

The Glass Transition in Polymers Theory 2 - Kinetics vs Thermodynamics

The formation of glasses can be understood from both a kinetic approach and a thermodynamic approach. In this section we will review both.

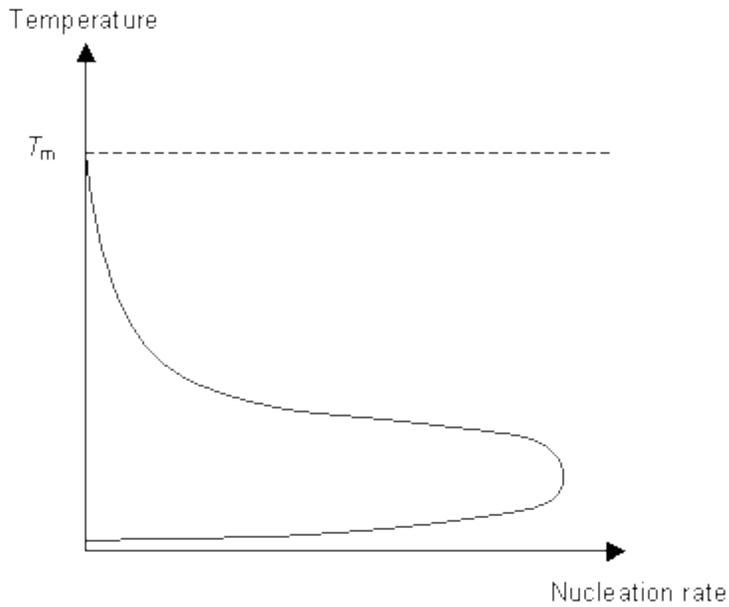
Kinetic Approach to Glasses

Consider a polymeric liquid being cooled towards its melting temperature. Once the temperature of the liquid reaches T_m the solid crystalline phase is thermodynamically favourable. In order for the liquid to undergo a phase transition to the solid state a two-step process must take place:

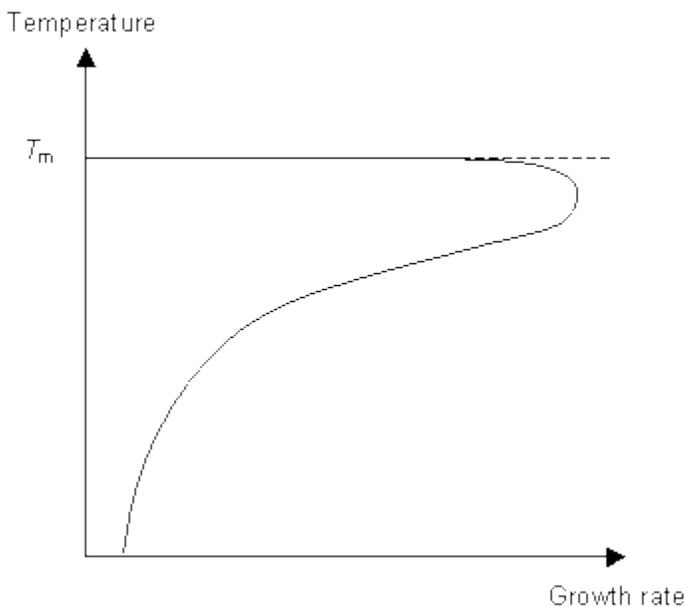
1. Nucleation of solid seeds
2. Growth of the seeds

Nucleation is the formation of small crystalline solid particles in the liquid. As a result a new interface is formed in between the solid particle and the liquid. This interface has an associated energy, the interfacial energy. For a successful nucleation event to occur the polymer must find extra energy from somewhere to "pay" for the energy cost of creating a new interface.

This energy is called the "driving force" for nucleation. As we cool the liquid just below T_m we see no nucleation at first. Instead nucleation occurs at a temperature $T < T_m$, below the expected temperature. When the polymer is still liquid below T_m it is said to be undercooled. The amount of "undercooling" is limited by the nucleation rate.

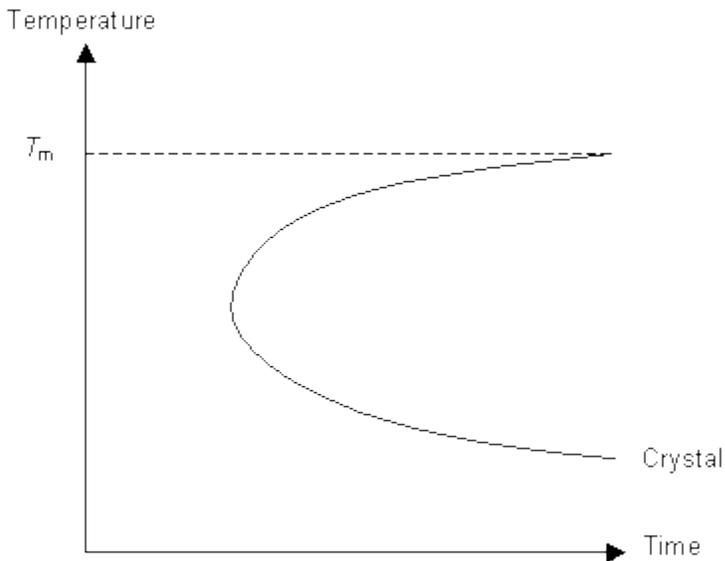


The second stage of the phase transition is the growth of the nucleated seeds. This is a thermally activated process, which means that its rate is dependent on the temperature. So for fast crystal growth the ideal method is to cool the polymer to just above T_g to allow for nucleation to occur and then raise the temperature to just below T_m to allow growth to occur.



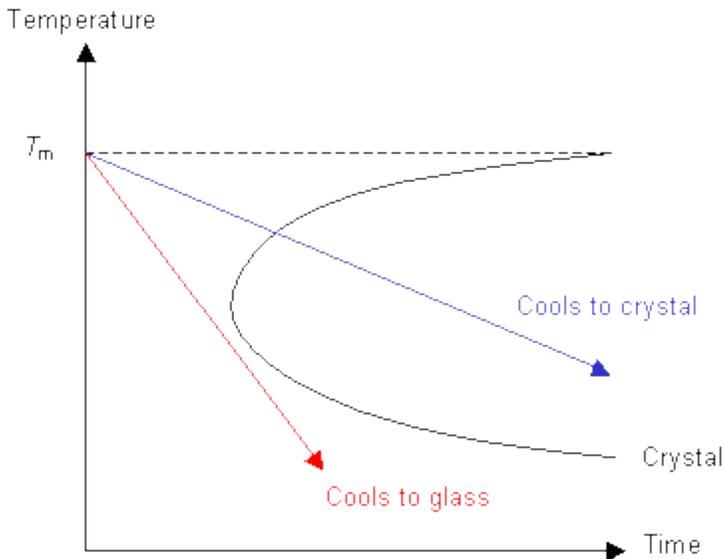
Understanding these concepts we can now think about how best to cool a liquid in order to form a glass. To ensure we form a glass we want to reduce the number of nucleation events as much as

possible (otherwise we will have crystals not an amorphous solid) and not allow growth to occur. By cooling the liquid very quickly (i.e. *quenching* it) it is possible to reduce the mobility of the molecules to the point where they can not move around to order themselves periodically as they do not have the energy to diffuse far enough. This concept can be expressed on a TTT (time temperature transformation) graph.



The graph represents the degree of crystallinity of the polymer as it is cooled. The line marked "crystal" indicates a specific degree of crystallinity (for example it may indicate 90% crystallinity in the sample). The TTT graph is used for isothermal transformations, but here it is loosely applied to continuous cooling.

If the cooling rate is fast enough then the polymer can be cooled so that it does not enter the crystal region of the graph. In this case, although the polymer is below T_m , it does not crystallise because the molecules can not move to order themselves periodically (as in a crystal). Instead the polymer has formed an amorphous solid, or a glass.



Thermodynamic Approach to Glasses

Consider the red line from the graph above. Above T_m the polymer is a liquid. At temperatures a long way below T_m the polymer behaves like a solid, although it is not crystalline. In this state the glass has the properties of a solid, but may exhibit aspects of liquid behaviour over long time scales.

(There is a common misconception that inorganic glasses behave in this same way. This liquid behaviour is incorrectly thought to be responsible for the windows of old buildings often being thicker at the bottom than at the top. This is discussed briefly, with citations, below)

Do Cathedral Glasses Flow?

A popular world-wide myth about inorganic glasses based on silica frameworks, such as glass windows in cathedrals, is that over hundreds of years noticeable flow is able to occur under the influence of gravity, as a result of which cathedral glass windows are thicker at the bottom than the top.

There are a number of useful references in the scientific literature where this is discussed at some length. In a letter entitled 'Fact or fiction? Can cold glass flow under its own weight and what happens to stained glass windows?' sent to the



Editor of Glass Technology, 37, 143 (1996) R.G. Newton notes that at room temperature inorganic glass can flow if a large enough compressive stress is applied, so that for example hardness indents can be made in inorganic glass. However, irreversible flow can only occur if stresses of at least one tenth of the theoretical breaking strength of glass are applied. Such stresses are not achievable in inorganic glass because of the presence of surface defects, which will cause the glass to shatter well before such a stress can be applied.

Further discussions of this myth, with calculations to show conclusively why cathedral glass will not flow under its own weight over hundreds of years, are to be found in:

- *F.W. Preston, 'The post-instantaneous creep of long-loaded glass specimens', Glass Technology, 14, 20-30 (1973)*
- *E.D. Zanotto, 'Do cathedral glasses flow?', American Journal of Physics, 66, 392-395 (1998)*
- *E.D. Zanotto and P.K. Gupta, 'Do cathedral glasses flow?-Additional remarks', American Journal of Physics, 67, 260-262 (1999)*

A telling point made by Zanotto and Gupta from their calculations is that the timescale over which flow might be seen at room temperature (termed the relaxation time) of 10^{23} years is well beyond the age of the Universe (10^{10} years). The explanation for why cathedral glasses are thicker at their bottom than at their tops lies in the manufacture of ancient glass. Such glass was made by blowing the glass into large cylinders that were split and flattened manually. This manufacturing process produced glass that was inherently not of a uniform thickness, unlike the glass made by the float glass process that we have today.

Instinct would make fitters of window panes in cathedrals put thicker sides of glass at the bottom, little realising that their actions would give rise to the urban myth that would sweep the globe hundreds of years later.

Important points relating to phase transitions within polymers

- Glass formation can be explained both kinetically and thermodynamically
- Glasses can be formed by quenching (rapidly cooling) the polymer so that the molecules do not have time to order themselves into a periodic crystal
- Glasses exhibit the properties of a solid, but over long time scales can flow like a liquid
- Below the Kauzmann temperature the polymer must either be a crystalline solid or a glass as the liquid phase is thermodynamically unstable

Source: <http://www.doitpoms.ac.uk/tlplib/glass-transition/theory2.php>