Nature of steady flow in entangled fluids revealed by superimposed small amplitude oscillatory shear

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Synopsis

We carry out a systematic investigation into steady-state shear behavior of six entangled solutions based on a superposition of continuous shear and small amplitude oscillatory shear (SAOS). During steady shear in the shear thinning regime the superimposed SAOS frequency sweep measurements reveal characteristics of viscous liquids, e.g., terminal dynamics, on the experimental time scale of the reciprocal shear rate. The residual entanglement network retains the same level of elastic stiffness as the equilibrium system does. Consistent with the convective constraint release idea, chains in the network are forced to pass around each other as they must do so to undergo steady flow. When such a sample is examined at a significantly short time scales, chains are unable to pass around, and the signature of this residual entanglement is that the storage modulus is greater than the loss modulus at higher frequencies than the applied shear rate. The particle-tracking velocimetric observations confirm that whether shear banding is present or not does not affect the basic "terminal flow" character revealed by the superimposed SAOS.

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I. Introduction

Continuous shear and oscillatory shear are two commonly employed protocols to investigate rheological properties of complex fluids such as granular matters, suspensions, colloids, emulsions, foams, liquid crystals, surfactant aggregates and polymers [Larson (1999); Wyss et al. (2007)]. One key issue to address in the field of rheology of viscoelastic materials is to understand how these materials arrive at their final steady-state flow. For entangled polymeric liquids, a major task is to explain observed rheological phenomena such as shear thinning in terms of the state of chain entanglement.

Linear viscoelastic (LVE) properties of entangled polymeric liquids appear to be well described by combination of the reptation idea of de Gennes and Doi-Edwards (DE) tube model [Doi and Edwards (1986)]. The most common way to measure the linear viscoelastic properties is to perform small amplitude oscillatory shear (SAOS) and measure storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ as a function of frequency $\omega$. For monodisperse systems, the reptation time $\tau$ can be shown to be within 2% from the inverse of $\omega_c$, for which $G'(\omega_c) = G''(\omega_c)$ [Doi and Edwards (1986)]. It is also useful to superimpose such an SAOS upon a steady shear flow [Ferry (1980)]. Commercial rotational rheometers have an option to enable such a combination. This approach was first applied by Osaki et al. (1965) on polymer solutions such as polystyrene in toluene, poly-(methyl methacrylate) and poly-(n-butyl acrylate) in diethyl phthalate. Similar measurements were subsequently performed of other polymer solutions including ethylene-propylene copolymer [Booij (1966a), (1966b)], polyisobutylene [Tanner and Simmons (1967); Macdonald (1973); Isayev and Wong (1988)], poly-(ethylene oxide) [Laufer et al. (1975a), (1975b); Powell and Schwarz (1975)], aqueous polyacrylamide [Vlastos et al. (1997)], associative polymers [Tirtaatmadja et al. (1997); Mewis et al. (2001)], worm-like micellar solutions [Anderson et al. (2006)] and polyethylene and isotactic-polypropylene melts [Kataoka and Ueda (1969); Costello (1997); Somma et al. (2007)]. All of these studies were made with the implicit assumption that the steady flow involves homogeneous shear.

Recent studies by a combination of particle tracking velocimetric (PTV) and rheometric measurements revealed that entangled fluids may undergo inhomogeneous shear in the form of either interfacial wall slip or bulk shear banding for Weissenberg number $Wi = \dot{\gamma} \tau > 1$ [Boukany et al. (2008); Ravindranath and Wang (2008a,b) Boukany and Wang (2009a,b)]. Such inhomogeneous shear in steady state would make it difficult to interpret the characteristics of the superimposed SAOS. The shear banding occurs apparently because well-entangled polymeric liquids, though initially uniform, are unable to undergo yielding in a homogeneous manner. The signature for yielding shows up in the form of a shear stress overshoot during suddenly started simple shear [Wang et al. (2007), Wang and Wang (2009)]. More detailed studies of the scaling characteristics associated with the yield point have been carried out [Ravindranath and Wang (2008c), Boukany, Wang and Wang (2009)]. It was shown that yielding indeed occurs beyond the stress overshoot because the elastic recovery can no longer be 100% beyond the shear stress maximum.

In the present work, we have carried out systematic parallel superposition and PTV measurements on several entangled DNA and polybutadiene (PBD) solutions with different entanglements per chain $Z = 13 \sim 155$ in various flow conditions involving either uniform flow or shear banding. Most of SAOS superposition measurements were
obtained from the non-shear-banding systems to avoid difficulty in interpretation although the features of SAOS are not even quantitatively different for the same sample that suffers shear banding.

II. EXPERIMENT

A. Materials

Six entangled solutions based on DNA and PBD are investigated in this work. The DNA solutions were made by dissolving 0.5 ~ 2.2 wt % of DNA (75 kbp ~ 50×10^6 g/mol, USB Co., which is not monodisperse) in a glycerol (Fluka). They are the same materials and prepared in the same way as described previously [Boukany and Wang (2009a,b)]. The PBD based solutions were prepared by dissolving 5 and 10 wt % PBD (M_w = 0.75×10^6 g/mol, M_n = 0.74×10^6 g/mol, Bridgestone-America) in low molecular-weight polybutadiene of M_w=1.8 K (Aldrich, Cat. No. 20,043-3, which has a significantly higher T_g, and thus is rather sluggish) and 9.0 K g/mol (Bridgestone-America) respectively, and 10 wt % PBD (M_w = 1.052×10^6 g/mol, M_n = 1.014×10^6 g/mol, Quirk’s lab, Akron, USA) in a polybutadiene solvent with M_w =15.0 K g/mol. More details on the sample preparation of these PBD solutions can be found in Ravindranath and Wang (2008a,b).

B. Methods

Linear viscoelastic measurements in quiescence

Rheological measurement was carried out on the controlled-stress rheometer (Physica MCR-301, Anton Paar USA). This is a multifunctional rheometer that can perform in both controlled-torque (CS) and controlled-displacement (CR) mode. The rheometer is equipped with a cone of 2° angle and diameter of 25 mm. The small amplitude oscillatory shear (SAOS) measurements were first carried out. Fig. 1(a) and Fig. 1(b) show storage and loss moduli G' and G'' at γ = 5 % for both the DNA and PBD solutions at different concentrations in absence of continuous shear. The shapes of G' and G'' in Fig. 1(a) reveal that the DNA is not monodisperse. The characteristics of these samples based on the SAOS measurements are listed Tables 1 and 2, where the plateau modulus G_pl is estimated from the value of G' at the frequency where G'' shows a minimum, and the crossover modulus G_c = G'(ω_c) = G''(ω_c). The terminal relaxation time τ is estimated as 1/ω_c. The critical entanglement molecular weight M_c(φ) is estimated from the elastic plateau modulus G_pl according to M_c(φ) = CRT/G_pl, where C is the concentration, R the gas constant and T temperature. Here G_pl is obtained as the value of G' at the frequency where G'' shows minimum. When there is no minimum in G'', we apply the well-established scaling law for the concentration dependence of M_c(φ) = φ^{−1.2}M_c(φ=1) to estimate M_c(φ) for a low concentration from that at a higher concentration, as previously done by Ravindranath and Wang (2008a) for PB solutions and Boukany and Wang (2009a) for DNA solutions. All measurements were carried out at room temperature (T = 24 °C).

Parallel superposition measurements

In the CS mode, the Physica rotational rheometer allows us to superimpose an oscillatory shear during a continuous shear. In this study, at first we imposed constant shear rate in CR mode to obtain the steady-state value of the shear stress. Then, the
rheometer is switched to the CS mode at the same shear stress to maintain the same steady shear rate meanwhile a SAOS is superimposed. Fig. 2 illustrates how Physica is programmed for the 0.5% DNA/glycerol solution to perform the mode switching experiment. For the superimposed oscillatory shear measurements in the CS mode, the peak value of the oscillatory shear stress is chosen to produce a strain amplitudes $\gamma$ in the range from 1% to 40% as the sweeping frequency decreases from high to low values, so that the superimposed SAOS is not expected to perturb the state of chain configurations produced by the steady continuous shear.

For 10 wt % PBD(0.7 M)-9.0K and 10 wt % PBD (1.0 M)-15K solutions, a stationary plastic film (PMMA) with inner diameter of 30 mm and height of 5.0 mm is wrapped around the meniscus to prevent edge instability and sample loss during steady shearing. Oscillatory frequency sweep test from $\omega=100$ to 0.1 s$^{-1}$ are performed after each steady-shear experiment to evaluate whether appreciable edge fracture had occurred or not. If a noticeable decrease of storage and loss moduli $G'$ and $G''$ is observed after prolonged shearing, a fresh sample will reloaded. Without wrapping a film, it is impossible to approach steady state for the 10 wt % entangled PBD solutions. In DNA-based solutions and 5% PBD (0.7M)-1.8K, all rheometric measurements were performed without the plastic film since negligible edge instability occurs during prolonged shear.

**Particle-tracking velocimetry (PTV)**

For PTV measurements, a cone and plate geometry with a 4° cone angle and diameter of 25 mm is employed. About 300 ~ 500 parts per millions (ppm) weight percent of silver-coated particles (Dantec Dynamic HGS-10 having a size range from 1 to 20 µm) are uniformly dispersed in the samples. The PTV observation plane is 3 ~ 4 mm from the meniscus. The details of PTV setup have been provided elsewhere [Boukany and Wang (2009a, b)].

### TABLE 1. Characteristic properties of DNA solutions

<table>
<thead>
<tr>
<th>DNA solutions</th>
<th>$G_p$ (Pa)</th>
<th>$G_c$ (Pa)</th>
<th>$M_e(\phi)$ (g/mol)</th>
<th>$Z(\phi)$</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt% DNA (50M)/glycerol</td>
<td>5.8</td>
<td>1.4</td>
<td>$2.1\times10^6$</td>
<td>24</td>
<td>512</td>
</tr>
<tr>
<td>1.1 wt% DNA (50M)/glycerol</td>
<td>32</td>
<td>5.3</td>
<td>$0.84\times10^6$</td>
<td>60</td>
<td>780</td>
</tr>
<tr>
<td>2.2 wt% DNA (50M)/glycerol</td>
<td>169</td>
<td>26.1</td>
<td>$0.32\times10^6$</td>
<td>156</td>
<td>1590</td>
</tr>
</tbody>
</table>

### TABLE 2. Characteristic properties of PBD solutions

<table>
<thead>
<tr>
<th>PBD solutions</th>
<th>$G_p$ (Pa)</th>
<th>$G_c$ (Pa)</th>
<th>$M_e(\phi)$ (g/mol)</th>
<th>$Z(\phi)$</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 wt% PBD (0.7M)/oBD (1.8K)</td>
<td>1766</td>
<td>324</td>
<td>$54\times10^3$</td>
<td>13</td>
<td>29.8</td>
</tr>
<tr>
<td>10.0 wt% PBD (0.7M)/PBD (9K)</td>
<td>5490</td>
<td>1530</td>
<td>$26\times10^3$</td>
<td>27</td>
<td>17.7</td>
</tr>
<tr>
<td>10.0 wt% PBD (1.0M)/PBD (15K)</td>
<td>6100</td>
<td>1570</td>
<td>$27\times10^3$</td>
<td>40</td>
<td>65.5</td>
</tr>
</tbody>
</table>
III. RESULTS AND DISCUSSIONS

A. Viscoelastic state in non-shear-banding DNA solution ($Z=24$)

Our PTV observations have confirmed, consistent with a previous report of Boukany and Wang (2009a), that the 0.5% DNA/glycerol solution does not undergo shear banding because of its low concentration. So this sample serves as an ideal system to probe the state of viscoelasticity during steady shear in the shear thinning regime. Fig. 3 shows that the crossover frequency $\omega_c(\dot{\gamma})$ systematically shifts with the imposed steady shear rate in the range from 0.004 to 1.2 s$^{-1}$. In particular, $\omega_c(\dot{\gamma}) < \dot{\gamma}$, implying that in the steady shear at any rate $\dot{\gamma}$ the system is flowing as if it is undergoing terminal flow. For example, at $\dot{\gamma} = 0.08$ s$^{-1}$, the system has clearly transformed from its initial, equilibrium state of a fully entangled elastic network to an eventual homogeneously flowing liquid: At a Weissenberg number of 41, the entanglement network would have undergone 41 shear strain units of quasi-elastic deformation had the network not been forced to yield. In reality, the system yields as shown by the shear stress overshoot around $\gamma_y = 2.4$ in Fig. 2. Beyond the yield point, flow (irrecoverable deformation) takes place. In other words, it is necessarily true that the condition of $\omega_c(\dot{\gamma}) < \dot{\gamma}$ emerges during steady-state homogeneous shear. This condition is what we mean by flow. The inset of Fig. 3 indicates that the steady shear is essentially homogeneous.

Fig. 4 confirms that indeed $\omega_c(\dot{\gamma})$ increases approximately linearly with $\dot{\gamma}$ to make the ratio $\omega_c(\dot{\gamma})/\dot{\gamma}$ nearly a constant around 5 and $G_c(\dot{\gamma})$ hardly changes with $\dot{\gamma}$. The phenomenon is fully consistent with, in other words, offers support for the idea of convective constraint release [Marrucci (1996), Somma et al. (2007)]. It is of great significance that the level of $G_c(\dot{\gamma})$ remains approximately unaltered. This fact gives us penetrating insight into the essence of chain disentanglement. For example, it is inappropriate to think about chain disentanglement in terms of an increase in the critical molecular weight $M_c$ such that $Z = M/M_c$ would be reduced. $Z$ is at best a useful concept to depict the level of chain entanglement in quiescence.

There must not be chain entanglement during steady flow in the following sense. Entanglement is a concept to depict the fact that chains do not pass around one another until the molecular diffusion brings them out of each other's way. Loss of entanglement is simply a statement that chains are now able to pass around one another on the experimental time scale. When there is steady flow, the chains necessarily are being forced by external continuous deformation to pass around one another on the experimental time scale of the reciprocal $\dot{\gamma}$ as if their effective relaxation time $\tau_{\text{eff}}(\dot{\gamma}) \sim 1/\omega_c(\dot{\gamma})$ is shorter than $\dot{\gamma}$. Fig. 4 shows that the effective Weissenberg number $\dot{\gamma} \tau_{\text{eff}}(\dot{\gamma})$ is around 1/5. On the other hand, when the steady-sheared sample is probed on time scales significantly shorter than the experimental time scale, it exhibits a similar level of elasticity, i.e., a magnitude of $G'$ comparable to that of the equilibrium plateau modulus $G_{\text{pl}}$. In the other words, the stiffness of network remains the same when examined on a time scale, on which the chains are unable to move past one another.

B. Comparison between homogenous vs. inhomogeneous shear

The DNA solution at 1.1 wt% concentration is more entangled than the 0.5 wt% solution studied in the preceding subsection III.A. In contrast, at a shear rate of 0.5 s$^{-1}$,
strong shear banding occurs even in steady state as shown in the inset of Fig. 5(a). We have recently demonstrated [Boukany and Wang (2009c)] that with a gradual ramping-up in the applied shear rate, a state of much reduced shear banding can be attained as shown in the inset of Fig. 5(a). For the different velocity profiles, the superimposed SAOS reveals identical characteristics as shown in Fig. 5(a). In other words, it is not possible to infer from Fig. 5(a) whether homogeneous shear prevails. Fig. 5(b) summarizes similar superimposed SAOS results at other applied shear rates. Clearly, rheological characterizations alone are insufficient to delineate the state of flow in these entangled DNA solutions.

The results of Fig. 5(a) and 5(b) appear surprising at first sight. On a second thought, it seems reasonable that the apparent rheological response, as measured by the superimposed SAOS, may be dictated by the response of the high shear band. The more entangled portion of the sample, i.e., the low shear band, however, does still influence the overall rheological characteristics of the SAOS measurements. Actually a model made of two Maxwell elements in series can be used to account for the insensitivity of $\omega_c$ to the state of shear deformation.

At sufficiently high shear rates close to the end of the stress plateau, uniform velocity profiles reemerge across the gap after transient banding even in startup shear mode [Ravindranath and Wang (2008a), Boukany and Wang (2009a)]. This can be understood because at high enough rates full disentanglement must occur. The superimposed SAOS reveals in Fig. 6 for the 1.1 wt. % DNA solution that at an applied shear rate of 3.5 $s^{-1}$ the SAOS frequency sweep data no longer indicate any crossover between $G'$ and $G''$, where the inset shows the normalized velocity profile that has a uniform velocity gradient in contrast to the inset of Fig. 5(a).

C. Superimposed SAOS results for non-shear-banding PBD solutions

To test the universality of the findings based on DNA solutions, we carry out similar experiments on three entangled polybutadiene solutions: 5% PBD (0.7M)-1.8K, 10% PBD (0.7M)-9K and 15% PBD (1.0M)-15K where the level of entanglement $Z$ ranges from 13 to 40. It has been reported previously that there is no wall slip and shear banding across the gap for these samples during steady shear due to the low level of entanglement and use of polymeric solvents [Ravindranath and Wang (2008a,b)]. Fig. 7 (a) and 7(b) show the storage and loss moduli measured from the superimposed SAOS as a function of frequency at different imposed $\dot{\gamma}$ for 5% PBD (0.7M) and 10% PBD (0.7M) respectively. The insets confirm that uniform shear prevails across the sample thickness during steady shear for these entangled solutions.

Finally, the characteristics of these superimposed SAOS, e.g., the coordinates at the crossover point, $\omega_c(\dot{\gamma})$ and $G_c(\dot{\gamma})$, can be summarized in universal master curves for all entangled DNA and PBD solutions at different levels of chain entanglement. Specifically, Fig. 8(a) shows the normalized crossover frequency $\omega_c(\dot{\gamma})/\omega_c(0)$ increases linearly with the Weissenberg number $Wi$. Moreover, $G_c(\dot{\gamma} \tau)/G_c(0)$ very gradually increases with $Wi$ with a small slope of 1/7 as shown in Fig. 8(b).

IV. Summary

The main purpose of this work is to gain insight into the nature of steady shear flow in entangled polymeric liquids. Apparently, the effect of the applied shear rate is
simply to force chains to pass around one another without altering the stiffness of the residual entanglement network. When chains in one layer pass around each other at a different rate from chains in another layer, shear banding occurs. However, strikingly, the parallel superposition of SAOS was unable to reveal noticeable difference between a sample homogeneously sheared and the same sample that undergoes shear banding.

The frequency sweep of a SAOS superimposed upon steady homogeneous shear of both DNA and polybutadiene solutions (with the number of entanglement per chain ranging from 13 to 156) shows that the equilibrium chain entanglement does not survive during steady shear. In other words, the state of flow is similar to a steady shear in the Newtonian regime, where the effective polymer relaxation time is shorter by a factor of 5 than the reciprocal shear rate. The feature is favorably consistent with the convective-constraint release (CCR) idea advocated by Marrucci (1996), Marrucci and Ianniruberto (2003).

For an entangled polymer liquid with an overall relaxation time $\tau$, at a Weissenberg number $Wi = \dot{\gamma} \tau \gg 1$, a sudden startup shear must cause it deform elastically at the beginning when no chains can pass around one another, i.e., chain entanglement is initially intact. In other words, in response to the externally imposed fast shear, the "liquid" initially undergoes deformation elastically, i.e., without chains passing by each other. Eventually, the dynamic strength of the entanglement network is overcome, and the system yields. The signature of yielding is the shear stress overshoot, beyond which the chains are forced, during the continuing external deformation, to move past one another [Wang et al. (2007), Wang and Wang (2009)]. It is in this sense that the chains have lost entanglement and flow has occurred.

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Figure Captions

1. Storage and loss moduli $G'$ and $G''$ as a function of frequency $\omega$ from small-amplitude oscillatory shear (SAOS) measurements in quiescence. (a) 0.5 ~ 2.2% DNA solutions in glycerol with $Z$ from 24 to 155. (b) PBD solutions: 5.0% PBD(0.7M)-1.8K, 10% PBD (0.7M)-9K and 10%PBD (1.0M)-15K whose $Z$ from 13 to 40.

2. Non-stop switching from CR measurements at $\dot{\gamma}=0.08$ s$^{-1}$ to CS measurements at $\sigma = 3.3$ Pa for the 0.5%DNA/glycerol solution.

3. The frequency dependence of $G'$ and $G''$ from superimposed SAOS at different shear rates $\dot{\gamma} = 0.004 \sim 1.2$ s$^{-1}$. The inset shows the PTV measurements of the normalized steady-state velocity profiles during startup shear at these applied shear rates.

4. The changes of $\omega_c(\dot{\gamma})/\dot{\gamma}$ is nearly a constant around 5 and $G_c(\dot{\gamma})$ only increases slightly with $\dot{\gamma}$.

5. (a) The frequency dependence of $G'$ and $G''$ from superimposed SAOS onto a final shear rate $\dot{\gamma} = 0.5$ s$^{-1}$, which is produced by either a startup shear or a gradual rate ramp-up. The inset shows the PTV measurements of the normalized steady-state velocity profiles obtained either during startup shear or ramp-up shear. (b) The dependence of the crossover frequency $\omega_c(\dot{\gamma})$ as a function of $\dot{\gamma}$ on the left-Y axis.

6. $G'(\dot{\gamma})$ and $G''(\dot{\gamma})$ from the superimposed SAOS onto a sufficiently high shear rate of 3.5 s$^{-1}$, where all chain entanglements are lost and the system displays homogeneous shear as shown in the inset.

7. The frequency dependence of $G'$ and $G''$ from superimposed SAOS experiments for (a) 5.0% PBD(0.7M)-1.8K and (b) 10% PBD (0.7M)-9K. The inset shows the linear normalized velocity profiles across the gap during shear at two representative shear rates of 0.1 and 1.0 s$^{-1}$.

8. Mater curves depicting how the coordinates of the crossover point change in a universal way for all the entangled DNA and PBD solutions: (a) The linear increase of $\omega_c(\dot{\gamma})/\omega_c(0)$ as a function of $Wi$ in shear thinning regime. (b) The gradual rise of $G_c(\dot{\gamma})/G_c(0)$ as a function of $Wi$ with a slope of 1/7.
Figures

(a) DNA solutions

(b) PBD solutions

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5(a)
Blue diamonds: Homogenous shear
Red circles: Inhomogenous shear

Fig. 5(b)

Fig. 6

(a) 5%PBD (0.7M)-(1.8K)  
Z = 13

(b) 10%PBD(0.7M)-(9K)  
Z = 27

(a) 5%PBD (0.7M)-(1.8K)  
Z = 13

(b) 10%PBD(0.7M)-(9K)  
Z = 27

Newtonian Region
Shear thinning Region

Fig. 7(a)

Fig. 7(b)

Fig. 8(a)

Fig. 8(b)
References


Vlastos, G., D. Lerche, B. Koch, O. Samba, and M. Pohl, “The effect of parallel


