Relaxation in silicate melts

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Abstract: The glass transition is a kinetic barrier that divides the behavior of silicate melts into two types, liquid and glassy. Liquid behavior is the equilibrium response of a melt to an applied perturbation, resulting in the determination of an equilibrium liquid property. The equilibrium may be stable (superliquidus) or metastable (subliquidus). Glassy behavior occurs when the timescale of the perturbation is too short for melt equilibration. This can occur when the frequency of an applied sinusoidal perturbation is too high or when the observation time of an experiment is too short. The time- or frequency-dependent response of the structure and properties of a melt to a perturbation is termed relaxation. Liquid and glassy behavior are relaxed and unrelaxed behavior, respectively.

Linear viscoelastic theory provides mechanical models for the prediction of the isothermal transition from liquid to glassy behavior. A simple series combination of Hookean spring and Newtonian dashpot (a Maxwell element) is capable of predicting the timescale corresponding to the glass transition from the ratio of the relaxed viscosity to the infinite frequency elastic modulus. We review some experimental work on silicate melts that can be used to constrain the location of the glass transition in time-temperature space at 1 atm pressure (e.g., ultrasonic wave propagation, fiber elongation, torsional testing, scanning calorimetry).

The microscopic origin of the glass transition in silicate melts is related to the exchange of Si-O bonds. Recent $^{29}$Si NMR work indicates that the Si-O bond exchange frequency matches the timescale of the glass transition. This explains the Newtonian viscosity of silicate liquids. No extended species (e.g., “polymers”) can exist at higher temperatures and longer timescales than the lifetime of the fundamental Si-O bond. Silicate melts, however, become non-Newtonian as the strain rate approaches the equilibration rate of the Si-O bonds. Such a correlation between Si-O bond exchange and the viscous flow mechanism, in turn, explains the success of the Eyring relationship in relating high temperature oxygen and silicon self-diffusion to viscosity.

Knowledge of the structural relaxation timescale is important in extracting equilibrium information from studies of the structure and properties of quenched glasses. Quench rate-dependent speciation data for glasses imply a temperature-dependence of the species equilibrium in the liquid state. Estimation of the relaxation times associated with the quench rates allows reconstruction of the temperature-dependence of homogeneous equilibria in liquids.

Experimental work on silicate melts should consider the location of the experimental method in time-temperature space, with respect to the glass transition. Diffusivity measurements, for example, are influenced by the glass transition. When the duration of a diffusivity experiment crosses the volume relaxation time, an inflection in the temperature-dependence of diffusivity of cations is observed. A second “transition” in diffusivity behavior is expected to occur at higher temperatures when the diffusivity of network oxygen and silicon approaches that of other cations.

Key-words: structural relaxation, viscosity, diffusivity, speciation, non-Newtonian, quench rate, silicate melt, liquid, glass.

1. Introduction

The glass transition has been described as “that phenomenon... in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties such as heat capacity and thermal expansivity from crystal-like to liquid-like values” (Wong & Angell, 1976). The development of frequency domain methods for experimental methods

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