

The physical potential energy landscape sampled by molecular and polymeric liquids in the landscape-dominated regime

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Abstract:

Complex behaviour of viscous liquids at $T < T_x$ (the crossover temperature) is dominated by the potential energy landscape (PEL). An intriguing aspect of this behavior is the connection between dynamics and thermodynamics embodied in the Adam–Gibbs equation using the excess entropy (S_{ex}) of a liquid over its crystal phase. This connection indicates that the physical PEL in real liquids will obey a topographic scaling relation that links basin populations at a given depth to the barrier heights at that depth. Theoretical analyses indicate that such physical PEL must arise ultimately from aspects of molecular structure (shape, symmetry, flexibility, etc.). However, concrete physical PEL like this in various real glass-forming liquids has been scarce and what and how aspects of molecular structure determine its basic properties remain poorly understood. Here, we present such physical PEL and a realistic way to determine its basic properties in terms of molecular flexibility. We fit the AG equation along with the Richert–Angell's expression for S_{ex} to the experimental data of a series of prototype molecular and polymeric liquids. We find that, first, the resulted value of the parameter C of the AG equation for each liquid equals the total energy barrier to its intramolecular rotations, second, S_{ex} is determined by the ratio of intramolecular rotations and energy barrier to conformation conversion, and third, the rapidity of change with temperature of S_{ex} is controlled by that of the entropy associated with conformation conversions. These results indicate that S_{ex} and C are a measure of the number of the stable conformations sampled by the liquid and the heights of the transition states along paths connecting neighbouring sampled conformations, respectively. In other words, the dynamics at $T < T_x$ are dominated by the liquid's exploration of its own potential energy landscape for intramolecular rotations. The mechanism that connects intramolecular rotations with the α processes at $T < T_x$ is given. We derive an equation for prediction of the fragility index m in terms of the physical PEL, which accurately predicts m values of all types of pure glass-formers, especially the molecular weight dependence of m of polymers for which neither existing theories nor available correlations have met much success.