Triplet Correlations in Tetrahedral Liquids

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Abstract:

The total, triplet and pair contributions to the entropy with increasing tetrahedrality are mapped out for the Stillinger-Weber liquids to demonstrate the qualitative and quantitative differences between triplet-dominated, tetrahedral liquids and pairdominated, simple liquids with regard to supercooling and crystallization. We show that as a function of tetrahedrality, the liquid state can be subdivided into pair- and tripletdominated regimes, separated by a narrow, glass-forming region where orientational disorder within the first neighbour shell is significant. The three regimes show qualitatively different thermodynamic behaviour on supercooling, with the lowtetrahedrality liquids conforming to the temperature scaling and melting rules expected of simple liquids, while the triplet-dominated systems show a characteristic heat capacity anomaly reflecting local ordering due to pair and triplet correlations prior to crystallization. The results suggest that structural correlations can be directly related to thermodynamic anomalies, phase changes and self-assembly in other atomic and colloidal fluids.

References:

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