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ASPECTS OF VISCOELASTICITY IN POLYMER SIMULATIONS

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When asked what the difference between a liquid and a solid is, presumably we would answer spontaneously like this: "Liquids flow, solids don't!" This experience from everyday life can be tested experimentally by subjecting a material to an infinitesimal shear deformation: A solid responds elastically to such a deformation; it has a finite shear modulus (i.e., elastic constant). For a liquid the shear modulus vanishes; instead, liquids have a finite viscosity. However, this distinction between the liquid and solid states needs to be taken with some care because it depends on the considered time scale. Also a liquid can have a nonzero elastic response to shear, provided short enough times are probed. For ordinary liquids, like water, the associated time scale is extremely short, on the order of a picosecond. Therefore, the elastic response of water is unimportant in everyday life. However, if the viscosity increases, the liquid may display both elastic behavior for short times and viscous flow for long times. This phenomenon is called viscoelasticity and is a characteristic property of soft matter materials, such as polymers, and of all liquids when they are cooled toward their glass transition.

In this presentation we describe some aspects and consequences of viscoelasticity as seen in molecular dynamics (MD) simulations of polymer melts. One aspect is concerned with the dynamics of a polymer in a nonentangled melt. A longstanding, puzzling issue in the field is that the motion of the center of mass (CM) of a chain is subdiffusive, contrary to established theoretical concepts. By MD simulations and theoretical analysis we explain this subdiffusive motion through the coupling of the CM dynamics to the viscoelasticity of the melt (see [1] and Figure; symbols = MD, line = theory). A second aspect addresses the slowing down of the dynamics on

cooling a polymer melt toward its glass transition. In the cold melt one observes that monomers are localized for a long time and that these periods of solid-like behavior are punctuated by a jump-like motion of the monomers [2,3]. Along with that, shear rigidity emerges on an intermediate time scale. It is a currently actively debated question how this precursor of shear rigidity is related to the (finite) shear modulus found below the glass transition temperature in the amorphous solid [4]. The presentation ends with a sketchy description of some of the current projects in this context.
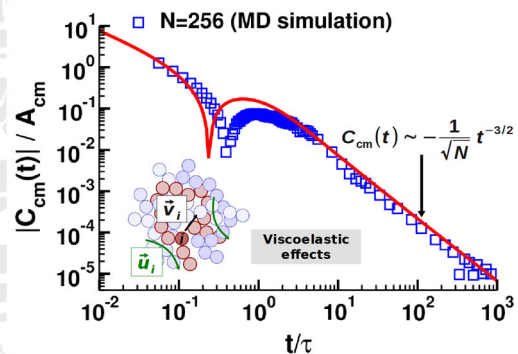
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