Entropy and relaxation time. Lessons learnt from simple liquids' isomorphs and their quasiuniversality

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Abstract:

The relaxation time of a supercooled liquid is extremely temperature and density dependent, approaching hours and even longer upon cooling or compression. Is the relaxation time controlled by the entropy? Or is it controlled by high-frequency elastic properties, as assumed in the shoving and related elastic models - or possibly by a third physical property? Given that glass-forming liquids have quite different chemistry, it is far from certain that there is a simple and generally valid answer to this question for, but as physicists we like to think this is the case.

We first discuss the possible relation between entropy and relaxation time of liquids, in particular glass-forming systems. Besides the well-known and popular Adam-Gibbs model, we also consider the 1964 experimental observation by Chang and Bestul of the apparently universal excess entropy at the glass transition and Rosenfeld’s excess entropy scaling.

To put these things into perspective, the paper proceeds by summarizing recent results on the isomorphs in certain systems. An isomorph is a curve in the thermodynamic phase diagram along which structure, dynamics, and some thermodynamic properties in reduced units are invariant to a good approximation. Glass-forming liquids with good isomorphs (e.g., van der Waals bonded liquids or metallic glass-forming liquids) have a Prigogine-Defay ratio close to unity. Systems with good isomorphs are generally characterized by having a single-parameter family of reduced-coordinate constant-potential-energy hypersurfaces. The excess entropy is the logarithm of the area of this hypersurface, and the high-frequency elastic properties are basically the surface’s curvature. Since the relaxation time is also encoded in the manifold via “NVU dynamics” (geodesic motion on the hypersurface, equivalent to Newtonian dynamics), both quantities will appear to control the relaxation time - as will in fact any isomorph invariant.

If time permits, we finally discuss briefly recent results on quasiuniversality, among which is the prediction that all liquids with good isomorphs have a universal value of the constant-volume fragility.