Direct determination of the kinetic fragility index of glassforming liquids by differential scanning calorimetry

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Abstract

A calorimetric method of obtaining directly the fragility of liquids from the fictive temperatures of variably quenched glasses, is outlined. "Steepness indexes" $m$, have been determined for a group of molecular liquids of diverse character, and vary in the range 50-150. The values obtained mostly agree well with those from earlier studies using dielectric relaxation, heat capacity spectroscopy, and viscosity data. In our method there is the advantage that the fragility is determined from the most fundamental relaxation process, that of the enthalpy. The same calorimetric measurements yield the liquid and glass heat capacities $C_p$, and entropies of fusion, permitting relationships between thermodynamic and kinetic responses to be examined simultaneously. We find that decalin is the most fragile molecular liquid, $m=145$. Surprisingly it has the smallest increase in heat capacity at the glass transition (scaled by the glass $C_p$) of the liquids studied here, while the strongest liquid, glycerol, has the largest increase. However, the thermodynamic fragility, assessed from the scaled rate of increase of the excess entropy above $T_g$, is nevertheless found to be highest for decalin due to the very small value of the excess entropy at $T_g$. By contrast glycerol, with the largest jump in heat capacity, has the smallest entropy-based fragility, because of its large residual entropy at $T_g$. Thus, despite the heat capacity results, the approximate correlation of kinetic and entropy-based thermodynamic fragilities reported in recent work [xx] is upheld, while the basis for any correlation of fragility with the jump in heat capacity itself, is removed.

With data from this study we can test the notion that the condition for breaking ergodicity at cooling rate $Q$ is $Q^*d\tau/dT=1$. This shows that the reason that the "Deborah number" is found to be approximately unity at the ordinary glass transition is that it must always be approximately unity at the "midpoint cooling" glass transition, i.e., the fictive temperature of the glass.

Keywords: glass transition, structural relaxation of supercooled liquids, fragility of liquids, heat capacity, differential scanning calorimetric

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