Abstract for an Invited Paper
for the MAR05 Meeting of
The American Physical Society

Kinetics and Thermodynamics of the Glass Transition: Kovacs and Kauzmann Revisited

SINDEE SIMON, Texas Tech University

The tau-effective paradox was observed by Kovacs in early work on volume recovery; the crux of the paradox is that the effective relaxation times at equilibrium for up-jumps made from different initial temperatures do not agree with one another (i.e., an expansion gap is observed). Our new volume recovery measurements show that the paradox exists to much smaller departures from equilibrium than previously observed and also show that the expansion gap disappears and the paradox resolves itself very near equilibrium. Another paradox related to the glass transition is that of Kauzmann who observed that the entropy of a glass-forming liquid extrapolates to zero at a finite temperature; one proposed resolution is the existence of a thermodynamic Tg below the experimentally observed transition. In an attempt to address whether a thermodynamic Tg exists, the absolute heat capacities of polymethylstyrene and its mixtures with the pentamer were measured. Extrapolation of these measurements to pure polymer gives the equilibrium liquid heat capacity for the polymer at temperatures as much as 180 K below the Tg and 130 K below the Kauzmann temperature. No evidence of a second order transition is observed.