

The role of heat capacity in arguments for a new glassformer paradigm.

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Heat capacity measurements can provide a powerful probe of both energetic and kinetic processes in condensed matter systems¹, and with the right expertise can be made with great precision. In this contribution we use heat capacity measurements provided by different practitioners of the laboratory art^{1,2,3} (aided by computer simulation studies (that provide data at temperatures where all known calorimeters would be vaporized⁴) to lay out a pattern of heat capacity behavior for glassformers that is a challenge to theory⁵. At one end of the temperature range, focused on strong liquids of the familiar silica type, we find heat “excess” capacity behavior reminiscent of (but smeared from) the lambda transition in metallic alloys⁶, and C-60⁷, where glass-like transitions are also found, and where the disordering kinetics above T_g also exhibit Arrhenius behavior until the disordering is complete. The peak heat capacity is associated with the fragile-to-strong transition for these liquids⁸. In the middle we find systems with liquid-liquid transitions which usually crystallize^{3,9}, and at the other end we find the familiar fragile molecular glassformers where the heat capacity behavior looks more like the mirror image of a lambda transition except that the sudden decrease (now at the low temperature extreme) is entirely kinetic in character (viz. the glass transition). However, in this case the only theoretical model that can fully describe the form of excess heat capacity¹⁰, requires that the ordering process be terminated by a *first* order transition to the glassy state at a temperature somewhat below T_g . Accordingly the process would not normally be observable. An unexpected route to a new low entropy glass state, which may be related to the hidden phase, has recently been discovered by the Ediger group¹¹. This phenomenology and its significance, form the subject of another symposium at this meeting.

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