Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Free Volume, Energy, and Entropy at the Polymer Glass Transition: New Results and Connections with Widely Used Treatments[1]
RONALD WHITE, JANE LIPSON, Dartmouth College — Free volume has a storied history in polymer physics. To introduce our own results, we consider how free volume has been defined in the past, e.g. in the works of Fox and Flory, Doolittle, and the equation of Williams, Landel, and Ferry. We contrast these perspectives with our own analysis using our Locally Correlated Lattice (LCL) model where we have found a striking connection between polymer free volume (analyzed using PVT data) and the polymer's corresponding glass transition temperature, $T_{\rm g}$. The pattern, covering over 50 different polymers, is robust enough to be reasonably predictive based on melt properties alone; when a melt hits this T-dependent boundary of critical minimum free volume it becomes glassy. We will present a broad selection of results from our thermodynamic analysis, and make connections with historical treatments. We will discuss patterns that have emerged across the polymers in the energy and entropy when quantified as "per LCL theoretical segment". Finally we will relate the latter trend to the point of view popularized in the theory of Adam and Gibbs.

[1]The authors gratefully acknowledge support from NSF DMR-1403757

Ronald White
Dartmouth College

Date submitted: 05 Nov 2015 Electronic form version 1.4