

Abstract Submitted
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Entropy Theory of Polymer Glass-Formation Revisted JACK DOUGLAS, JACEK DUDOWICZ, KARL FREED, James Franck Institute, University of Chicago — Considerable physical evidence supports the idea of Gibbs and DiMarzio that glass-formation arises when the configurational entropy of a liquid becomes critically small and the subsequent arguments by Adam and Gibbs (AG) that quantitatively relate the configurational entropy to the rate of long wavelength structural relaxation. We revisit this classical ‘entropy theory’ of glass-formation, based on a minimal lattice model that incorporates monomer structure and the different rigidities of the polymer chain backbone and side-groups into a thermodynamic description of compressible polymer melts with van der Waals interactions. Previous observations of an apparent breakdown of the AG theory at elevated temperatures (20- 30 K above the glass-transition temperature T_g) led us to identify the ‘configurational entropy’ of the AG model with the site rather than mass normalized configurational entropy. This reinterpretation of the entropy theory has little effect near the glass transition, but it completely revises the theory at more elevated temperatures. In particular, we predict a series of characteristic temperatures describing respectively, the onset of a drop in s upon cooling, an inflection point in sT and the extrapolation of s to 0. The T -dependence of s is quite distinct above and below the inflection point ‘crossover temperature’. We complete our specification of the characteristic temperatures of glass-formation by defining kinetic transition temperature T_g through a Lindemann criterion.

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