

Clear transparent plastics – Why does a glass form?

Praveen Chaddah

Email: chaddah.praveen@gmail.com

Abstract: *Two turning points in human civilization are the ability to control and exploit the power of steam, and the ability to fabricate clear transparent glass out of various different constituents. Exploiting the power of steam was driven to a large extent by the innovations of James Watt, and resulted in the Industrial Revolution with its huge impact on our civilization. The invention and fabrication of clear transparent glass as a turning point may not be so recognized by many others, and it shall be my endeavour to convince the reader that it has really been a turning point. Physicists have helped in enhancing our ability to exploit the power of steam, but have not really contributed to the discovery of newer materials that form clear transparent glass. That has been mainly the contribution of engineers and innovators. Turning points benefit not only from those who are trying to understand what is, but also from those who ask why not and try to create what is not. In these chapters from a forthcoming book “**Steam Power and Transparent Glass: Two phase transition related turning points in human civilization**”, we discuss the development and impact of clear transparent glasses.*

1. Clear transparent plastics

Plastics are materials that have polymers as a main constituent. Many plastics are partially crystalline and partially amorphous, while many are completely amorphous. Like glass, plastics have been with us for a few thousand years with natural rubber being the most prominent example and having been in use for over three thousand years. Plastics have evolved with the development of partially synthetic plastics that use polymers as their main ingredient until in 1907 the Belgian chemist Baekeland invented the first fully synthetic plastic that used only man-made molecules, and was called Bakelite after its inventor. Baekeland also coined the term plastics.

Plastics have a large number of very useful properties, and have become a material that has literally swamped our industry and civilization. It has also been targeted as plastics cause widespread environmental problems. This is because they decompose very slowly in natural ecosystems. I must point out that this is also true of silica-based glasses, where this slow decay is used as a positive attribute, to encapsulate and store radioactive waste. But I am diverting from my theme.

There are two types of plastics, broadly classified as thermoplastics and thermosets. Thermosets are polymers that undergo a chemical reaction when

heated, accompanied by melting. They take shape and solidify, and after they have solidified they stay solid. But this happens only once. If this solid is heated again, the plastic does not melt, but decomposes because a chemical reaction occurs in the thermosetting process, and this chemical reaction is irreversible. A very commonplace example of this is the vulcanization of rubber when polyisoprene is heated with sulphur. The initial viscous material becomes rigid after vulcanization.

Thermoplastics, on the other hand, do not undergo change in their composition when they are heated. As they are heated there is a change in their physical properties before any chemical reaction can occur. Above a glass transition temperature these become pliable or mouldable, and solidify in the new physical shape on cooling. On heating further, thermoplastic materials become liquid and this is their 'melting point'. As an example, the glass transition temperature for Acrylic is about 105C and melting temperature is about 160C. A major attribute of these thermoplastics, like of silica-based glass, is that they can be heated to their melting point, cooled, and reheated again. While silica-based glass has to be cooled back faster than a critical cooling rate to again form a glass, thermoplastics can be cooled back slowly since they vitrify and do not crystallize even under slow cooling. (They vitrify at arbitrary cooling rates, but their kinetics has not been investigated enough by those studying glass formation.) Thermoplastics can be thermally cycled without any irreversible changes in their physical properties. When cooled from the liquid state, they reform into their initial amorphous state. Thus they qualify as glasses even in the rigorous definition of Greer [1] that the amorphous solid must form from the liquid, a definition used to state that amorphous silicon is not a glass because its density is not near that of liquid silicon [1].

There are a large number of thermoplastics that have been developed during the last hundred years (Acrylic was developed about ninety years ago), and many of them are transparent. A search on the internet for "transparent polymers" shows up a list of more than ten such materials. Some amongst these are replacing silica-based glasses in many applications. These have a refractive index that is close to that of silica-based glass, and generally are better bio-compatible than silica-based glass. They are also lighter, and easier and cheaper to manufacture. Further their forming under slow cooling rates should help physicists understand why glasses form, a question to which we shall return in our last chapter. The drawback for the broad category of polymer-based glasses is that their glass transition temperature T_g is lower than that of silica-based

glasses. Accordingly, the temperatures up to which they can be used are also lower than silica-based glasses. But these polymer-based glasses function well at the temperature encountered in our daily lives, and that is what has made them so useful.

The covid-19 pandemic has created a huge demand for transparent protective barriers that will allow humans to interact somewhat physically, without spreading the virus. Such barriers in the form of sheets (mostly rigid, but also thinner and flexible) have come up wherever eye-contact is desirable, and proximity is essential for exchange of material objects that cannot be done through tele-conferencing. The examples are immense such as shops, offices, pharmacies, library counters, public transport, conference rooms, restaurants, hospitals and diagnostic centres, public-facing areas like bank tellers, retail settings like store check-out clerks, and wherever it is difficult to maintain the stipulated separation in high-human-density spaces. In all such cases sheets are used, and these sheets have to be frequently sterilized. This feature of clear transparent barriers allowing us to interact semi-physically without communicating the virus has allowed medical treatments. The visual picture of medical workers within a PPE is synonymous with this Covid-19 pandemic, and clear transparent barriers have been the turning point in our civilization that allowed humanity to survive this pandemic not just physically preventing transmission of the virus, but also ensuring our mental wellbeing by allowing us to *almost* touch. The visuals of grandparents hugging their grandchildren while wearing transparent screens have been very moving.

Such clear transparent (but rigid) barriers would have been possible with silica-based glasses, but not the flexible screens that transparent polymers provide. Further, the physical weight of silica-based glasses would be immense as their density is more than double that of polymer-based glasses. The easy breakage of silica-based glasses (into sharp pieces that can cause injury) would be another handicap. And the production process of polymer-based glasses is much less cumbersome than that of silica-based glasses. When we discuss that, it will bring me to why these might show an out-of-the-box approach for scientists to explain the physics of glass formation.

Amongst the dozen-or-so transparent polymer-based glasses, PMMA (polymethyl methacrylate) has been the most popular during the past year because sterilization neither affects its transparency nor its appearance. PMMA is also known as Acrylic, Plexiglass, Lucite, and Perspex, among several other

commercial names. It is used frequently in sheet form as a lightweight or shatter-resistant alternative to silica-based glass. Its usage has increased much faster during this pandemic than that of polycarbonate, which is also an extensively used polymer-glass.

The corresponding monomer methyl methacrylate has a density 0.94, and a melting point -48°C . The polymer PMMA has a density 1.18, a melting point (flows at) 160°C , and a T_g (glass transition temperature) 105°C . Polycarbonate has a density 1.21, a much higher T_g of 147°C , and flows at about 155°C . The characteristics of polycarbonate are comparable to those of PMMA, but polycarbonate is stronger and will hold up longer to extreme temperature. But PMMA is often preferred because of its moderate properties, easy handling and processing, and low cost. As mentioned earlier, the ability to withstand sanitizers makes PMMA much more useful in the pandemic situation.

To help us compare silica-based glasses and polymer-based glasses, we shall restrict ourselves to the polymer PMMA since both withstand sanitizers. PMMA has a density of 1.17-1.2 which is less than half of silica-based glass. It is strong, tough, and is a lightweight, as anyone who has tried spectacles made of silica-based glass will vouch! PMMA transmits up to 92% of visible light (3 mm thickness), and gives a reflection of about 4% from each of its surfaces due to its refractive index (1.4905 at 589.3 nm). It filters ultraviolet light at wavelengths below about 300 nm (similar to ordinary window glass). PMMA is also biocompatible and is used in medical implants, including as rigid intraocular lenses after the treatment of cataract. In particular, such lenses are useful for Uveitis patients as acrylic material induces less inflammation.

Silica-based glass is formed by mixing typical constituents like sand soda-ash and limestone in a specific ratio and feeding them together into a furnace that is heated to approximately 1500°C . In contrast, PMMA is formed from the monomer methyl methacrylate along with some additives, and heating required is only to about 100°C (the monomer is a liquid above -48°C and boils at 101°C) which is even above the melting point of PMMA. The polymer forms as a glass by the chemical polymerization of the monomer, and no 'rapid cooling of the liquid across the first order freezing transition' is required. The bypassing of the requirement of cooling the liquid faster than a critical cooling rate will be emphasized when we later seek an out-of-the-box approach to understand the physics of glass formation. In fact, the crystalline form of polymer-based glasses, or the process of their devitrification, is not discussed by the innovator-

engineers who invented and gave us these very important polymer materials for our civilization. All I could find was the statement that "No one has ever crystallized it," (attributed to Ediger by Robert Kunzig in his article titled 'The Physics of Glass' [2]) in the context of the polymer-based glass polystyrene. He re-emphasizes that "Glass is the only solid state (*read solid form*) common polystyrene can have".

We conclude this chapter by noting that our second turning point, viz. clear transparent glass (whether silica-based or polymer-based) is obtained by avoiding the first order freezing transition that would have given us crystallites. This solid would not be transparent because light would be scattered at the interfaces separating these crystallites in the bulk solid. The liquid state of an insulator is optically transparent, as would be its single-crystal form. The glass state being a frozen liquid, but without the temporal density fluctuations possible in a liquid, is clear transparent. Contrast this with the turning point of steam-power which was created by completing the first order boiling transition!

Do we always want a first order transition to be completed? We do want liquid water to vaporize into the atmosphere and then condense at locations other than where it evaporated from. Glass is an example where we do not want the first order freezing transition to be completed. Environmental experts tell us that we do not really want our glaciers to melt (though some must melt as they feed our rivers), though this melting has to be prevented by not allowing the temperature of the glaciers to rise. There are many examples where we want to *postpone* the transition rather than prevent it. Supercooled water flowing up trees in sub-zero temperature is the example Nature gives us. Supercooling or superheating across a first order transition are thermodynamic metastable states, and will convert to the stable (frozen or heated) phase beyond a limit (of supercooling or superheating). A glass obtained at temperatures below the freezing point will not, on the other hand, convert to the stable state even under extreme cooling. That is the difference between postponing and avoiding the transition.

2. Why does a glass form?

In this Chapter we look at the future possibilities. Steam power, described by Harari as 'the secret in the kitchen' is poised to now evolve towards power stations that run supercritical steam turbines operating at high pressures where the boiling of water is thermodynamically avoided. At pressures above 221 atmospheres and temperatures above 374C water does not boil. Supercritical water reactors for nuclear power are being discussed in great detail [3] while tapping steam-power and efficiencies for converting heat energy to electrical or mechanical energy are likely to rise to 45-to-50% compared to 30-to-35% for boiling water reactors. Technology, and the knowledge of materials would need to be enhanced for this to become a practical reality. However, there seems to be no conceptual or 'in principle' barrier to surmount for better utilization of steam power by thermodynamically avoiding the boiling transition.

We now come to the second 'turning point' invention of clear transparent glass. The cognitive phase transition in the human brain occurred as incremental growth in the human brain caused some interlinks to develop and gave us the ability to wonder, and to think about what does not exist [4]. It is a phase transition that fortunately was not avoided! But clear transparent glass is formed by avoiding the freezing transition of the liquid.

The concept that cooling at a rate faster than a critical cooling rate (the critical cooling rate is different for each material) is the requirement for forming a glass is something that all scientists agree on; at least in that no one will question this statement. But is this basic premise absolute and justified, especially since there is presently no accepted methodology on how to calculate this material-specific critical cooling rate? I mention here that in 2012 we had first stated an alternate view that "extract specific heat without extracting latent heat serves as a procedural definition of glass formation" [5,6]. This view emphasized that the method of cooling could be an alternative to the rate of cooling.

We note that the change from water to ice is a phase transition. So is any liquid changing to a solid. And we have a phase transition when molecules in a solution form a crystal, as when a solution of salt or of sugar dries out and we get crystals. In the book "**Gene Machine**" [7], Ramakrishnan describes the importance of using X-ray diffraction from crystals of complex molecules to determine where the atoms in a molecule are. In his attempt to determine the structure and function of the ribosome that contains hundreds of thousands of atoms, he describes the immense effort, sustained over many years, in growing good

crystals. He describes his attempts in initial years of growing good crystals of even proteins. He states that when “you let proteins dry out, though, they just form amorphous goop, not crystals”. He describes the slow and tedious process necessary to ensure that “the proteins will come out of solution by packing regularly against each other to form crystals”. Ribosome contains over a million atoms, including a large number of proteins. The molecule is large and floppy and during crystallization, even if it finds its way to the correct position in the growing crystal lattice, it may not sit in exactly the correct orientation as its neighbouring molecules. A major part of Ramakrishnan’s book describes his work, leading to the Nobel Prize, ensuring completion of the phase transition resulting in single crystals. But there are phase transitions that we try to prevent, to obtain transparent glass. Glass, in the strict definition of physicists (and most other scientists), is actually a family of materials where a liquid became a solid without undergoing the phase transition associated with freezing.

A small crystallite would be transparent for any insulator with a large band gap, but a solid consisting of an agglomeration of crystallites would scatter light at every crystallite boundary and would only be translucent. Liquids of such materials would be transparent, like water is. If a bulk material could be formed by solidifying the liquid to a glass (as ‘a liquid with time held still’), then the solid would be clear and transparent. The drawback is that the process requires cooling of the liquid at high rates. These “critical cooling rates” are easily achievable for some special cases, like for silicates that form window glass. In many other metallic materials also the crystallization process is arrested, but only at cooling rates that are around a million degrees per second [1].

About ninety years ago, some insulating materials were found that do not need to be formed through a chemical reaction at high temperature. These materials form as a solid that is amorphous, form directly into this ‘a liquid with time held still’ state. These materials are insulators with a large band gap, and are clear and transparent because they are homogeneous liquids that are ‘frozen in time’ to form solids. They do not form through a high temperature process, do not first form as hot liquids like the window glass that we were just talking about, and the ‘glass’ is formed without the need for rapid cooldown of the hot liquid. These materials called thermoplastics can be heated to above their melting point to a liquid, and then cooled to form the same solid glass. The heating and cooling is *reversible*, and this can be done several times without any change in the chemical or mechanical properties of the solid glass. They do not crystallize, and one can only reiterate Ediger’s statement [2] for polystyrene “No one has

ever crystallized it". The critical cooling rate has simply vanished to zero! I believe that the newer polymer-based complex materials may also hold the key to why thermodynamics becomes less important than kinetics, and thus to why glasses form. But physicists are not looking at these materials, probably because they are too complex! As mentioned at the beginning of this book while defining a turning point, turning points are non-incremental changes that humanity kept building further on and did not try to undo. And, building on the engineer-driven discovery of clear transparent polymer-based glass requires a proper understanding of why the freezing transition is arrested.

As I proceed to counter the emphasis on rate of cooling, I repeat the quote from Ramakrishnan's book "**Gene Machine**" that when "you let proteins dry out, though, they just form amorphous goop, not crystals" [7]. This critical cooling rate is obviously very, very, slow for some materials! There is increasing incidence of innovators coming up with newer materials that form an amorphous glass without the need for fast cooling or any other effort, and like Ramakrishnan's experience with ribosome, require immense effort to form crystallites of. It is my guess that these materials may also hold the key to understanding why glasses form. I believe that materials like thermoplastics that have exceedingly slow kinetics need to be understood because a proper understanding does pave the path to better utilization.

Physicists are still trying to understand what will make a liquid avoid the first-order phase transition of freezing, and form a glass-solid under rapid cooling. They are still trying to predict which liquids will form a glass and which liquids will not. Meanwhile, innovators and engineers have created some extremely useful polymer glasses that form as glass-solids, and they have created these without first creating the corresponding liquid! Physicists try to understand why things are the way they are, whether they are created that way by Nature or, as in this case, by some adventurous and innovative humans. Such innovative humans (who we refer to as engineers!) do not seek an understanding, but just ask "why not?". They create things that do not exist or, sometimes, are not even expected to exist. What is important to these innovators is whether their question "why not" has a convincing answer on why something cannot be. They can, perhaps, be dissuaded from trying a process only if there is a proof that the process cannot work! And there is no such proof about why metastable states ('a liquid with time held still' is a metastable state) cannot be formed when thermodynamic routes (just varying temperature is a thermodynamic route) are

not followed. Polymer glasses are examples of metastable phases being formed by following non-thermodynamic routes.

I now mention some recent research efforts that follow out-of-the-box ideas on the kinetics of the freezing transition, and may take us beyond the 'critical cooling rate' path. I mention two ideas on completing a freezing (more generally a first order) phase transition. An observation that has been pursued actively for about a decade is that sometimes a liquid close to the freezing point takes more time to freeze than a liquid farther from the freezing point. This observation on water was first reported by Aristotle and has also been noted by Bacon and Descartes and is believed to have been known even well before the scientific revolution. In modern times, this was first observed by a Tanzanian schoolboy in 1963. Erasto Mpemba was making ice cream when he noticed that the hot liquid sometimes freezes faster than when it is cold. He and his teacher Osborne then did experiments on water and published the results in 1969 [8]. This report captured the scientific imagination on what has since been called the "Mpemba effect". The freezing of water is a first order transition, as is the liquid to crystalline transition that has to be arrested if a glass is to be formed.

Half-doped manganite materials showed possibilities of applications in computer memory devices due to a first order magnetic transition that also led to a very large change in electrical resistance with magnetic field. These magnetic materials were being studied extensively in the 1990's, and we had also got attracted to this problem. We concluded by 2005 [9] that these magnetic first order transitions could be avoided and the kinetics of the first order transition could be 'arrested' by changing temperature and magnetic field in some particular ways. In these studies we also found in 2010 [10] an analogue of Mpemba effect in that a starting state farther from the equilibrium state could 'overtake' a starting state closer from the equilibrium state. This has been reinforced by a recent assertion that a material is more likely to fall into the minimum energy deep well if it starts far from equilibrium [11]. (Avinash Kumar, Nature). Our studies have been noticed in last few years by those looking at Mpemba effect in water and other liquid to solid transitions, stating that "to complicate matters further, a similar effect has also been observed in magnetic systems, for other phase transitions" [12] (Physics World 2020). While these studies on Mpemba effect do investigate non-equilibrium features giving counter-intuitive behaviour in the kinetics of phase transitions, they do not directly address the prevention or arrest of the transition that we had started investigating in magnetic systems.

In a recent work that follows on our pioneering work on these magnetic systems, Matsuura et al [13] have argued that the kinetics of the first order transition can be avoided or arrested if there is a state that is competing in energy with the ground state. They show that if there is another state with energy close to the ground state then the critical cooling rate for getting trapped becomes very small, and the first order transition can be easily avoided. Is this what happens in polymer glasses?

In a very recent work unrelated to magnetic systems recent preprint, Persch et al [14] have shown that increasing covalency slows down crystallization by six orders of magnitude and promotes vitrification. This could be directly applicable to polymer glasses, and may also provide an out-of-the-box idea for understanding why glasses form. ***It needs to be checked with the fact that while PMMA has a T_g of 105C and a melting point of 160C, and is typically having about a thousand to ten thousand monomers. The starting monomer MMA ($C_5H_8O_2$) does not vitrify and is a colourless liquid that has a melting point of -48C (and a boiling point of 101C). Clearly the covalency in the monomer is not dominating the kinetics, and some crucial change is caused by polymerization. The entropy that contributes to the latent heat of melting becomes less 'accessible' after polymerisation. As another interesting material, we look at terphenyl ($C_{18}H_{14}$) that has three isomers. One of these O-terphenyl is a prototype glassy material that melts at -33C, but forms a glass even at very slow cooling rates. Another isomer para-terphenyl melts at a much higher temperature of 110C and does not show easy vitrification. The difference between these two isomers is that the two carbons in the central benzene ring that do not bind to hydrogen are near neighbours in the former isomer, and have two carbons in-between in the latter isomer. Obviously small changes dictate the tendency to vitrify.***

My worry is also that the underlying idea for tendency to arrest freezing has to be relevant to the arrest of the first-order freezing transition of a liquid, and must also extend to the arrest of various other first-order phase transitions, including in magnetic systems. This brings me back to our alternate out-of-the-box prescription that “extract specific heat without extracting latent heat serves as a procedural definition of glass formation” that we enunciated in 2012 [5,6]. We might then be able to solve and exploit what Anderson told us viz. “The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition” [15]. Understanding the conditions under which a liquid would vitrify, rather than crystallize into a

solid, has been recognized as an outstanding scientific problem for a long time. Only after physicists develop such an understanding would the invention of glass by engineer-innovators be fully utilized.

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