

1 Glasses

Sometimes, instead of possessing the carefully arranged crystalline bonds we've been talking about, materials end up partially or completely jumbled. In particular, elements that have flexibility in the rotational orientation of bonds can form these disordered structures, like long, interlinked chains frozen in a random orientation. We refer to these amorphous structures as *glasses*. In 3.091 we'll focus primarily on silica: a glass based on silicon dioxide.

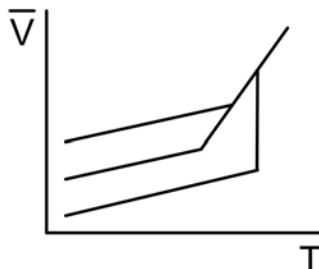
The scale from order to disorder is a spectrum. Single crystals have near-perfect order: everything is oriented the same way, and there is long-range order in the crystalline lattice. Then there are polycrystalline materials, which possess multiple crystalline regions arranged in grains. Near the grain boundaries, there are defects; the sudden change in crystal orientation can add local strain. Polycrystalline materials have short-range order, on the scale of the grains, but they lack the homogeneity of single crystals. At the other end of the spectrum are amorphous materials. These glassy materials lack any semblance of order: the complete rotational freedom of the silicon bond provides little constraint on the arrangement of bonds.

As it turns out, it is possible to control whether a melt forms a crystal or a glass by carefully engineering the cooling process. Although silica glasses are able to form, the regular structure of the crystalline lattice is still the most energetically favorable structure. In a crystal, the atoms are optimally arranged to minimize energy by balancing the Coulombic attraction between protons and electrons with the repulsion of like charges.

2 Cooling curves

In summary, the primary knob we can turn to determine whether a melt ends up as a crystal or a glass is *processing*. One metric that allows us to keep track of the affect various processing steps have affected the melt is the *molar volume*. You can think of molar volume as a proxy for disorder. For the optimally-arranged crystal, the atoms are minimally spaced, and the molar volume is minimized. The more disordered the material becomes, the more space each atom takes up, and the larger the molar volume is! By measuring the molar volume as a function of temperature, we can compare how ordered or disordered different processing methods are.

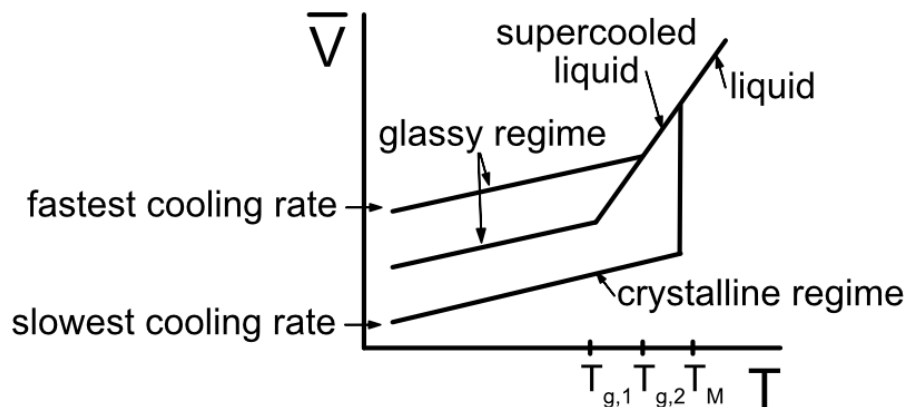
Example: Label the plot with the following features of cooling curves: liquid, supercooled liquid, T_m , T_g , the crystalline and glassy regimes, and the curves with the fastest and slowest cooling rates



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Do yourself a solid.

Liquid is the state of matter at high temperatures, when the material forms a melt. It has a higher slope than the solid regions because the coefficient of thermal expansion ($\frac{\partial \bar{V}}{\partial T}$) is generally higher for liquids than solids. The melting point, T_m , can be determined by looking for a discontinuity in the plot: during the phase transition from liquid to solid involves a big change in molar volume at constant temperature. Correspondingly, the *crystalline regime* is the low temperature solid that follows the phase transition. *Supercooled liquid* is any liquid that remains at temperatures below the melting point— it has the same slope as the liquid above the melting point. The points in the supercooled liquid regime where the slope changes are the *glass transition temperatures*, T_g . Unlike the crystalline phase transition, the glass transition is continuous (but not smooth): you can think of the glass transition as just freezing the viscous liquid melt in place, as is. Remember that depending on the specifics of the processing, glasses with different T_g and different molar volumes can form. Below T_g , the glass becomes a solid: this is the *glassy regime*. Finally, it takes a long time atoms to rearrange into ordered structures, so crystals are processed with the *slowest cooling rates*. The glasses with the highest molar volumes are the most disordered: these melts have to freeze rapidly, and they have the *fastest cooling rates*.



Example: Which of the following samples will yield a glass with higher molar volume?

melt is very viscous OR melt is very fluid

melt is cooled rapidly OR melt is cooled slowly

equilibrium crystal structure is complex OR equilibrium crystal structure is simple

A viscous melt does not flow easily: it is more difficult for the atoms to move around than in a very fluid melt. Therefore, with all other factors held constant, **the viscous melt** should produce a glass with higher molar volume. Following the rationale from the previous section, **the melt that is cooled rapidly** will yield a glass with higher molar volume compared to a melt that is cooled slowly. Finally, if the equilibrium crystal structure formed by a melt is very complicated, it takes time for all of the atoms to make it to their optimal lattice sites. With all other factors held constant, **the melt with a more complex equilibrium crystal structure** will yield a higher molar volume glass than the melt with a simple equilibrium crystal structure.

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