

The Elastically Cooperative Nonlinear Langevin Equation: A unified, predictive theory of activated relaxation in colloids, molecular liquids, and polymers in the bulk and under confinement.

The Elastically Cooperative Nonlinear Langevin Equation (ECNLE) theory is a first principles, microscopic, no adjustable parameter approach to describing the dynamical behavior of supercooled liquids. Written at the level of microscopic forces, the theory is able to provide a unified framework for understanding activated relaxation in colloids, small molecule liquids, and polymer melts, over nearly 14 orders of magnitude in relaxation time, both in the bulk and under confinement. The theory provides a fundamentally new picture of the alpha relaxation event as involving local cage-scale hopping coupled to a long range cooperative elastic distortion of the surrounding liquid. This results in two inter-related but distinct contributions to the total barrier. I will show material specific, no adjustable parameter calculations of dynamical behavior in molecular and polymeric liquids.

The theory has been extended to treat the case of geometrically confined liquids. Generically, confinement of supercooled liquids by a free surface leads to a speeding up of the dynamics (with a consequent depression of the glass transition temperature) extending on the order of tens of molecular diameters away from a free surface, while interactions with a solid substrate are complex and highly material dependent. At present, this behavior is not theoretically well understood. ECNLE theory interprets the effect of a surface or substrate in terms of two coupled effects. First, is a direct surface effect, extending two to three molecular diameters from the interface, and related to local cage-scale hopping. The second is a longer ranged “confinement” effect, extending tens of molecular diameters from a free surface and related to the collective elastic barrier. The theory allows for the calculation of relaxation time and T_g profiles within a given geometry and first principles calculations of relevant length scales. Comparison to both dynamic and pseudo-thermodynamic measurements shows reasonable agreement to experiment with no adjustable parameters.