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Role of Fluctuations in Predicting the Glass Formation Line
GRIGORI MEDVEDEV, JAMES CARUTHERS, Purdue University — Problems with application of the Ehrenfest relations to predicting pressure dependence of the glass transition temperature are well documented in the literature. The resolutions of this problem proposed by various authors range from claiming general inapplicability of the standard phase transition theory to glasses to postulating additional thermodynamic variables to describe glassy state. In this paper we follow a different approach based on explicit acknowledgement of the dynamic heterogeneity of materials observed at a nanometer length scale in and near the glassy state. As a result, the macroscopic relaxation response of a material (defining the glass transition) emerges as an average over an ensemble of local responses which vary from one location to another due to thermodynamic fluctuations. Because of the strong non-linearity of the relaxation time as function of its variables, regions with different values of thermodynamic parameters unevenly contribute to the average effectively shifting the macroscopic relaxation time and, thus, the glass transition point. Moreover, since the magnitude of fluctuations depends on temperature, the glass formation line rotates in the volume-temperature plane. We show that the fluctuation model provides improvement in predicting the glass formation line in PMMA and a number of other polymeric glass formers for which literature data are available.

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