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.

This Comment has benefited from communications with Peter Olmsted, Hiroshi Watanabe, David Mead, Ron Larson, Jack Douglas, Ken Schweizer, and Zhen-Gang Wang.

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[1] J. M. Adams and P. D. Olmsted, Phys. Rev. Lett. **102**, 067801 (2009).
[2] (a) For simple shear, see P. Tapadia and S. Q. Wang, Phys. Rev. Lett. **96**, 016001 (2006); P. Boukany and S. Q. Wang, J. Rheol. **51**, 217 (2007); S. Ravindranath and S. Q. Wang, Macromolecules **41**, 2663 (2008); J. Rheol. **52**, 957 (2008); (b) For uniaxial extension, see Y. Wang *et al.*, Phys. Rev. Lett. **99**, 237801 (2007); J. Rheol. **52**, 1275 (2008).
[3] (a) For simple shear, see S. Q. Wang *et al.*, Phys. Rev. Lett. **97**, 187801 (2006); Macromolecules **40**, 8031 (2007); (b) for uniaxial extension, see Ref. [2(b)].
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[8] Chain retraction upon stretching occurs on Rouse time scale at any stage of external deformation of any magnitude in a DE type tube model due to its inability to account for any intermolecular interactions. There is no chain retraction upon shear cessation from slowly generated step shear, making it difficult to assert that the nonquiescence after step shear reported in Ref. [4] would be due to chain retraction.
[9] F. Brochard and P. G. de Gennes, Langmuir **8**, 3033 (1992).

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Adams and Olmsted Reply: Wang [1] makes the following points about our Letter [2]: (1) He infers that, "contrary to its title, shear banding [in [2]] emerged from monotonic curves only if there was a stress gradient," and he points out that nonquiescent relaxation was found (experimentally) after step strain in geometries *without* a stress gradient [3]. (2) He disagrees with the values of the parameters we used. (3) In some recent experiments the flow was homogeneous after cessation of step strain, and only *subsequently* developed nonquiescent macroscopic motion [3]. We only showed step strains that developed an inhomogeneity *before* cessation of flow, as in [4].

(1) As our title stated [2], we showed that a fluid with a monotonic constitutive curve based on Doi-Edwards (DE) theory can have signatures similar to shear banding. These signatures arise from a stress gradient (e.g., the bowed steady state velocity profile obtained in the stress gradient of a cone and plate rheometer [5] or transient bandinglike profiles during startup). Flat geometries can have *transient* bandinglike signatures: e.g., two clearly defined bands of shear rates during large amplitude oscillatory shear (LAOS) [2,6], or inhomogeneous bandinglike transients during startup flows in the presence of inhomogeneous spatial fluctuations (noise) (Fig. 1) [2].

(2) Our parameters were matched to experiment, for a nonlinear model in which the parameters τ_d and τ_R roughly correspond to their rigorously defined counterparts in linear rheology. Because we use (the best available) crude nonlinear theory, the parameters do not correspond precisely. We used $\epsilon = \eta/(G\tau_d) \simeq 10^{-5}$ based on a plateau modulus $G \simeq 3$ kPa, reptation time $\tau_d \simeq 20$ s, and solvent viscosity $\eta \simeq 1$ Pa s [7]. Although $\tau_d/\tau_R \sim 10^3$ implies too many entanglements, it fits the nonlinear constitutive behavior of the experiments well [5]. This inconsistency is an unsatisfactory feature of current theory.

(3) The step strain results in [2] should be compared with [4] (Fig. 5), where the velocity profile became inhomogeneous before cessation. Figure 2 shows a calculation in which inhomogeneities develop only after cessation of flow, during a strong recoil. This is for startup in a flat geometry with noisy initial conditions, and resembles [4] (Fig. 3) if there were no experimental wall slip.

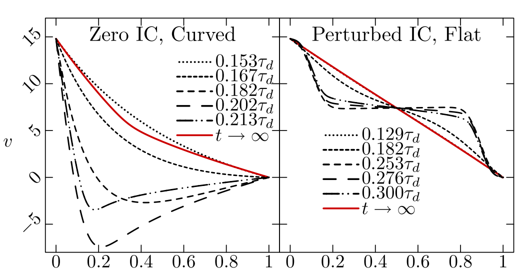

FIG. 1 (color online). Startup transients for (left) a cone angle of 4° ($q = 2 \times 10^{-3}$); and (right) a flat geometry with noisy initial polymer shear stress $\Sigma_{xy}(0)$ of a few percent, with $\dot{\gamma}\tau_d = 14.8$, $\beta = 0.728$ and $\epsilon = 10^{-5}$, and $\tau_d/\tau_R = 10^3$.

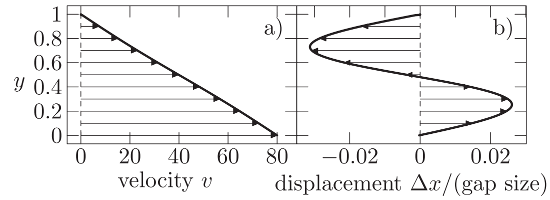

FIG. 2. Recoil displacement (b) at $t = 0.08\tau_d$ after cessation of homogeneous shear (a) at $t_{\text{stop}} = 0.0375\tau_d$ with $\dot{\gamma}\tau_d = 80$, i.e., $\gamma = 3$ for the Rolie-Poly model with $\beta = 0.728$, $\epsilon = 10^{-5}$, and $q = 0$, with initial noise.

Wang's newest experiments show dramatic rupture and internal fracture, despite a homogeneous velocity before cessation [3] (similar fracture planes could be interpreted in [8], Fig. 3(f), but in a cone-and-plate geometry; moreover, those data are also consistent with wall slip and simple recoil). Our calculations (Fig. 2) go some way towards modeling this phenomenon, but do not capture the rupture, and have not yet been adequately modified to incorporate slip. It remains a strong challenge to distinguish which experimental features are captured by tube models, and which (e.g., rupture) require new physical insight. One suggestion is the "elastic yielding" in [1] which may be similar to modifying the DE model to incorporate the instability of the spatial distribution of entanglement [9]. In fact, the instability in the DE model occurs when the shear rate greatly exceeds the reptation time, which is one criterion for elastic yielding postulated in [1].

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