Comment on "Nonmonotonic Models are Not Necessary to Obtain Shear Banding Phenomena in Entangled Polymer Solutions"

A recent Letter [1] attempted to explain some emerging yielding phenomena involving both continuing [2] and interrupted [3,4] (shear or extensional) deformations by taking the standpoint that if numerical calculations based on a Doi-Edwards (DE) tube model [5] could produce something resembling the experimental observations, then the DE tube model must already contain the required physical ingredients, and there should be no need to introduce "new physics." Others followed a similar philosophical line to study instability in extension [6].

Contrary to the title of [1], shear banding would emerge from monotonic curves only if there was a stress gradient as in circular Couette geometry. Moreover, in their model calculations, no motions would show up during relaxation from a preceding homogeneous step strain. See their response to the present Comment. Experiment reveals nonquiescent relaxation from *homogeneous* step strain produced in parallel disks [3(a)] and parallel-sliding plates [4]. It appears that high elastic deformation, not any preexisting stress gradient, is responsible for the observed postdeformation failure, which we have termed elastic yielding [7].

Second, there is a conceptual and numerical error in Ref. [1], making it unrealistic for comparison with experiment: The authors had mistaken the experimental plateau width of 10^3 as the number of entanglements per chain $Z = N/N_e \sim \tau_d/\tau_R$. The experimental systems actually had $Z < 50$. Moreover, Adams and Olmsted (AO) chose an exceedingly small viscosity ratio of solvent to solution, i.e., $\varepsilon = 10^{-5}$. The experiment actually always avoided this limit, for which significant wall slip would dominate the rheological response. Yet AO calculation could not demonstrate dominance of wall slip under such a condition.

Third, the Letter considered only the condition that shear inhomogeneity has already occurred before shear cessation to produce a residual stress gradient and thus missed the essential phenomenon [3(a),4] that macroscopic motions occur after *homogeneous* step strains. The calculation had little to do with the observed elastic yielding in Figs. 3 and 4 of [3(a)] that was known to them since 2006.

It is not uncommon for models containing inadequate physics to generate results in resemblance with experiment. Therefore, the calculations made in these Physical Review Letters articles do not expel the likelihood that new physics is required to describe large deformation behavior of entangled polymeric liquids. Experiments have revealed that the relaxation of a deformed polymer is stable against any macroscopic motions only when the deformation is below a critical level. The DE type model [8] does not and cannot identify this threshold that reflects an intrinsic level of cohesion. Sufficient elastic deformation produced by a step strain can result in yielding of the entanglement network [7]. Chain entanglement exists due to the entropic barrier, and temporary structural integrity of an entangled polymer liquid exists because of this entanglement. Dynamically speaking, entanglement means that the chains cannot pass around one another without spending some time to do so. Disentanglement or cohesive failure occurs whenever the chains spend *less* time passing around one another than they do in equilibrium. It is clear that the emerging phenomenology including nonquiescent relaxation requires new concepts such as finite cohesion and elastic yielding. More elementarily, any theoretical treatment has to be able to account for such heterogeneous responses as interfacial wall slip or internal slip. Actually, long ago, Brochard and de Gennes recognized [9] that tube models cannot adequately elucidate wall slip.

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