
Retrospective on the development of glass science over the last 50 years. A personal account, and some current aspects

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Abstract

When my research career started at the M. Sc. level at Melbourne University, 1954, the study of liquid silicates of industrial interest was still at a primitive level. Even at MIT, the slags of pyrometallurgical processes were still being discussed in terms of mixtures of oxide molecules. My supervisor, G. M. Willis, preferred the ideas of "ionic" liquids being pioneered by electrochemist John Bockris and so, on his advice, I joined the Bockris group, intending to complete the write-up of my Ph. D. work back at Melbourne. Instead I went to Imperial College as a "name" post doc, listened to the Gurus at the first Faraday Discussion on Ionic Liquids, and wrote a thesis about Ionic diffusivity and the Cohen-Turnbull free volume theory¹. It won me the Armstrong Medal.

Back at Melbourne University as asst. prof. I read Turnbull's papers on glass formation² including the case (Russian work) of the simple salt mixture, $\text{KNO}_3 + \text{Ca}(\text{NO}_3)_2$, now known as the model system CKN. The liquid solution is easily made by gentle heating. Pulling clear strong glass fibres from the cooling ionic liquid was a transforming experience, and I was hooked on simple glasses for life. The aqueous solutions of inorganic salts nearly all form glasses, and salt hydrates, like many molecular liquids, provide excellent examples of the Kauzmann paradox³. But water itself is weird and provocative and its study suggests some liquids might like to form second liquid phases before vitrifying- so the glassy state, when it can be obtained, is not as expected from the known liquid. This is currently a forefront area of research as I will emphasize with unfamiliar examples.

Liquids approach their glassy states in different ways, manifested by very different rates of viscosity increase per unit temperature. Some with network structures, obey the Arrhenius law. Others with less specific structuring show hair-raising violations of the Arrhenius law. A Tg-scaled Arrhenius plot⁴ was helpful in demonstrating the difference and gave new impetus to understanding the origin of what had long been known as "long" vs "short" glass behavior in the classical glass field. In the case of the super-Arrhenius glassformers a close relation between the viscosity divergence temperatures indicated by the Vogel-Fulcher-Tammann equation and the Kauzmann vanishing excess entropy temperature could be demonstrated using short extrapolations, as attributed to Julian Gibbs and co-authors⁵, thus putting the understanding of the provocative viscosity behavior ("fragile" vs "strong"⁴) squarely in the lap of thermodynamic modelers, as will be explained.

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Understanding the rate of excess entropy loss demands understanding the origin of the excess heat capacity, but how to scale the excess heat capacity for comparisons amongst different substances is a long-standing problem. We have recently suggested a way of doing this⁶ which will be put up for criticism. The scaled excess heat capacity, hence the liquid fragility, should be determined by the entropy change in the fundamental configurational excitation, which we discuss in terms low frequency vibrational mode generation, as originally suggested by Granato⁷.

One of the fascinations of glassforming systems is the hint of some underlying universality, which remains to be elucidated. An important question for evaluation is whether there exist glassformers that have no crystalline ground state. "Crystal-free" routes to the glassy state⁸ will be given some consideration.

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