Structure of Molecular Liquids: the Minimal Requirements to Form a Glass and its Relation to Fragility

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Abstract:

What causes the viscous slowing down of molecular liquids is most of the time related to an increase of dynamical correlation lengths, whose signatures are not found in any static structure factor measurements and radial pair correlation functions. Most of the studies are therefore focussing on thermodynamical and dynamical properties and the fragility indices, expressed in various ways, collect nearly all the significant features of the phenomenon. However at a first glance looking at the seminal Angell plot, we are tempted to classify the systems also according to their chemical formula and bond type, from covalent to van derWaals: the tendency is thus to consider silica as a model system for strong liquids and the ortho-terphenyl or the toluene as the simplest fragile liquids. Each class can evolve towards the other: the addition of Na or Ca to silica makes it less strong and changing the aromatic character of toluene to its saturated analogue methyl-cyclohexane will decrease its fragile character. But the latter differences have their strongest impacts in the high temperature or Arrhenius regime, where an effective activation energy E□ of already several kT above the melting temperature can be related to intermolecular interactions and specific motions due to the molecular shape. The specific magnitude of this E□ will therefore strongly affect the value of the fragility and support revisiting its definition. Above all it encourages focusing on chemical architecture and local structure of liquids forming a 'laboratory' glass and resisting to crystallisation. This issue might have considerable operational and conceptual significance for a better understanding on how the local order evolves as Tg is approached. As suggested by Turnbull decades ago, "it not well established whether or not every substance can be put into a glass form.", thus we propose here to analyse the minimal requirements, focussing on the simplest molecular and most fragile liquids distinct from the most studied computer-liquid, the two-component Lennard-Jones fluid.