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The Challenge of Understanding the "Complexity" of Polymeric Fluids and Solutions

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It is well known that the complexity of polymer conformational shapes makes this class of molecules prone to glass formation and that high molecular mass polymers exhibit rubbery viscoelastic flow properties associated with their topological and packing interactions. Many natural and synthetic polymers also exhibit complex associative interactions arising from the variation of chemical species and the presence of charged and polar groups within the molecule that can give rise to polymer supermolecular organization into a wide range of fragile structures at the nanoscale and larger. There are changes in both the thermodynamics and dynamics of these fluids associated with these general patterns of "complex fluid" behavior that provide a fundamental challenge for theoretical understanding so that this field remains at the frontier of materials science. The high level of regularity observed in the relatively high frequency glassy dynamics of polymer fluids, and other glass forming liquids more broadly, and in the viscoelastic properties that define chain "entanglement" in high molecular mass polymers, provides some hope for a general theoretical framework describing the complex fluid dynamics of polymeric fluids. Specifically, it is argued, and supported by evidence, that the complex fluid behavior underlying glass formation, entanglement and self-assembly in polymeric fluids all involve emergent collective behavior taking the form of supermolecular polymer structures that form and disintegrate in dynamic equilibrium. This "dynamic heterogeneity" paradigm, which is not addressed by conventional mean field theories such as the mode-coupling model of glass formation and the reptation model, provides a framework for understanding many aspects of the linear and non-linear dynamics of polymer complex fluid behavior such as stretched exponential stress relaxation, and shear thinning and "aging" following cessation of flow. It also provides a framework for understanding the influence of nanoparticles, and other additives to polymeric fluids, that modify the fluid mesoscale structure, often with significant changes in material properties.