

# STRUCTURE, DYNAMICS AND PROPERTIES OF SILICATE MELTS

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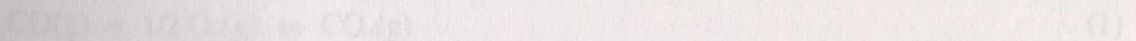
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## INTRODUCTION: THE NATURE OF STRUCTURAL RELAXATION

In spite of the enormous activity and interest in the subject over the past thirty years or so, the nature of the glass transition and the structural relaxation process in liquids is frequently poorly understood by otherwise knowledgeable scientists or engineers. The purpose of this chapter is to introduce the glass transition, the structural relaxation process and the phenomenology associated therewith in a fairly basic fashion aimed more at qualitative concepts than at quantitative details. Extensive treatments of much of this material can be found in the books of Braver (1983), Scherer (1986a) and Novikov (1975) and a number of review papers (Moynihan et al., 1976; Durgwell and Webb, 1989, 1990; Bohlen, 1990; Simpson, 1993; Moynihan, 1994; Hodge, 1994; Angell, 1995).

At the macroscopic thermodynamic level, structural relaxation and the glass transition can be viewed as a phenomenon in which the state of the system depends not only on variables such as temperature  $T$ , pressure  $P$ , shear stress, electric field, etc., but also on what are commonly called order parameters, internal parameters or (in chemistry) progress variables (Alymkin and Gupta, 1978). If one has such a system initially in equilibrium and makes a sudden change in one of the variables (change in  $T$ ,  $P$ , chemical composition, etc.) the system will respond and seek a new equilibrium state consistent with the imposed change. However, the adjustment of the order parameters to new equilibrium values may be kinetically impeded and, in the extreme, be so slow as to be unobservable on any practical experimental timescale.

Examples of this sort of kinetically impeded adjustment of order parameters to imposed changes abound in our everyday world. Consider, for example, the chemical reaction



where the order parameter describes the relative amounts of reactants and products. At ordinary composition (1%  $\text{CO}$  in ordinary Earth atmosphere,  $P_{\text{O}_2} = 0.21$  atm,  $P_{\text{CO}_2} = 3.5 \times 10^{-4}$  atm) and the same pressure of  $\text{CO}$  in chemical equilibrium is extremely small ( $P_{\text{CO}} = 8 \times 10^{-11}$  atm). If we perturb the system by adding additional  $\text{CO}$  at ordinary temperatures, we might expect most of the added  $\text{CO}$  to be consumed by reaction with oxygen. This of course will not occur in real time, as demonstrated by the ease with which the  $\text{CO}$  content in the car tail in and around the toxic level ( $P_{\text{CO}} = 5 \times 10^{-2}$  atm). The reaction is too slow at ordinary temperatures. However, this is not the case at higher temperatures, where noticeable (1%) reacts quite readily with  $\text{O}_2$ .

Equilibrium constants for chemical reactions are in general temperature dependent. The main point is one starts with a system at chemical equilibrium and lowers the temperature, the relative amounts of reactants and products (the order parameter) will also