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Unified Theory of Activated Relaxation in Cold Liquids over 14 Decades in Time KENNETH SCHWEIZER, STEPHEN MIRIGIAN, University of Illinois, Urbana-Champaign — We formulate a predictive theory at the level of forces of activated relaxation in thermal liquids that covers in a unified manner the apparent Arrhenius, crossover and deeply supercooled regimes (J.Phys.Chem.Lett.4,3648(2013)). The alpha relaxation event involves coupled cage-scale hopping and a long range cooperative elastic distortion of the surrounding liquid, which results in two inter-related, but distinct, barriers. The strongly temperature and density dependent collective barrier is associated with a growing length scale, the shear modulus and density fluctuations. Thermal liquids are mapped to an effective hard sphere fluid based on matching long wavelength density fluctuation amplitudes. The theory is devoid of fit parameters, has no divergences at finite temperature nor below jamming, and captures the key features of the alpha relaxation time in molecular liquids from picoseconds to hundreds of seconds. The approach is extended to polymer liquids based on the Kuhn length as the key variable. The influence of chain length and backbone stiffness on the glass transition temperature and fragility have been studied where degree of polymerization enters via corrections to asymptotic conformational statistics.

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