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A Re-evaluation of the Physiochemistry of Glass on the Basis of Recent Developments and its Relevance to the Glass Industry

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The classical image of glass is that of a rigid, transparent brittle material characterized by a non-crystalline microstructure. This 19th and 20th century image however is mostly based on the contrast between soda lime glass and metals. It does not really make sense in the 21th century where more modern testing methods have increased our understanding of the physiochemistry of glass. Based on recent results and the development of computational molecular dynamic software modelling a new approach to the physiochemistry of glass is outlined. The consequences this view has on glass properties and processing are explained.

Keywords: Glass structure, Hot working glass, Glass processing, Effect of glass composition

1. Introduction

Most classical text books on physics, for example Muncaster, divide matter in three types, solid, liquid and gas. Some authors such as Morozov consider plasma as a fourth type of matter. Glasses however are neither fish nor fowl in this type of division. Many classic physics text, which consider solids from the point of view of crystalline materials, have a problem with glasses. Some of them consider glasses as a super cooled liquid rather than a solid. A simple overview is given by Curtin.

From an engineering point of view it strange to consider lead, which flows under pressure at room temperature as a solid, and float glass, which does not flow under pressure as a liquid.

From a modern physicists point of view; which accepts that solids can change into other solids or into liquids or gasses, examples being the ferrite-austenitic phase change in iron, the melting of copper and the sublimation of ice; the rigid categorisation into states of matter is dangerous, yet it still common in both secondary schools and in bachelor programmes of engineering and natural science programmes. If we take a modern materials science text, such as Callister, chapter 3 deals extensively with the crystalline structure, the next 10 chapters (400 pages) build on this, then in chapter 14 there are 4 pages which deal with glasses before going onto ceramics. In chapter 15 there is some mention of amorphous polymers. So less than 1% of the book is spent on non-crystalline materials.

In general unless one follows some specialised master course in glasses, where typically Shelby is used, 99+% of engineers and scientists, including those that deal with the processing of float glass typically have no formal training in glass science.

The danger of this is that glass is always viewed from the perspective of metals, specifically a strange solid that becomes liquid at a certain point like steel; and like steel needs to be annealed and can be heat treated. Even the terminology, tempered glass is based on the practice of metallurgical technique. The mind-set our conventional preference for metals and other crystalline materials induces an automatic prejudice against glasses and does not provide a basis to understand the behaviour of glasses.

2. Low and high temperature structure of glass

The structure of glass is something that cannot be easily determined. X-Ray Diffraction (XRD) only reveals patterns if the material tested is crystalline, which glasses by definition are not. The nano-level structures in glass cannot be seen with conventional microscopes or electron microscopes. Even meso-structures in transparent glasses at the 10 to 100 µm level, such as the bubbles and inclusions in float glass described by Molnar et al. , cannot be seen easily using optical microscopy because there is almost no contrast.

Zachariasen, a noted crystallographer, published a model for the structure of glass in 1932. This model is still used even though aspects of Zachariasen’s rules for glass formation have been proven wrong, as shown by Rao. Huang et al. proved the basis concept of the Zachariasen model is true in 2012, at least for a 2 dimensional glass lattice. Basically this means that glasses are randomly formed 3d networks of covalently bonded atoms at room temperature. Essentially a single piece of glass is a macro-molecule. The network can be locally broken up by ionic species, the so called fluxes, which reduce the melting point and improve workability.

The problem however occurs when we heat the glass. It is well known that glass can be bend at a certain temperature, for soda lime glass about 800ºC, while it melts at a much higher temperature. The problem is that we know nothing about the structure of glass at these temperatures. We do know that as glass is not a metal, the hot bending deformation is not a dislocation based plastic mechanism as we find in metals and which is used in rolling, extruding or bending metals.

As a single macro molecule cannot deform, this implies that the glass that we are bending is not a single macro molecule. It must by logic be a series of large molecules bonded together by van der Waals forces. Conceivably the molecules might break down and reconnect during the bending, but nothing is known of the structure or the change of structure of glass at these temperatures, as we cannot measure anything.

If we melt the glass again our preconceptions from our studies of metals lead to a dangerous view. The macro molecule cannot break down into atoms. The oxygen molecules would combine and form a gas. The glass would largely sublimate rather than melt. The fact that glass exists as a liquid implies that the glass is still composed of molecules in the liquid state. The minor problem is that there is not the single liquid state which we find for metals. If we cast glass normally at 1400ºC or more the glass is liquid in the sense that it is free flowing, as shown in Fig. 1, note however the scissors which are necessary to cut the viscous glass stream. If we kiln cast at 950ºC the glass is very viscous, flowing like treacle, as in Fig. 2. Melting and casting takes several hours. At 800ºC the glass can be hot bend. In all these three processes the glass is by definition not a single macro-molecule but a molecular liquid. The difference that determines the viscosity is the molecular weight. There might be dynamic break downs and reconstitutions of the molecules, but this cannot be determined using current experimental technologies.

Fig. 1: Casting glass at Poesia

Fig. 2: Kiln casting at TU Delft.

3. Molecular modelling of glass

Lacking experimental tools to investigate the high temperature structure of glass there have been developments in analytical and numerical modelling of glass structures in recent years. Analytically the physiochemistry of glass has been developed into a new model called the topological constraint theory. A good introduction is given by Mauro. Essentially the topological constraint theory explains many reasons why glasses are formed and predicts the glass transition temperature. Fig. 3, taken from Mauro, shows the principles how a glass temperature, T_g, is calculated. Fig. 4, taken from Mauro, shows a ternary diagram and the T_g prediction which follows from the topological constraint theory. The predictions from the model have been proven to be quite accurate. Following on from the topological constraint theory is molecular dynamics modelling of the formation and changes in glasses. This is a numerical technique where atoms are modelled assembling and disassembling into structures. A good example and explanation can be found in the PhD thesis of Konstantinou.

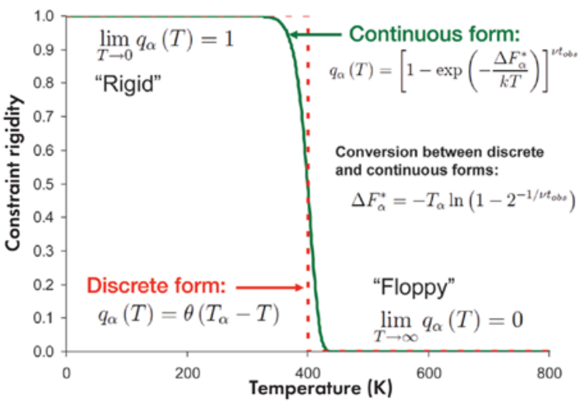

Fig. 3: Glass transition predicted from topological constraint model, from Mauro

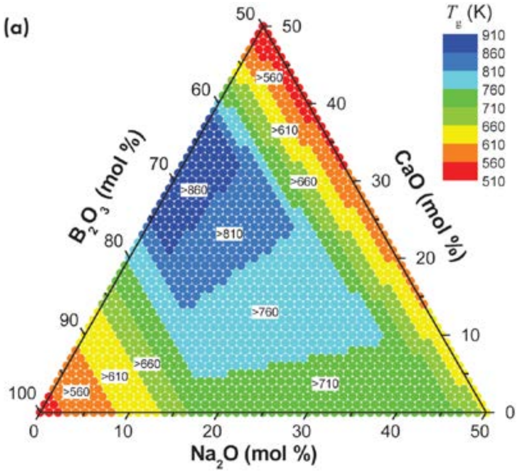

Fig. 4: T_g as a function of composition, from Meuro

Konstantinou’s modelling allows the prediction of local structures in glasses. A specific example is how Molybedenum atoms are incorporated into a glass structure designed for storage of nuclear materials. An example is shown in Fig. 5, with the specific local structure around the Mo atom in Fig. 6. These modelling techniques allow for close study of the solid glass. Currently exact modelling what happens above the glass transition temperature is beyond the technique but this should be possible within the next 10 years. As the strain in the chemical bonds and the strength of the chemical bonds can be calculated the weakest links in the structure can be identified can be identified. Is is thus possible to calculate which links break in succession as the temperature increases. Thus the breakup of the macro molecule can be preeicted and the development of the molecular liquid modelled. To model the interaction between the molecules is however beyond the current state of the art. Additionally to model the transition of a large enough molecules to several molecules which break down at successively higher temperatures and interact however require a large starting model of the order of 10.000 atoms and preferably more. This is beyond the current capacity of ab initio molecular dynamic modelling.

An important result from both the topological constraint theory and the molecular dynamic modelling is that the glass temperature is very sensitive to compositional changes, as can be seen in Fig. 4. The practical relevance of which will be shown later.

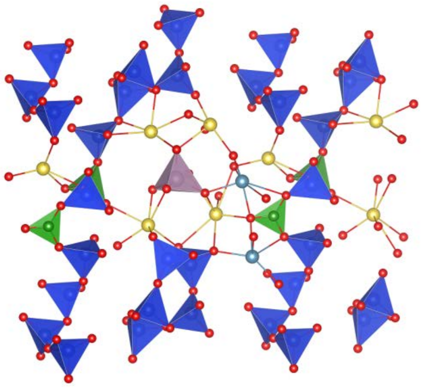

Fig. 5: Local structure of glass containing Mo, from Konstantinou

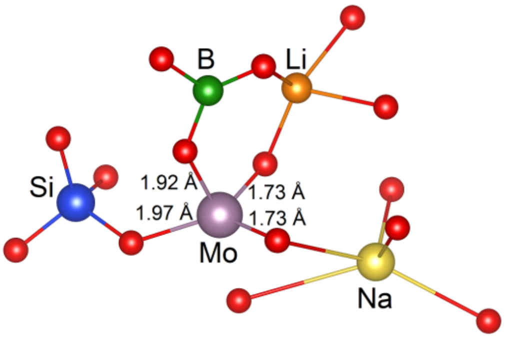

Fig. 6: detail of the structure, from Konstantinou

4. DSC analysis

The one experimental tool that does work on glasses is Differential Scanning Calorimetry (DSC). In this technique a small sample is heated up and the amount of energy needed to increase the temperature by 1 K is measured. Phase changes are detected in this way because of the increased energy required at the phase change temperature. In glasses these are commonly used to determine the glass transition temperature, T_g. Lopes et al. give a good introduction and example how the DSC technique can be used. DSC analysis has been used to study several float glass samples, such as those in table 3. A result is shown in Fig. 7. If we compare these to literature DSC curves from Lopes et al, shown in Fig. 8. Some differences are observed. The float glass sample shows a minimum enthalpy change for the glass temperature transition. All the other transitions are also less distinct to almost invisible. The float glass sample there has a progressive molecular breakup and no clear transitions. If we do a DSC test on PPG Starphire glass, with the same settings as before, we get the result shown in Fig. 9. This is distinctly different from Fig. 7. A clear T_g is observed.

Another important observation can be made from Fig. 8. Tests with slower heating rates show that the glass temperature seems to shift, similar to that in Fig. 8. Konstantinou also concludes the same as the result of his ab initio modelling.

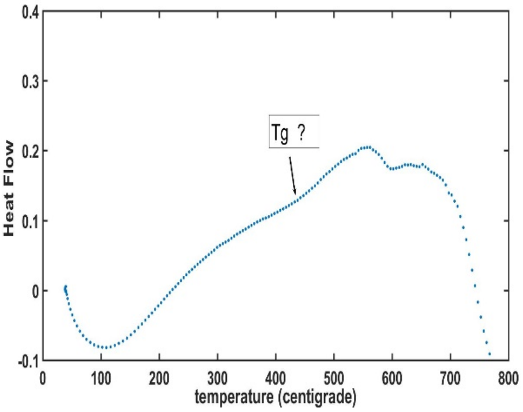

Fig. 7: DSC of sample a of table 3.

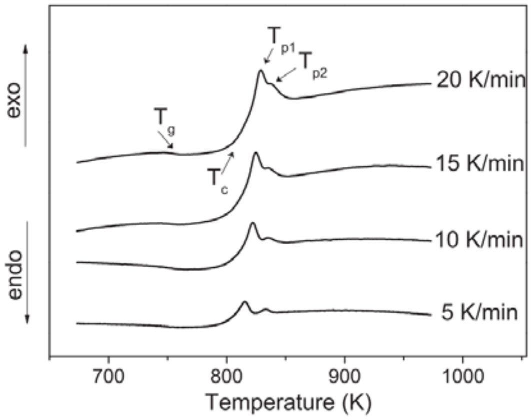

Fig. 8: reference DSC curves from Lopes.

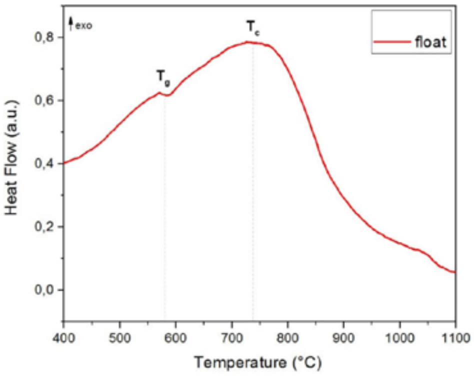

Fig. 9: DSC analysis of PPG Starphire float glass, from Bristogianni. et al.

5. Actual chemical compositions of commercial glasses

Although there are some norm compositions for normal, mid iron and low iron float glass, these are rarely checked by the end user. In recent years during consultancy work it was necessary to check on the chemical composition of several glass types to explain industrial problems. This was done using X-Ray Fluorescence (XRF) analysis. Table 1 contains the results of 3 samples of 1 mm thin glass supplied to a manufacturer of a specific product, involving 3 different factories and 2 producers. Table 2 contains the results of one type of bulk coloured glass with multiple samples produced at a single factory at different times. Table 3 contains the results of several types of float glass which a single processor bought from different European suppliers and also contains the norm composition for float glass as a reference. It is clear that the compositions differ significantly. Table 1 shows that different factories even from the same owner have different compositions. Limiting the glass that was bought to a single factory, in this case producer A factory 2, significantly reduced the failure rate during production of the product. This reduced the drop-out rate significantly making the product much more economical to produce. Table 2 shows that the chemical composition of a single float line is reasonably constant, although there is a clear variation in time. Table 3 shows that many modern float glasses have compositions that are modified for lower melting temperature to reduce the cost. This will also affect the temperatures for correct processing of the glass for tempering and bending. There are also considerable differences between different suppliers. As glass which is bought by a processor is not tested in terms of composition, there is no guarantee that the glass is processed at optimal temperatures. All glass that is used is assumed by the end user to be the same and is processed the same, irrespective of whether a supplied batch needs slightly different settings. In practice most end users do not know where the glass they buy was produced and if they buy from different sources the glass is routinely mixed up in the store house. The methodological way of checking and inventorying materials in the aerospace industry is the complete reverse of how the glass industry treats it materials.

Table 1: chemical composition of 3 types of thin glass in wt.%

Compound	Producer A factory 1	Producer A factory 2	Producer B
SiO_2	74.83	73.84	74.36
Na_2O	12.84	12.83	12.25
CaO	7.24	7.17	8.30
MgO	4.29	4.35	4.07
Al_2O_3	0.82	1.24	0.48
Fe_2O_3	0.023	0.077	0.019
ZrO_2	0.005	0.008	0.006

Table 2: chemical composition of bulk glass produced at different times in one factory, wt%

Compound	Float glass composition by norm	Sample a	Sample b	Sample c
SiO_2	71.9	74	72.7	74
Na_2O	13.1	12.8	12.3	12.6
CaO	9.23	7.7	7.7	7.9
MgO	5.64	4.1	3.9	4.1
Al_2O_3	0.008	0.7	0.5	0.4
Fe_2O_3	0.04	0.52	0.50	0.62
K_2O	0.02	0.06	0.12	0.11

Table 3: chemical composition float glasses produced by different factories, wt%

Compound	Float glass composition by norm	Sample a	Sample b	Sample c	Sample d
SiO_2	71.9	64.72	68.54	66.59	70.41
Na_2O	13.1	12.61	12.35	12.41	12.89
CaO	9.23	16.83	13.20	15.67	11.31
MgO	5.64	4.00	3.82	3.94	4.43
Al_2O_3	0.008	0.79	0.68	0.71	0.02
Fe_2O_3	0.02	0.18	0.15	0.22	0.19

6. Effect of composition on glass viscosity

In glasses the various working temperatures are related to the viscosity. Martlew gives these as:

Melting point	2.0
Working point	4.0
Flow point	5.0
Littleton’s softening point	7.65
Deformation point	11.5
Annealing point	13.0
Strain point	14.5

The values are the 10 base logarithm of the viscosity in poise. 10^2 means 100 poise, etc. These are however arbitrary definitions based on the practices of traditional glass working. Actual values for the different viscosities are difficult to find. Martlew gives an incomplete series of values for different groups of glasses. For Na_2O –SiO_2 melts the data is summarized in table 4.

Table 4: melting point as function of composition for Na_2O SiO_2 melts

Na_2O mol%	SiO_2 mol%	Temperature ºC
10	90	1728
15	85	1568
20	80	1455
25	75	1372
30	70	1294
35	65	1205
40	60	1015
45	55	1057

Increased Na_2O content decreases the melting point, from 10 to 15% by 32K per mol% increase. From 25 to 30% by 15.6K per mol% increase. The other glass working temperatures are similarly affected.

7. Discussion

In the artistic glass world there is a significantly greater appreciation of the different behaviour of different glasses. This arises simply from the need to work many different glasses into complex objects. Their publications are however not widely read in the general glass community. Stone gives for many types of glasses a range of temperatures. There is also a clear need to be cautious in using these. To quote several relevant passages from Stone (p 6.28 en 6.29) :

“The most significant variable after thickness is the glass type being fired. Glasses differ in their heat cycle requirements in four important areas:

1. the rates of temperature change, both up and down
2. the amount of annealing time
3. the annealing temperature
4. the subsequent down phase temperature settings.”

“The following specific temperatures for the annealing stage are approximate, especially regarding glass from producers that supply a range of colours and forms.”

“Remember that glass has an annealing range rather than a single point where stress is relieved . It’s just as well, because not all manufacturers test the temperature at which the viscosity of their glass 10^{13} Poises, the accepted measurement of an annealing point.”

These points derived from practical experience in the artistic glass community, do however translate into problems for the current float glass industry. If we look at the most important quality control problems in the float glass industry:

1. uneven tempering
2. optical anisotropy
3. roller wave distortion

The first of these have been studied by Chen et al. and Veer et al. Tempered float glass is quite inhomogeneous in terms of the surface pre-stress. This varies widely in a single specimen and is also highly variable between specimens. Although Chen et al. correctly attribute this uneven cooling, different physiochemical response between within float glass specimens and between specimens with different compositions cannot be ruled out. As the glass point varies between different compositions and is also dependent on the heating rate and cooling rate; equal treatment of chemically different float glass panels will result in different compressive pre-stresses. Additionally inhomogeneous cooling rates will affect the glass temperature locally of the glass. The different compressive pre-stresses cause visual anisotropy as the different compressive pre-stresses cause different polarisation effects which cause blotchy patterns. This effect and the problems it creates are described quite well by Pasetto and are shown to be a significant problem in the current glass industry. The lack of quality control norms regarding optical anisotropy of course does not help. There is some anecdotal evidence that some Chinese glass producers that single source their float glass and optimise the settings on their tempering furnaces for this glass have (significantly) less problems with an-isotropy. Although this would argue for a role of composition effects, anecdotal evidence is however not scientific evidence. It is however clear that some producers have a much bigger problem with an-isotropy than others.

Roller wave distortion is another quality control problem, again beset by a lack of standards in the industry for what is acceptable. A good overview of the problem is given by Abbot and Maddocks. There is however a clear relation between roller wave distortion and a temperature which is too high for the glass used. Abbot states that for tempering:

"In theory, heat treatment requires uniform heating of the glass to 621 +/- 3 deg C, while holding the glass in a flat state"

This might be true for a certain float glass, for instance the PPG Starphire from Fig. 9, it is very doubtful if this is correct for the glass from a different supplier in Fig. 7, where the T_g is clearly lower and not very well defined.

As it is clear from the previous paragraphs that the glass temperature is dependent on the heating rate and that glass producers that do not single source their glass by necessity have to deal with different chemical compositions and thus (slightly) different glass temperatures; some panels will inevitably be tempered at too high a temperature. As Fig. 4 and table 4 show, a couple of % difference in one or two components of the glass can shift the glass transition by tens of degrees. The resultant decreased viscosity will cause roller wave distortion. The differences in composition in table 3 are large enough to cause the differences in T_g that would significantly increase the risk of roller wave distortion. Some of these glasses also have an indistinct T_g point as shown by DSC measurements, such as in Fig. 7, which makes it difficult to determine the correct processing temperature.

Quality control in the glass industry is thus more than proper cutting and grinding, and setting the right temperature settings on the tempering furnaces. It needs to either single source the glass and optimize the machinery for this glass. Table 2 shows that glass from a single float line is reasonably consistent in terms of composition. Or the industry needs to adjust the process settings to the actual chemical composition of the glass being processed.

However the current logistics of the industry do not allow for differences in composition other than normal float, mid iron and low iron glass. This also because the effect of differences in composition are not recognised as important. If we compare this to the metallurgical industry where exact compositions are controlled and the logistics setup allows for streams of materials being correctly controlled allowing for differences in composition and in different heat treatments there is much too learn for the glass industry.

8. Conclusions

From the previous paragraphs the following conclusions are drawn:

- There are significant differences in the float glass composition if we look at glass from different suppliers.
- These differences are sufficient to shift the glass temperature potentially by 10 K or more as shown by both DSC tests and modern analytical and numerical modelling.
- These differences can contribute to industrial problems such as uneven tempering, optical anisotropy and roller wave distortion.
- Quality control in the glass industry should allow for compositional differences.

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