

The low temperature end of the fragile liquid state: experimental evidence for a new paradigm.

C. Austen Angell,
Dept. of Chemistry and Biochemistry,
Arizona State University, Tempe, AZ-85287 USA

When a molecular substance is unable to find a 3D-ordered packing state that is of low energy, the intrinsic entropy of the liquid state leads the substance to melt far below its boiling point. Substances, with melting points less than half their boiling points, are viscous liquids on melting and are always slow to crystallize on cooling. In rare cases designated “ideal glassformers” ($T_m < T_g$), crystallization may even be impossible before the glass transition is reached.

For most of the last half century, it has been supposed that such glassforming substances would pass continuously into the glassy (non-ergodic) state at a temperature that depends on the cooling rate and finds its limit, on infinitely slow cooling, at the Kauzmann temperature. The Kauzmann temperature can often be defined within narrow limits, by a “vanishing excess entropy” extrapolation, starting either from crystal state in the case of experiments [1,2] or from the ideal gas state in the case of simulations [3]. Viscosity and relaxation time extrapolations seemed to support the continuous approach to the ideal glass using plausible, mathematically simple, extrapolations (VFT fittings).

In the last decade, however, starting with models by Tanaka [4], and experimental findings on such substances as triphenylphosphite TPP by Kivelson and coworkers [5], and again Tanaka’s group [6], an alternative has arisen, namely that the glassy state may be reached ideally in a discontinuous manner, through a first order liquid-glass transition. Such transitions had also been invoked to explain the existence of some apparently boson-peak free “superstrong” inorganic glasses[7]. Most recently a full theoretical model predicting the occurrence of a first order transition to a nearly-ideal glass state, generally hidden below the experimental glass transition, has been developed by Matyushov[8] and is the first to give a satisfying account of the observed heat capacity and excess entropy behavior for a variety of fragile glassformers. With the exception of occasional cases like TPP, the actual transitions appeared improbable of detection until very recently when Ediger’s group [9] using special vapor deposition techniques, stumbled across (and then investigated carefully) the apparent existence of very low enthalpy, below $-T_g$, states, that are inaccessible by simple annealing. These have been followed by similar discoveries for a variety of toluene derivatives [10], and the findings start to look general for very fragile liquids [8]. Thus a new paradigm for the low temperature end of the *fragile* liquid state, with an abrupt first order termination, seems on the point of establishment. Structural characterizations of the low temperature glass phase are currently being reported by the Ediger lab (MDE, private commun.)

References

1. W. Kauzmann, *Chem Rev.* 43, 218 ((1948).
2. G. Adam, J. H Gibbs, *J. Chem. Phys.* **43**, 139.(1965)
3. G. Parisi, *J. Phys. A* 30, 8523, (1997): Sciortino et al, PRL, 83, 3214 (1999)
4. H. Tanaka, *J. Phys. Condensed Matter* 10, L207, (1998).
5. A. Ha, I. Cohen, X.-L. Zhao, M. Lee, D. Kivelson, *J. Phys. Chem.* 100, 1, (1996).
6. R. Kurita and H. Tanaka, *Science* **306** (2004), p. 845.
7. Angell, Moynihan and M. Hemmati. *J. Non.-Cryst. Solids* 274:319-331 (2000).
8. D. Matyushov and C. A. Angell, *J. Chem. Phys.* **126** (2007), p. AN094501.
9. S. F. Swallen, Kearns, K. L., Mapes, M. K., Kim, Y. S., McMahon, R. J., Wu, T., Yu, L. & Ediger, M. D. *Science* **315**, 354-356 (2007).

10. K. Ishii, H. Nakayama et al., Chem. Phys. Lett. 459 109–112 (2008)