Fundamental Importance of the Dispersion of the Structural Relaxation Time in Solving the Problem of Vitrification of Liquids

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In conventional theories of glass transition, the dispersion of the structural relaxation is either not addressed, or derived with additional assumptions as a consequence, which is independent of the structural relaxation time τ_α. Thus, the dispersion or the time dependence of the structural relaxation bears no fundamental relation to the value of τ_α and its dynamic properties. However, such approaches appear incompatible with a variety of general experimental facts indicating that the dispersion either governs the properties of τ_α or correlates with them. A striking example is the recently discovered general experimental fact in glass-formers: for a given material at a fixed value of τ_α, the dispersion is constant, independent of thermodynamic conditions (temperature, pressure and volume); that is, the shape of the α-relaxation function is a single function of the relaxation time. We found this generally in more than thirty molecular and polymeric glass-formers. Examples are shown in Figs.1 and 2. Thus, if the dispersion of the structural relaxation is derived independently of τ_α as in conventional theories, it is unlikely that it would be uniquely defined by τ_α.

Furthermore, secondary relaxations belonging to what we call the Johari-Goldstein (JG) β-relaxation have properties remarkably similar to the structrual α-relaxation. It is universal and found in small molecular, polymeric, plastic crystalline, metallic, and inorganic glass-formers. We found the relation of its relaxation time, τ_{JG}, to τ_α is entirely determined by the dispersion of the structural relaxation, independent of T, P and V. All these general experimental facts of the JG β-relaxation are pointing to the fundamental role it plays in vitrification and as the precusor to the structural relaxation. Conventional theories of glass transition either do not consider the JG relaxation or merely acknowledge its existence but give no relation of it to the structural relaxation. Hence, their task is not yet complete.

From the above, we see that conventional theories and models of the glass transition either do not address the dispersion or derive it independently of τ_α; and do not take into consideration of the fundamental role of the JG relaxation. They are not consistent with the general experimental facts, and are in need of revision. On the other hand, the Coupling Model of the presenting author is the exception. It emphasizes many-molecule dynamics, which gives rise to the dispersion, and its primitive relaxation time is nearly the same as τ_{JG}.
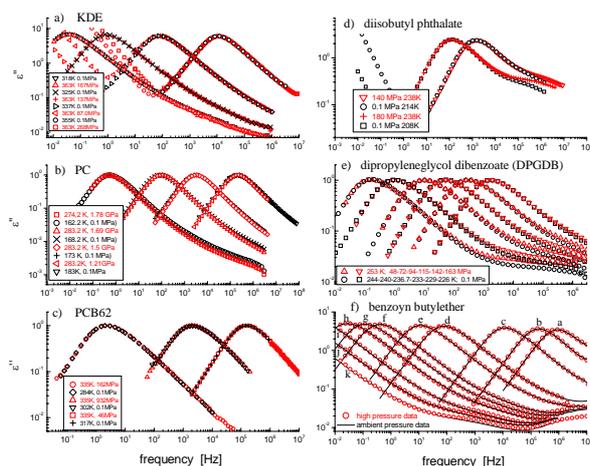
Figure 1: Dielectric loss data at various combinations of temperature and pressure as indicated to demonstrate the invariance of the dispersion of the α-relaxation at constant α-loss peak frequency ν_α or equivalently at constant α-relaxation time τ_α. for: a) Cresolphthalein-dimethylether (KDE) b) Propylene carbonate (PC), c) chlorinated biphenyl (PCB62); d) diisobutyl phthalate (DiBP) e) Dielectric loss of dipropyleneglycol dibenzoate (DPGDB).
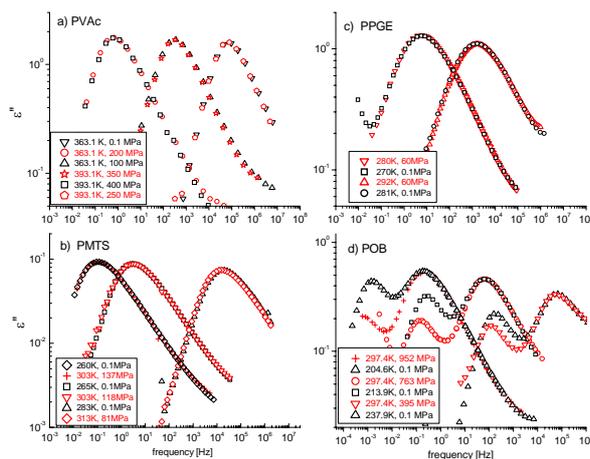
Fig.2: a) poly(vinylacetate) (PVAc); b) poly(methyltolylsiloxane) (PMTS). c) poly(phenyl glycidyl ether)-co-formaldehyde (PPGE); d)poly(oxybutylene) (POB). The remarks in Figure in Figure 1 applies here as well.