

# Stress distribution and the fragility of supercooled melts

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We formulate a minimal ansatz for local stress distribution in a solid that includes the possibility of strongly anharmonic short-length motions. We discover a broken-symmetry metastable phase that exhibits an aperiodic, frozen-in stress distribution. This aperiodic metastable phase is characterized by many distinct, nearly degenerate configurations. The activated transitions between the configurations are mapped onto the dynamics of a long range classical Heisenberg model with 6-component spins and anisotropic couplings. We argue the metastable phase corresponds to a deeply supercooled non-polymeric, non-metallic liquid, and further establish an order parameter for the glass-to-crystal transition. The spin model itself exhibits a continuous range of behaviors between two limits corresponding to frozen-in shear and uniform compression/dilation respectively. The two regimes are separated by a continuous transition controlled by the anisotropy in the spin-spin interaction, which is directly related to the Poisson ratio  $\sigma$  of the material. The latter ratio and the ultra-violet cutoff of the theory determine the liquid configurational entropy. Our results suggest that liquid's fragility depends on the Poisson ratio in a non-monotonic way. The present ansatz provides a microscopic framework for computing the configurational entropy and relaxational spectrum of specific substances.

If cooled sufficiently rapidly, a liquid may fail to crystallize, but will instead remain in a metastable, *supercooled* state. Upon further cooling, the relaxation times in a supercooled liquid grow very rapidly as the mass transport becomes activated, in contrast with the mainly collisional transport near the fusion temperature. Because the local structures are much longer-lived than the vibrational equilibration times, the activated-transport regime represents a state with a broken translational symmetry, even though the corresponding, aperiodic structure shows no obvious distinction from a snapshot of an ordinary, uniform liquid. (It is said the heterogeneity is “dynamical.”) Since the symmetry is broken *gradually* with lowering the temperature - beginning with the highest frequency motions - a transition into this “aperiodic-crystal” state is not sharp, but, instead, is a soft cross-over centered at a temperature  $T_{cr}$ ,<sup>1,2</sup> corresponding universally to viscosity 10 Ps or so.<sup>2,3</sup> The cross-over into the activated regime is a finite-dimensional analog of a mean-field kinetic catastrophe of the mode-coupling theory (MCT), whereby the motional barriers would diverge at a temperature  $T_A$ , even though the configurational entropy is still extensive.<sup>4,5</sup>

In additional contrast to the mean-field transition at  $T_A$ , the cross-over at  $T_{cr}$  exhibits two emerging length scales: One length scale is the molecular length  $a$  that signifies the volumetric size of a chemically rigid unit - often called the “bead” - that is not significantly perturbed during activated transport. Conversely, the beads interact with each other weakly, comparably to the Lennard-Jones interaction.<sup>2</sup> The bead may be thought of as a coarse-graining length, beyond which activated motions are largely independent of chemical detail, but fully characterized by a single, *bulk* quantity. This bulk quantity is the excess liquid entropy relative to the corresponding crystal, usually called the configurational entropy. The magnitude of the configurational entropy per bead,  $s_c$ , directly gives the number of alternative aperiodic con-

figurations available to a region of a supercooled liquid containing  $N$  beads, i.e.  $e^{s_c N/k_B}$ . The bead usually contains two-three atoms, but could be bigger for molecular liquids containing large rigid units such as benzene. The other length scale emerging during the crossover is the so called Lindemann length  $d_L$ ,<sup>1,6,7</sup> which is the molecular displacement at the mechanical stability edge. This length is nearly universal:  $d_L \simeq a/10$ , and characterizes bead displacements during transitions between distinct aperiodic packings in the metastable, aperiodic crystal phase. One may view the crossover into the activated liquid regime as a “localization” transition, whereby the emerging metastability of local structures is signaled by a *discontinuous* transition from a uniform liquid to a state with a non-zero force constant of the Einstein-oscillator.<sup>1</sup> The random first order transition (RFOT) theory utilizes this view to analyze the activated transport in chemically distinct (non-polymeric) fluids in a *unified* fashion.<sup>8-10</sup> (See Ref.<sup>11</sup> for a review.) The RFOT theory predicts that in a fully developed activated regime, the structural relaxation time is determined solely by the configurational entropy per bead:<sup>2,9</sup>

$$\tau = \tau_{\text{vibr}} \exp(32k_B/s_c), \quad (1)$$

where  $\tau_{\text{vibr}} \simeq 1$  psec is the microscopic time scale characterizing vibrational relaxation. By Eq.(1), system-specific deviations from the pure Arrhenius temperature dependence of  $\tau$  result from variations in the value of the heat capacity jump at the glass transition temperature  $T_g$  per bead:  $\Delta c_p \equiv T(\partial s_c/\partial T)|_{T=T_g}$ . The so called fragility index  $m \equiv d(\log \tau)/Td(1/T)|_{T=T_g}$  gives a quantitative measure of that deviation. Small and large deviations from the Arrhenius  $T$ -dependence (corresponding to small and large  $m$  respectively) are often called strong and fragile behaviors.<sup>12,13</sup> The RFOT theory predicts  $m \simeq 34.7\Delta c_p$ ,<sup>2,9,14</sup> in excellent agreement with experiment.

Hall and Wolynes have put forth a simple specific