of viscosity or viscoplasticity is not a good way to distinguish solids from liquids. Another way to define the distinction between solid and liquid is to say that, if there is a minimum shear stress required to produce a permanent deformation then it is a solid. This is just a precise way of saying it has some rigidity. A liquid can then be defined as a material that will flow. If it is placed in a container it will eventually flow to fill the lower reaches until its own surface is flat. The difficulty is that these two definitions do not cover all cases. There are materials that have some limited flow known as viscoelasticity. The material will deform elastically under stress. If the stress is held for a long time, the deformation becomes permanent even if the stress was small. Materials with viscoelasticity may seem to flow slowly for a while but then stop. It is futile to try to make a clear cut distinction between liquids and solids in cases of such behaviour.

**Types of Glass**

To be sure that glass in old windows has not flowed, we need to recognise the different properties of different glasses. Glass can be made from pure silica, but fused silica has a high glass transition point at around 1200° C which makes it difficult to mould into panes or bottles. At least 2000 years ago it was learned how to lower the softening temperature by adding lime and soda before heating, which resulted in a glass containing sodium and calcium oxides. Soda-lime glass used for windows and bottles today contains other oxides as well. Measuring the glass transition temperature for different glasses is not easy because it changes according to how slowly the glass is cooled. In the case of modern soda-lime glass, a quick cooling will produce a glass transition at about 550° C. There is thought to be a minimum glass transition temperature at about 270° C, and if it is cooled very slowly it can still be a supercooled liquid down to just above that temperature. Glass such as Pyrex (used for test-tubes and ovenware) is usually based on boro-silicates or alumino-silicates, which withstand heating better and typically have a higher glass transition temperature. Some glasses, such as the leaded variety, have lower transition temperatures.

Sometimes people say that good evidence that glass does not flow is provided by telescope lenses which after 150 years still maintain excellent optical qualities. They would be spoiled by the slightest deformation. In fact, optical glass is usually not the same as the glass used in windows and bottles. It may be based on boro-silicate or soda-lime glass with other metallic oxides added to improve its thermal and optical properties. So old telescope lenses and mirrors provide good evidence that some glasses do not flow, but little evidence to support the claim that glass in old windows has not flowed. Another example is Stone Age arrow heads made of obsidian, a natural glass. These are found to be still razor sharp after tens of thousands of years, but again, this glass is mainly silica and alumino-silicates and is much tougher than window glass.

For definitive evidence that glass has not flowed in old windows we must examine the oldest examples. Early glass used to make bottles and windows was usually formed by adding soda and lime to silicates. Sometimes potash was added instead. Usually there were other impurities that made it softer than modern soda-lime glass. Other compounds were often added to give colour or to improve its properties. The Romans were making glass objects of this sort in the 1st century AD, and despite being very delicate, some examples remain—such as the elaborately decorated Portland Vase kept at the British Museum. Roman glassware provides some of the best available evidence that types of soda-lime glass are not fluid, even after nearly 2000 years. The oldest remaining examples of stained glass windows that remain in place have lasted since the 12th century. The oldest of all are the five figures in the clerestory of Augsburg Cathedral in Germany, which are dated to between 1050 to 1150. Many other early examples are found in France and England including the magnificent North Rose window of Notre Dame, Paris dating from 1250.

There have been many claims (especially by tour guides) that such glass is deformed because the glass has flowed slowly over the centuries. This has become a persistent myth, but close inspection shows that characteristic signs of flow, such as flowing around, and out of the frame, are not present. The deformations are more consistent with imperfections of the methods used to make panes of glass at the time. In some cases gaps appear between glass panes and their frames, but this is due to deformations in the lead framework rather than the glass. Other examples of rippling in windows of old homes can be accounted for because the glass was imperfectly flattened by rolling before the float glass process came into use.

It is difficult to verify with absolute certainty that no examples of glass flow exist, because there are almost always no records of the original state. In rare cases stained glass windows are found to contain lead, which would lower the viscosity and make them heavier. Could these examples deform under their own weight? Only careful study and analysis can answer this question. Robert Brill of the Corning glass museum has been studying antique glass for over 30 years. He has examined many examples of glass from old buildings, measuring their material properties and chemical composition. He has taken a special interest in the glass flow myth and has always looked for evidence for and against. In his opinion, the notion that glass in Mediaeval stained glass windows has flowed over the centuries is untrue and, he says, examples of sagging and ripples in old windows are also most likely physical characteristics resulting from the manufacturing process. Other experts who have made similar studies agree. Theoretical analysis based on measured glass viscosities shows that glass should not deform significantly even over many centuries, and a clear link is found between types of deformation in the glass and the way it was produced.

# Conclusion

There is no clear answer to the question "Is glass solid or liquid?". In terms of molecular dynamics and thermodynamics it is possible to justify various different views that it is a highly viscous liquid, an amorphous solid, or simply that glass is another state of matter that is neither liquid nor solid. The difference is semantic. In terms of its material properties we can do little better. There is no clear definition of the distinction between solids and highly viscous liquids. All such phases or states of matter are idealisations of real material properties. Nevertheless, from a more common sense point of view, glass should be considered a solid since it is rigid according to everyday experience. The use of the term "supercooled liquid" to describe glass still persists, but is considered by many to be an unfortunate misnomer that should be avoided. In any case, claims that glass panes in old windows have deformed due to glass flow have never been substantiated. Examples of Roman glassware and calculations based on measurements of glass visco-properties indicate that these claims cannot be true. The observed features are more easily explained as a result of the imperfect methods used to make glass window panes before the float glass process was invented.

## References

"Antique windowpanes and the flow of supercooled liquids", by Robert C. Plumb, (Worcester Polytech. Inst., Worcester, MA, 01609, USA), J. Chem. Educ. (1989), 66 (12), 994–6

Ernsberger, F. M. "In Glass: Science and Technology"; D.R. Uhlmann, N.J. Kreidle, Eds; Acad. New York, 1980; Vol. V, Chapter 1.

"Physics of Amorphous Materials" by S.R. Elliott (London: Longman Group Ltd, 1983)

C. Austin Angell, Science, March 1995

Robert H. Brill, "A Note on the Scientist's definition of glass", Journal of Glass Studies, vol. 4, 127–138, 1962

Florin Neumann, "Glass: Liquid or Solid — Science vs an Urban Legend"

"Do Cathedral Glasses Flow?", Am. J. Phys. v**66**, pp 392–396, May 1998

Edgar Zanotto, American Journal of Physics **66** p392, May 1998

Paul Steinhardt, "Crazy Crystals", New Scientist, 25 January 1997