Note: Thermorheological complexity in polymers and the problem of the glass transition

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The “glass transition problem,” which refers to the spectacular change in dynamic properties of liquids cooled towards their glass transition, remains unsolved. The difficulty is that there are many properties associated with vitrification of a liquid, and these have interrelationships which complicate any analysis. Recently attention has been directed at the spatial heterogeneity of the dynamics; this “dynamic heterogeneity” is a general feature of supercooled liquids, investigated both experimentally and by computer simulations. Whether dynamic heterogeneity is the key to resolving the glass transition problem remains to be seen. Our interest herein is a seemingly related problem—the thermorheological complexity of polymers. This refers to the different temperature dependences of modes of motion in polymers, which leads to a breakdown of the time-temperature superposition principle. The differing response of local and global motions extends to changes in various thermodynamic quantities (Figure 1; Ref. 2), the failure of time-temperature superpositioning being the most often observed manifestation of the phenomenon.

There is a common belief that dynamic heterogeneity underlies thermorheological complexity, and that upon resolution of the glass transition problem, further investigation of the polymer problem will no longer be required. This idea arises from the notion that the different temperature-dependences of the segmental and chain motions are due to dynamic heterogeneities affecting the former but being averaged out over the longer length and time scales of the latter. The purpose of this note is to point out that neither dynamic heterogeneity as currently applied nor an eventual solution of the glass transition problem can provide an explanation for the thermorheological complexity of polymers.

The traditional assumption in the field of polymers is that all viscoelastic mechanisms are governed by the same monomeric friction coefficient, and thus have the same dependences on temperature, pressure, etc. This ideal behavior leads inter alia to time-temperature superpositioning, and is inherent to classic theories of polymer dynamics. Deviation from the single friction factor idea was first observed in entangled polymers, and subsequently in unentangled polymers. These findings have since been confirmed in a large number of materials, so that thermorheological complexity can be considered a general property of polymers. The fact that this behavior cannot be directly connected to dynamic heterogeneity and the glass transition problem is indicated by several experimental facts:

(i) The self-diffusion constant and viscosity of entangled polymers are decoupled, with the activation energy for self-diffusion being smaller than for the viscosity. This difference is similar to the difference in temperature dependences for the segmental and chain dynamics. Since the self-diffusion constant and the viscosity both involve global motions (length scales large compared to the segmental dynamics), spatially heterogeneous dynamics cannot be the origin of the decoupling; i.e., distinct averaging over the length and time scales cannot underlie differences in properties that involve similar length and time scales.

(ii) The viscosity of polymers has a different temperature dependence than do the relaxation times governing the chain dynamics. Depending on the molecular weight and temperature, the viscosity can exhibit a stronger temperature dependence than even the local segmental modes. Such behavior cannot be explained as a consequence of averaging over different length scales, since the viscosity and chain relaxation are both global processes. Moreover, use of the averaging argument to explain the stronger temperature dependence of the local segmental dynamics obviates its use to explain a weaker temperature dependence.

(iii) The diminished role of dynamic heterogeneity for polymers is also evident in the decrease of the steady state recoverable compliance, $J^0$, of low molecular weight polymers on cooling towards $T_g$. The product of this compliance and the viscosity yields the terminal relaxation time, so that the changes of $J^0$ with temperature cause another failure of the “single time scale” picture that cannot be ascribed to the spatially heterogeneous dynamics.

(iv) The difference in temperature variations of chain and segmental friction has been observed mostly by mechanical measurements, and occasionally by dielectric relaxation, but not from chain diffusion. Thus, the argument that dynamic heterogeneity is averaged out for chain diffusion differently than for the segmental dynamics cannot be applied to the problem of thermorheological complexity. This argument, used to account for the breakdown of the Stokes-Einstein relation in glass-formers, has been contradicted by both experiments and simulations.

(v) The heterogeneous dynamics has been quantified for various materials, and for 1,4-polyisoprene the number of dynamically correlated repeat units, $N_c$, is of the order of 100,
A complete understanding of supercooled liquids requires multiple interrelated lines of inquiry.\(^4\) For polymers the task is even more daunting—neither dynamic heterogeneity as currently applied nor an eventual solution of the glass transition problem will explain the thermorheological complexity of long chain molecules. Determining the mechanisms giving rise to different friction factors for different modes of motion is of fundamental importance, although it is neglected by mainstream viscoelastic theories. One approach with some success is the coupling model, wherein the dependences of molecular mobility on thermodynamic quantities are magnified by the many-molecule dynamics, which exert different effects on the segmental and chain dynamics.\(^9, 18, 19\)

Even though a resolution to the glass transition problem through concepts based on dynamic heterogeneity may be tantalizingly near, thermorheological complexity will remain unsolved because it is a different issue involving different mechanisms.

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\(^{14}\)The domain of cooperative segments contains repeat units from many different chains, given the interspersed nature of polymer melts. However, the argument is that the chain modes would average over these dynamically heterogeneous regions, while the local segmental modes would not.


