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MOLECULAR ORIGINS OF HIGHER HARMONICS IN LARGE-AMPLITUDE OSCILLATORY SHEAR FLOW: SHEAR STRESS RESPONSE

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ABSTRACT

Recent work has focused on deepening our understanding of the molecular origins of the higher harmonics that arise in the shear stress response of polymeric liquids in large-amplitude oscillatory shear flow. For instance, these higher harmonics have been explained by just considering the orientation distribution of rigid dumbbells suspended in a Newtonian solvent. These dumbbells, when in dilute suspension, form the simplest relevant molecular model of polymer viscoelasticity, and this model specifically neglects interactions between the polymer molecules [R.B. Bird et al., *J Chem Phys*, **140**, 074904 (2014)]. In this paper, we explore these interactions by examining the Curtiss-Bird model, a kinetic molecular theory designed specifically to account for the restricted motions that arise when polymer chains are concentrated, thus interacting and specifically, entangled. We begin our comparison using a heretofore ignored explicit analytical solution [Fan and Bird, *JNNFM*, **15**, 341 (1984)]. For concentrated systems, the chain motion transverse to the chain axis is more restricted than along the axis. This anisotropy is described by the link tension coefficient, ϵ , for which several special cases arise: $\epsilon = 0$ corresponds to reptation, $\epsilon > 1/8$ to rod-climbing, $1/2 \geq \epsilon \geq 3/4$ to reasonable predictions for shear-thinning in steady simple shear flow, and $\epsilon = 1$ to the dilute solution without hydrodynamic interaction. In this paper, we examine the shapes of the shear stress versus shear rate loops for the special cases $\epsilon = (0, 1/8, 3/8, 1)$, and we compare these with those of rigid dumbbell and reptation model predictions.

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CONTENTS

I. INTRODUCTION.....	6
II. METHOD.....	8
III. COMPARISONS.....	9
A. Reptation Theories ($\epsilon = 0$).....	9
B. Chains and Dumbbells with Hydrodynamic Interaction ($\epsilon = \frac{1}{8}$).....	10
C. Chains with Hydrodynamic Interaction: Best Fit ($\epsilon = \frac{3}{8}$)	11
D. Dilute Solutions of Chains, Dumbbells, and Polygons ($\epsilon = 1$)	11
IV. CONCLUSION.....	15
V. APPENDICES.....	16
A. Curtiss-Bird Theory.....	16
B. Reptation Through Slip-Links (With IAA).....	20
C. Reptation Through Slip-Links (Without IAA).....	22
D. Paul and Mazo Plane-Polygonal Polymer	24
E. Paul correction to Kirkwood and Plock.....	26
VI. ACKNOWLEDGMENT.....	30
VII. REFERENCES.....	67

TABLES

Table I: Literature on Analytical Solutions for Molecular Models in LAOS.....	31
Table II: Dimensional Variables.....	33
Table III: Dimensionless Variables and Groups.....	35
Table IV: Molecular models compared in this paper	37

FIGURES

Figure 1: Diagram for LAOS illustrating the complex, dimensionless generalized non-Newtonianness, G_n . Newtonian behavior is observed well inside the unit circle, where $ G_n \ll 1$. The magnitude of G_n thus reflects how far the system departs from Newtonian behavior and the inclination ϕ identifies the type of departure.....	38
Figure 2: Kramers freely-jointed chain (a), chain through slip-links (b), rigid dumbbell (c), and planar polygon (d).....	39
Figure 3: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = 0$ corresponding to reptation.	40
Figure 4: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain	

(Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = 0$ corresponding to reptation.	41
Figure 5: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = 0$ corresponding to reptation.	42
Figure 6: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = \frac{1}{8}$	43
Figure 7: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = \frac{1}{8}$	44
Figure 8: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = \frac{1}{8}$	45
Figure 9: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = \frac{3}{8}$	46
Figure 10: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = \frac{3}{8}$	47
Figure 11: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = \frac{3}{8}$	48
Figure 12: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.	49
Figure 13: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.	50
Figure 14: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a	

fixed Deborah number of 10, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.	51
Figure 15: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.....	52
Figure 16: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 1.....	53
Figure 17: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 10.....	54
Figure 18: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 0.1.....	55
Figure 19: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 1.0.....	56
Figure 20: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 10.....	57
Figure 21: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.	58
Figure 22: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 1.0.	59
Figure 23: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 10.	60
Figure 24: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell according to the Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 0.1.	61
Figure 25: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell according to the	

Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 1.	62
Figure 26: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a rigid dumbbell according to the Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 10.	63
Figure 27: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.	64
Figure 28: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 1.	65
Figure 29: Counterclockwise loops of dimensionless shear stress <i>versus</i> dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 10.	66

I. INTRODUCTION

Since its conception [1,2,3], oscillatory shear flow has become, by far, the most popular method for measuring the viscoelastic properties of liquids. For polymeric liquids, when this test is carried out at large amplitude, the shear stress responds as a Fourier series, the higher harmonics of which are caused by fluid nonlinearity. This growing subdiscipline of the physics of fluids is called *large-amplitude oscillatory shear* (LAOS).

To generate oscillatory shear flow, after confining the fluid to a simple shear flow apparatus, we subject one solid-liquid boundary to a coplanar sinusoidal displacement, and thus, a cosinusoidal shear rate [4,5]:

$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t \quad (1)$$

Using the characteristic relaxation time of the viscoelastic fluid, λ , we can make Eq. (1) dimensionless:

$$\begin{aligned} \lambda \dot{\gamma}(t) &= \lambda \dot{\gamma}_0 \cos \lambda \omega (t / \lambda) \\ &\equiv \text{Wi} \cos \text{De} (t / \lambda) \end{aligned} \quad (2)$$

where:

$$\text{De} \equiv \lambda \omega \quad (3)$$

and

$$\text{Wi} \equiv \lambda \dot{\gamma}_0 \quad (4)$$

are called the Deborah and Weissenberg numbers. The dimensionless Eq. (2) suggests that dimensionless solutions to LAOS problems shall be written in terms of Wi or De only, and we follow this throughout this work. Specifically, in dimensionless solutions, we resist the temptation to replace the ratio Wi/De with the shear strain amplitude, γ_0 . Increasing either the Weissenberg number or the Deborah number in Eq. (2) causes the fluid response to depart from Newtonian behavior. We can construct a complex dimensionless number from the ordered pair (De,Wi) thus:

$$\text{Gn} \equiv \text{De} + i \text{Wi} \quad (5)$$

which defines a vector with magnitude:

$$|\text{Gn}| \equiv \sqrt{\text{De}^2 + \text{Wi}^2} \quad (6)$$

and with angle:

$$\phi \equiv \arctan \frac{\text{Wi}}{\text{De}} \quad (7)$$

The magnitude of Gn reflects how far the fluid behavior departs from Newtonian behavior. We call such departures non-Newtonian. We can associate behavior in steady shear flow or viscometric flow with $\text{De}=0$, where $\text{Gn} = i \text{Wi}$. We can further associate linear viscoelastic behavior with $\text{Wi}=0$, where $\text{Gn} \equiv \text{De}$. The angle ϕ reflects the type of departure from Newtonian behavior. The value $\phi = 0$ corresponds to linear viscoelastic behavior, and $\phi = \pi/2$, to steady shear flow. We call Gn the *generalized non-Newtonianness*, and ϕ the *inclination towards non-Newtonianness*, and Figure 1 illustrates these.

In this work, we consider the molecular origins of the higher harmonics that arise in the shear stress during large-amplitude oscillatory shear flow experiments [4,5,6,7]. We shall do this by examining the predictions for several special cases of the Kramers freely-jointed chain and then, by comparing these with corresponding predictions of rigid dumbbell [25,30,34,44] and reptation [37,38] theories. Table I summarizes the literature on molecular models including those that we investigate in this paper, with our equations enumerated in column 2. To explore the predicted behaviors, we follow Dealy *et al.* (1973) in plotting loops of shear stress versus shear rate, since these best bring out distortions from ellipticity [8,9,10]. Our recent work on suspensions of rigid dumbbells (FIG. 3 through FIG. 5 of [44]) provides the benchmark set of conditions with which we will make our comparisons: $(\dot{\gamma}_0/\omega = \frac{1}{10}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4})$ at each $(\lambda\omega = \frac{1}{10}, 1, 10)$ where λ is the characteristic time of the fluid arising from the molecular theory. Further, we scale the ordinates of our loops with the reciprocal of the Weissenberg number, $\lambda\dot{\gamma}_0$.

In the Curtiss-Bird theory [12] the polymer melt is modeled as an intertwined, interacting collection of freely jointed bead-rod chains with N beads separated from center-to-center by $N - 1$ equal lengths a (see Kramers freely-jointed chain in Figure 2a). A chain can move easily along its backbone ("reptation"), but its lateral movement is restricted by neighboring chains (see FIG. 1 of [11]). This anisotropy is described by the link tension coefficient, which we represent with *lunate epsilon*, ϵ , for which interesting special cases arise: $\epsilon = 0$ corresponds to reptation, $\epsilon > 1/8$ to rod-climbing, $1/5 \geq \epsilon \geq 3/4$ to reasonable prediction of shear-thinning, and $\epsilon = 1$, to the dilute solution without hydrodynamic interaction.

In the dilute rigid dumbbell theory, a pair of beads, rigidly-separated, reorient in oscillatory shear flow, without interacting with any other dumbbells. For the special case examined here, the beads are sufficiently distant that the disturbances caused by adjacent beads of the suspending solvent do not interfere with one another (*without hydrodynamic interaction*) [34,44]. Kirkwood and Plock [25] also developed a corresponding theory (see Figure 2c) for $2n+1$ evenly spaced identical beads in a row, called a shish-kebab. This shish-kebab may or may not include hydrodynamic interaction, with interaction $0 \leq \lambda_0 < 0.5$, and without $\lambda_0 = 0$. For the special case of two beads, where $n = \frac{1}{2}$, we compare this model of Kirkwood and Plock [25], corrected by Paul [30].

Doi-Edwards reptation theory includes hydrodynamic interaction by confining the polymer chain to a tube [16] representing maximum hydrodynamic interaction. During deformation, the chains may deform affinely with the tube, and this is called independent-alignment. When independent-alignment is imposed mathematically, we call this the independent-alignment approximation (IAA). Independent-alignment requires both tube and polymer to contract or expand together by forcing the tangent vectors along the chain to align with the tube wall throughout the deformation. For LAOS, reptation has been modeled using chains slipping through links (which we call slip-link reptation and illustrate in Figure 2b) with [37] and without [38] IAA. In this paper, we limit our analysis to slip-link reptation with IAA and compare it with Curtiss-Bird theory [12] at $\epsilon = 0$.

We complete our exploration of molecular theories in LAOS with a brief look at plane-polygonal polymer models (see Figure 2d). We analyze the solution by Paul and Mazo [33] for a rigid ring of N sides undergoing LAOS in the absence of hydrodynamic interaction and then, compare their results with those of the other molecular theories under investigation.

Each molecular theory examined herein attaches a characteristic time to the fluid predictions, and these times are in turn related to molecular dimensions (for the Curtiss-Bird model, see Eq. (6.17) of [12]; for the rigid dumbbell suspension, see Eqs. (6) and (7) of [44]; for the slip-link model, see the unnumbered equation following Eq. (5'') of [37]). In this paper, we confine our attention to the loop shapes, and specifically, to the distortions in the shear stress responses caused by the third harmonics.

We have organized this contrastive review of the molecular origins of LAOS into four subsections (III.A through III.D) of ascending link tension coefficients, $\epsilon = 0, \frac{1}{8}, \frac{3}{8}, 1$.

II. METHOD

To evaluate the shear stress for the Curtiss-Bird model in large-amplitude oscillatory shear flow, mindful of the errata appended to References [13,14], we use the results of Fan and Bird [14]:

$$\begin{aligned} \frac{\tau_{yx}}{NnkT\lambda\dot{\gamma}_0} = & - \left\{ \left\{ \frac{8}{5} f_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \right. \\ & + \left. \left\{ \frac{4}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) f_1(2\lambda\omega) - \left(1 + \frac{2\epsilon}{5} \right) f_1(\lambda\omega) + \frac{1}{160} \epsilon \right] \right\} (\lambda\dot{\gamma}_0)^2 \right\} \cos \omega t \\ & - \left\{ \left\{ \frac{8}{5} s_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \right. \\ & + \left. \left\{ \frac{8}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) \left[\frac{1}{2} s_1(2\lambda\omega) - s_1(\lambda\omega) \right] \right] \right\} (\lambda\dot{\gamma}_0)^2 \right\} \sin \omega t \\ & - \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) f_1(\lambda\omega) \right. \right. \\ & \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) f_1(2\lambda\omega) + f_1(3\lambda\omega) - \frac{1}{240} \epsilon \right] \right\} (\lambda\dot{\gamma}_0)^2 \cos 3\omega t \\ & - \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) s_1(\lambda\omega) \right. \right. \\ & \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) s_1(2\lambda\omega) + s_1(3\lambda\omega) \right] \right\} (\lambda\dot{\gamma}_0)^2 \sin 3\omega t \end{aligned} \quad (8)$$

Appendix V.A details the method used to obtain Eq. (8), where all dimensional and dimensionless variables are defined in Table II and Table III. We then use Eq. (8) to develop dimensionless shear stress versus shear rate curves for the Curtiss-Bird model to investigate the special cases arising from different values of the link tension coefficient, $\epsilon = 0, \frac{1}{8}, \frac{3}{8}, 1$ (see Figure 3 through Figure 14). For comparison with the special cases of the Curtiss-Bird model, we also evaluate the

shear stress expressions for slip-link reptation [37] (see Appendices V.B and V.C Figure 15 through Figure 17), rigid dumbbells [44] (see Figure 18 through Figure 20), and Kirkwood-Riseman theory [30,33] (see Appendices V.D and V.E; see Figure 21 through Figure 29) by developing dimensionless stress-shear rate loops. We follow the protocol of values: $De = 0.1, 1, 10$ with $Wi/De = 0.1, 0.5, 0.75, 1, 1.25$, established in [24].

III. COMPARISONS

Having introduced each molecular theory for which an analytical solution for LAOS has been reported, we next compare of these theories. We organize our comparisons in descending order of hydrodynamic interaction. By descending order, we mean that the link tension coefficient, ϵ , of the Curtiss-Bird model ascends from zero to $\frac{1}{8}$ to $\frac{3}{8}$ to unity. Table IV is a correspondence between our figure numbers and the five molecular models compared herein.

A. Reptation Theories ($\epsilon = 0$)

Doi and Edward envisaged chain motion, for concentrated solutions and melts, to be confined to an imaginary tube, where the chain moves more freely along the tube than transversely [15]. The Kramers freely-jointed chain (special case of $\epsilon = 0$) predicts an orientation distribution of the chains that matches the orientation distribution of Doi and Edwards (see comparison of Eq. (6.18) with Eq. (3.8) of [16] in [12]). In other words, for the special case of $\epsilon = 0$, we can compare the Curtiss-Bird model, at least approximately, with predictions from slip-link reptation [37].

We use the results for slip-link reptation to develop an expression for shear stress in LAOS:

$$\begin{aligned} \frac{\tau_{yx}}{(\lambda\dot{\gamma}_0)\rho kT/N_e} &= \frac{3}{5\lambda\omega} \left[f(\alpha, -\alpha)\cos\omega t + [1 - f(\alpha, \alpha)]\sin\omega t \right] \\ &+ \frac{3(\lambda\dot{\gamma}_0)^2}{14(\lambda\omega)^3} \left[\begin{aligned} &-\left[f(\alpha, -\alpha) - \frac{1}{2}f(\sqrt{2}\alpha, -\sqrt{2}\alpha) \right]\cos\omega t \\ &-\left[\frac{3}{2} - 2f(\alpha, \alpha) + \frac{1}{2}f(\sqrt{2}\alpha, \sqrt{2}\alpha) \right]\sin\omega t \\ &+ \frac{1}{2} \left[f(\alpha, -\alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3}f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right]\cos 3\omega t \\ &+ \frac{1}{2} \left[\frac{1}{3}f(\alpha, \alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3}f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right]\sin 3\omega t \end{aligned} \right] \end{aligned} \quad (9)$$

where:

$$f(x, y) \equiv \frac{1}{x} \frac{\sinh x + \sin y}{\cosh x + \cos y} \quad (10)$$

and $\alpha \equiv \pi\sqrt{\frac{1}{2}\lambda\omega}$. Appendix V.B shows how we obtained Eq. (9).

Figure 3 and Figure 4 show reasonable shear stress loop predictions for the Curtiss-Bird model at $\epsilon = 0$ and for Deborah numbers of 0.1 and 1. By *reasonable*, we mean that the loop shapes conform to shapes measured for polymer melts or solutions. As we move to $De = 10$ in Figure 5, we observe distortions to the shear

stress loops for large Wi/De . These unreasonable distortions originate from the third harmonic and are not observed experimentally. Specifically, the loops are concave (convex) in the first (third) quadrant. The Curtiss-Bird model loops, at $\epsilon = 0$, thus have the *wrong convexity*.

If we plot the shear stress predictions for slip-link reptation at these same values of De and Wi/De (see Figure 15 through Figure 17), we observe entirely different behavior. At $De = 0.1$, Figure 15, we no longer observe the linear-elastic response of Figure 3, but instead, we see the development of large self-intersecting loops. For $De = 1$ (Figure 16), we observe similar loop distortions to those seen for the Curtiss-Bird model ($\epsilon = 0$) at $De = 10$ in Figure 5, where they have the *wrong convexity*. Figure 5 ($\epsilon = 0, De = 10$) and Figure 16 ($\epsilon = 0, De = 1$) are qualitatively similar and thus share the same wrong convexity. We do not see any such similarity between the two models when compared at the same Deborah number, $De = 1$ (Figure 4 and Figure 16). Figure 17 ($\epsilon = 0, De = 10$) and Figure 5 ($\epsilon = 0, De = 10$) are also dissimilar at large Wi/De . However, the shapes in Figure 17 appear as a stretched version of those in Figure 5 without as much *wrong convexity*. We believe that these models might agree more closely if the IAA was dropped from the slip-link theory [38].

B. Chains and Dumbbells with Hydrodynamic Interaction ($\epsilon = \frac{1}{8}$)

Using Eq. (8) and Figure 6 through Figure 8, we find that the third harmonic plays an inconsequential role in defining loop shape for $0.1 \leq De \leq 1$ (Figure 6 and Figure 7). Conversely, at higher frequency ($De = 10$, Figure 8), we get *wrong convexity*. The loops in Figure 6 through Figure 8 are close to those in Figure 3 through Figure 5, where $\epsilon = 0$. However, in Figure 6 through Figure 8 we also see loop broadening (or widening) as we reduce the hydrodynamic interaction by increasing ϵ .

We next compare the results of Curtiss-Bird (Figure 6 through Figure 8) with those of the two-member rigid rod ($n = \frac{1}{2}$) of Paul [30] for moderate hydrodynamic interaction ($\lambda_0 = 0.25$) (see Appendix V.E and Figure 24 through Figure 26):

$$\begin{aligned} \frac{(\tau - \tau^0)_{xy}}{n\zeta b^2 \dot{\gamma}_0} = & \frac{1}{30} \left(\frac{(2\beta'' + 3\beta' + 2\beta''De^2)\cos\omega t + 3\beta'D\sin\omega t}{(1 + De^2)} \right) \\ & + \frac{3Wi^2}{350} \left(\frac{(5(7\beta'' - 92\beta') + (110\beta'' - 757\beta')De^2 + 3(25\beta'' - 51\beta')De^4)D\sin\omega t}{(1 + De^2)^2(1 + 4De^2)(25 + 9De^2)} \right. \\ & \left. + \frac{(25(4\beta'' - 19\beta') + 4(111\beta'' - 196\beta')De^2 + (380\beta'' - 21\beta')De^4 + 36\beta''De^6)\cos\omega t}{2(1 + De^2)^2(1 + 4De^2)(25 + 9De^2)} \right) \\ & + \frac{Wi^2}{70} \left(\frac{45(3\beta'' + \beta')De^4 + (78\beta'' + 17\beta')De^2 + (7\beta'' - 92\beta')}{(1 + De^2)(1 + 4De^2)(1 + 9De^2)(25 + 9De^2)} D\sin 3\omega t \right. \\ & \left. - \frac{324\beta''De^6 - 9(28\beta'' + 67\beta')De^4 - 4(53\beta'' + 223\beta')De^2 - 5(4\beta'' - 19\beta')}{2(1 + De^2)(1 + 4De^2)(1 + 9De^2)(25 + 9De^2)} \cos 3\omega t \right) \end{aligned} \quad (11)$$

At $De = 0.1$, they are qualitatively alike (Figure 6 and Figure 24). For $De = 1$, both models predict *wrong convexity* (Figure 7 and Figure 25), and the two-member rigid rod model predicts more *wrong convexity*. The flexibility of the Curtiss-Bird chain reduces the stresses and diminishes the *wrong convexity*. Additionally, the Paul model misbehaves at large Deborah number (Figure 26), predicting stresses with significant self-intersection and large secondary maxima.

Whereas the free surface of a polymeric liquid will climb a rotating rod, Hassager [17] has shown that the reptation model predicts that the free surface of a polymeric liquid will descend the rotating rod. The necessary condition for rod climbing is $\epsilon > 1/8$, and so, in this section we explore the special case of *climb-neutrality*: $\epsilon = 1/8$, that is, where the liquid surface around the rotating rod will neither climb, nor descend.

C. Chains with Hydrodynamic Interaction: Best Fit ($\epsilon = \frac{3}{8}$)

In this section, we examine $\epsilon = 3/8$, the special case of the Curtiss-Bird model that most closely fits the measured behavior of monodisperse polymer solutions of various molecular weights in steady shear flow (see FIG. 1 of [18]). This particular value of $\epsilon = 3/8$ lies within the range $1/5 \leq \epsilon \leq 1/2$, where the predictions of the Curtiss-Bird model also closely match the Cox-Merz rule (see FIG. 13 of [11]). By the Cox-Merz rule (see Fig. 1 of [19]) we mean, where:

$$\eta(\dot{\gamma}) = \left| \eta^*(\omega) \right|_{\dot{\gamma}=\omega} \quad (12)$$

a curious connection between the region near the abscissa of Figure 1 (along which $\eta^*(\omega)$ is measured) and the region near the ordinate of Figure 1 (along which $\eta(\dot{\gamma})$ is measured).

The Curtiss-Bird model predictions in Figure 9 through Figure 11 agree with our previous observation that the loops broaden as we increase ϵ . Furthermore, Figure 9 and Figure 10 do not differ significantly with the loops at $\epsilon = 0$ (Figure 3 and Figure 4) and $\epsilon = 1/8$ (Figure 6 and Figure 7) and have no *wrong convexity*. When $De = 10$, we see that the *wrong convexity* present at $\epsilon = 0$ (Figure 5) and $\epsilon = 1/8$ (Figure 8) nearly vanishes at $\epsilon = 3/8$ (Figure 11). Thus, $\epsilon = 3/8$ is not only the best value for fitting steady shear viscosity, but also for fitting LAOS data. Without exception, for $\epsilon \leq 1/5$, we find *wrong convexity* to be persistent.

D. Dilute Solutions of Chains, Dumbbells, and Polygons ($\epsilon = 1$)

In this subsection, we investigate how well a freely-jointed chain can be approximated by the simplest molecular model that is relevant to oscillatory shear flow behavior: the dilute suspension of rigid dumbbells. By *relevant*, we mean that the model predicts higher harmonics in LAOS. We investigate by comparing the particular case $\epsilon = 1$ for the Curtiss-Bird chain with with the prediction of the rigid dumbbell model. We also compare both of these models with the model predictions for the shish kebab (Kirkwood and Plock rigid rod

with $2n+1$ equally spaced beads, for which the rigid dumbbell is the special case $n = \frac{1}{2}$).

When $\epsilon = 1$, the chain motion transverse to the chain axis is unrestricted. In other words, the chain moves freely in any direction, without restriction from hydrodynamic interactions. The possibility for two-dimensional shapes arises since the chain is now allowed to bend and flex. In this subsection, we also investigate what happens when the molecular structure closes on itself, as for the case of a plane-polygon. To this end, we contrast the Paul and Mazo plane-polygonal polymer model predictions for LAOS with those of the Curtiss-Bird model without hydrodynamic interaction, and with the aforementioned rigid dumbbell models (both the Kirkwood and Plock rigid rod with $n = \frac{1}{2}$, and the rigid dumbbell model [20,44]). This comparison will uncover how polymer molecular configuration affects the loop shapes.

Figure 12 through Figure 14 show that the Curtiss-Bird chain with unrestricted chain motion ($\epsilon = 1$) exhibits no *wrong convexity*, except at large Weissenberg number. By contrast, the rigid dumbbell model results (Figure 18 through Figure 20) differ markedly from Figure 12 through Figure 14. Specifically, at $De \geq 1$, the rigid dumbbell model exhibits severe *wrong convexity*. In fact, the *wrong convexity* in Figure 19 and Figure 20 is worse than that of the Curtiss-Bird model, even at $\epsilon = 0$ (Figure 4 and Figure 5). At $De = 0.1$, however, neither molecular model predicts *wrong convexity* (compare Figure 12 with Figure 18).

For the Kirkwood and Plock rigid rod with $n = \frac{1}{2}$, without hydrodynamic interaction ($\lambda_0 \ll 1$), the results of Paul [30] derived in Appendix V.E (Figure 21 through Figure 23):

$$\begin{aligned}
\frac{(\tau - \tau^0)_{xy}}{n\xi b^2 \dot{\gamma}_0} = \text{Re} & \left\{ \frac{1}{30} \left(\frac{(4\text{De}^2 + 7)\cos\omega t + 3\text{De}\sin\omega t}{2(1 + \text{De}^2)} \right) \right. \\
& + \frac{3\text{Wi}^2}{350(1 + \text{De}^2)} \left(\begin{aligned} & -\frac{230\text{De}\sin\omega t}{(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} + \frac{35\text{De}\sin\omega t}{2(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & -\frac{196\text{De}^2\cos\omega t}{(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} + \frac{86\text{De}^2\cos\omega t}{(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & -\frac{475\cos\omega t}{4(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} + \frac{25\cos\omega t}{(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & -\frac{153\text{De}^5\sin\omega t}{2(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & -\frac{21\text{De}^4\cos\omega t}{4(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & +\frac{9\text{De}^4\cos\omega t}{(4\text{De}^2 + 1)(9\text{De}^2 + 25)} - \frac{757\text{De}^3\sin\omega t}{2(\text{De}^2 + 1)(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \\ & +\frac{75\text{De}^3\sin\omega t}{2(4\text{De}^2 + 1)(9\text{De}^2 + 25)} \end{aligned} \right) \\
& + \frac{\text{Wi}^2}{140(1 + \text{De}^2)} \left(\begin{aligned} & \frac{2 + 3\text{De}^2 + i\text{De}}{(5 + 13i\text{De} - 6\text{De}^2)} \\ & -\frac{19 + 15\text{De}^2 - 4i\text{De}}{2(1 + 2i\text{De})(1 + 3i\text{De})(5 + 3i\text{De})} \end{aligned} \right) (\cos 3\omega t + i\sin 3\omega t) \left. \right\} \quad (13)
\end{aligned}$$

resemble closely the results for the rigid dumbbell model at $\text{De} \leq 1$ (Figure 15 and Figure 16); both lack *wrong convexity* at $\text{De} = 0.1$ but predict *wrong convexity* at $\text{De} = 1$. Additionally, at $\text{De} = 1$, the two models nearly match. Neither model agrees with results of the Curtiss-Bird chain, $\epsilon = 1$, which predicts less *wrong convexity* at large Weissenberg number. This is especially true at $\text{De} = 10$ (Figure 23), where the model predictions of the two-member rigid rod give both self-intersection and *wrong convexity* similar to that of Kirkwood and Plock with hydrodynamic interaction (Figure 26). This limiting case of the Kirkwood and Plock model cannot accurately predict highly nonlinear and elastic behavior, while Curtiss-Bird does not give this poor behavior in the limit of zero hydrodynamic interaction, $\epsilon = 1$. Though the loop predictions for the two-member rigid rod are qualitatively similar for $\lambda_0 \ll 1$ and $\lambda_0 \approx 1$, as λ_0 increases, the overall loop shear stress amplitude increases due to hydrodynamic interactions, as it should. Additionally, increasing the hydrodynamic interaction parameter, λ_0 , worsens *wrong convexity*, as is true when ϵ is decreased for the Curtiss-Bird model (see Subsection III.B).

Lastly, we investigate the molecular model of Paul and Mazo [33], where the beads are arranged on the vertices of a plane-polygon. We find that the

predictions of Paul and Mazo, derived in Appendix V.D (Figure 27 through Figure 29):

$$\begin{aligned}
 \frac{(\tau - \tau^0)_{xy}}{c'\xi b^2 \dot{\gamma}_0} = \text{Re} & \left[\frac{1}{60} \left(\frac{\xi_A + 6\xi_B + 3\xi_C + (\xi_A + 6\xi_B)De^2}{1 + De^2} \right) \cos(\omega t) + \frac{1}{60} \left(\frac{3\xi_C De}{1 + De^2} \right) \sin(\omega t) \right] \\
 & + \frac{Wi^2}{1 + De^2} \left\{ \begin{aligned} & \left[\begin{aligned} & \frac{3\xi_A (50 + 159De^2 + 18De^4)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - \frac{9\xi_B (25 + 103De^2 + 12De^4)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - 3\xi_C \left(\frac{475 + 784De^2 - 9De^4}{1400(1 + De^2)(1 + 4De^2)(25 + 9De^2)} \right) \end{aligned} \right] \cos(\omega t) \\ & + \left[\begin{aligned} & \frac{3\xi_A (140 + 69De^2)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - \frac{9\xi_B (10 + 40De^2)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - 3\xi_C \left(\frac{920 + 2054De^2 + 306De^4}{1400(1 + De^2)(1 + 4De^2)(25 + 9De^2)} \right) \end{aligned} \right] \text{Desin}(\omega t) \\ & + \left[\begin{aligned} & \frac{5\xi_A (10 + 16De^2 - 18De^4) - 15\xi_B (5 - 19De^2)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - \frac{5\xi_C (95 - 892De^2 - 603De^4)}{1400(1 + 9De^2)(1 + 4De^2)(25 + 9De^2)} \end{aligned} \right] \cos(3\omega t) \\ & + \left[\begin{aligned} & \frac{5\xi_A (21 + 45De^2) - 15\xi_B (18 - 6De^2)}{1400(1 + 4De^2)(25 + 9De^2)} \\ & - \frac{5\xi_C (552 - 102De^2 - 270De^4)}{1400(1 + De^2)(1 + 4De^2)(25 + 9De^2)} \end{aligned} \right] \text{Desin}(3\omega t) \end{aligned} \right\} \quad (14)
 \end{aligned}$$

differ from those of the Curtiss-Bird model, $\epsilon = 1$ (Figure 12 through Figure 14). We next compare each of our non-interacting molecular models (i) the plane-polygonal (Figure 27 through Figure 29) *versus* (ii) the rigid dumbbell [20,44] (Figure 18 through Figure 20) *versus* (iii) the Kirkwood and Plock rigid dumbbell (Figure 21 through Figure 23). The predicted loop shapes for these three non-interacting models agree closely with one another, despite the differences in bead number or in configuration. We believe the agreement between the rigid dumbbell and plane-polygonal models results from their mutual rigidity. Furthermore, the loops for the non-interacting ($\epsilon = 1$) Curtiss-Bird chain (Figure 12 through Figure 14) differ markedly from any of our three non-interacting molecular models [(i), (ii) or (iii)]. Because the Curtiss-Bird model allows for

chain flexibility, it disagrees with the rigid molecular models [(i), (ii) and (iii)]. However, the non-interacting plane-polygonal model predictions for the overall shear stress amplitude agree closely with those of the non-interacting Curtiss-Bird model, but subceed those of the non-interacting rigid dumbbell models [(ii) and (iii)]. We believe that the plane-polygonal model is therefore intermediate between the Kramers chain in Curtiss-Bird theory and the rigid dumbbell, because it is both rigid and does not require its beads to be inline.

IV. CONCLUSION

In this paper, we have examined, under one notation [9] (for other notations, see Section 9. of [24]), all of the molecular models for polymeric liquids in LAOS for which analytical solutions exist (see Table I). Specifically, for our notation, we chose triplets of stress *versus* strain rate loops following the convention established in Figures 2-4 of [24], for which $De = \frac{1}{10}, 1, 10$ and $Wi/De = \frac{1}{10}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}$. In this paper, for molecular models, we have explored suspensions of rigid dumbbells (with and without hydrodynamic interaction), plane-polygons (without hydrodynamic interaction), and chains. Since the chain model, through its link-tension coefficient, ϵ , admits different amounts of motion transverse to the chain backbone. In order of ascending ϵ , we explored the special cases of reptation ($\epsilon = 0$; see Subsection III.A), climb neutrality ($\epsilon = 1/8$; see Subsection III.B), best-fit to steady shear ($\epsilon = 3/8$; see Subsection III.C), and zero hydrodynamic interaction ($\epsilon = 1$; see Subsection III.D). We next compared each of our non-interacting molecular models (i) the plane-polygonal *versus* (ii) the rigid dumbbell [20,44] *versus* (iii) the Kirkwood and Plock rigid dumbbell.

We discover the specific problem with loop shape, *wrong convexity*, to be prevalent amongst molecular models in LAOS. We find the Curtiss-Bird model to be the most successful at overcoming *wrong convexity*. Further, the Curtiss-Bird model captures the qualitative behavior of polymers at various degrees of hydrodynamic interaction in LAOS, that is, going from reptation ($\epsilon = 0$; see Subsection III.A) all the way up to non-interacting chains ($\epsilon = 1$; see Subsection III.D).

For its special cases of (a) reptation ($\epsilon = 0$; see Subsection III.A), (b) climb neutrality ($\epsilon = 1/8$; see Subsection III.B), and (c) zero hydrodynamic interactions ($\epsilon = 1$; see Subsection III.D), the Curtiss-Bird model disagrees with rival corresponding molecular models (a) slip-link reptation, and Kirkwood and Plock rigid dumbbells (b) with and (c) without hydrodynamic interaction. Specifically, whereas all three rival models give *wrong convexity*, for $\epsilon = 1$, the Curtiss-Bird model does not. We thus find that decreasing ϵ amplifies *wrong convexity*.

We also investigated the effect of rearranging the beads from the shish-kebab to the plane-polygon. We find that rearranging the beads from a line (Figure 21 through Figure 23) to the vertices of a plane-polygon (Figure 27 through Figure 29) dramatically reshapes the loops. The non-interacting rigid molecular models (rigid dumbbells and plane-polygonal) predict loops with greater *wrong convexity* than the flexible model, the Curtiss-Bird chain with $\epsilon = 1$ (see Subsection III.D).

Whereas, for continuum theory, analytical solutions for the normal stress differences in oscillatory shear are available (Section 4. of [24]; [21,22]), for molecular theory, only the rigid dumbbell [46] and the plane-polygon [33,36] have yielded analytical solutions (even for small-amplitudes). Other molecular models have thus failed to attract similar attention. This is why a comprehensive investigation of the normal stresses in LAOS, under one notation (Section 4. of [24]), is not yet possible. The finitely extensible (FENE) or the Fraenkel dumbbells have yet to be evaluated in LAOS for either the shear stress or for the normal stress differences [35,23]. Furthermore, loop shapes of normal stress differences in LAOS have yet to be measured [21].

V. APPENDICES

A. Curtiss-Bird Theory

To develop an equation for shear stress using Curtiss-Bird Theory [14], we begin with an expansion of the odd shear stress harmonics:

$$\tau_{yx} = \sum_{n,\text{odd}}^{\infty} \tau'_n \cos n\omega t + \tau''_n \sin n\omega t \quad (15)$$

$$\begin{aligned} \tau_{yx} = & \tau'_1 \cos \omega t + \tau''_1 \sin \omega t \\ & + \tau'_3 \cos 3\omega t + \tau''_3 \sin 3\omega t \\ & + \tau'_5 \cos 5\omega t + \tau''_5 \sin 5\omega t + \dots \end{aligned} \quad (16)$$

where:

$$\tau'_n \equiv - \sum_{p,\text{odd}}^{\infty} \eta'_{np} (\dot{\gamma}_0)^p ; p \geq n \quad (17)$$

$$\tau''_n \equiv - \sum_{p,\text{odd}}^{\infty} \eta''_{np} (\dot{\gamma}_0)^p ; p \geq n \quad (18)$$

so that:

$$\begin{aligned} \tau'_1 & \equiv - \sum_{p,\text{odd}}^{\infty} \eta'_{1p} (\dot{\gamma}_0)^p ; p \geq 1 \\ & = - \left(\eta'_{11} (\dot{\gamma}_0) + \eta'_{13} (\dot{\gamma}_0)^3 + \eta'_{15} (\dot{\gamma}_0)^5 + \dots \right) \end{aligned} \quad (19)$$

$$\begin{aligned} \tau''_1 & \equiv - \sum_{p,\text{odd}}^{\infty} \eta''_{1p} (\dot{\gamma}_0)^p ; p \geq 1 \\ & = - \left(\eta''_{11} (\dot{\gamma}_0) + \eta''_{13} (\dot{\gamma}_0)^3 + \eta''_{15} (\dot{\gamma}_0)^5 + \dots \right) \end{aligned} \quad (20)$$

$$\begin{aligned}\tau'_3 &\equiv - \sum_{p,\text{odd}}^{\infty} \eta'_{3p} (\dot{\gamma}_0)^p ; p \geq 3 \\ &= - \left(\eta'_{33} (\dot{\gamma}_0)^3 + \eta'_{35} (\dot{\gamma}_0)^5 + \eta'_{37} (\dot{\gamma}_0)^7 + \dots \right)\end{aligned}\quad (21)$$

$$\begin{aligned}\tau''_3 &\equiv - \sum_{p,\text{odd}}^{\infty} \eta''_{3p} (\dot{\gamma}_0)^p ; p \geq 3 \\ &= - \left(\eta''_{33} (\dot{\gamma}_0)^3 + \eta''_{35} (\dot{\gamma}_0)^5 + \eta''_{37} (\dot{\gamma}_0)^7 + \dots \right)\end{aligned}\quad (22)$$

and:

$$\begin{aligned}\tau'_5 &\equiv - \sum_{p,\text{odd}}^{\infty} \eta'_{5p} (\dot{\gamma}_0)^p ; p \geq 5 \\ &= - \left(\eta'_{55} (\dot{\gamma}_0)^5 + \eta'_{57} (\dot{\gamma}_0)^7 + \eta'_{59} (\dot{\gamma}_0)^9 + \dots \right)\end{aligned}\quad (23)$$

$$\begin{aligned}\tau''_5 &\equiv - \sum_{p,\text{odd}}^{\infty} \eta''_{5p} (\dot{\gamma}_0)^p ; p \geq 5 \\ &= - \left(\eta''_{53} (\dot{\gamma}_0)^5 + \eta''_{55} (\dot{\gamma}_0)^7 + \eta''_{57} (\dot{\gamma}_0)^9 + \dots \right)\end{aligned}\quad (24)$$

where:

$$\eta'_{11} = NnkT\lambda \left\{ \frac{8}{5} f_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \quad (25)$$

$$\eta'_{13} = NnkT\lambda^3 \left\{ \frac{4}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) f_1(2\lambda\omega) - \left(1 + \frac{2\epsilon}{5} \right) f_1(\lambda\omega) + \frac{1}{160} \epsilon \right] \right\} \quad (26)$$

$$\eta'_{33} = NnkT\lambda^3 \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) f_1(\lambda\omega) - 2 \left(1 + \frac{\epsilon}{5} \right) f_1(2\lambda\omega) + f_1(3\lambda\omega) - \frac{1}{240} \epsilon \right] \right\} \quad (27)$$

$$\eta''_{11} = NnkT\lambda \left\{ \frac{8}{5} s_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \quad (28)$$

$$\eta''_{13} = NnkT\lambda^3 \left\{ \frac{8}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) \left[\frac{1}{2} s_1(2\lambda\omega) - s_1(\lambda\omega) \right] \right] \right\} \quad (29)$$

$$\eta''_{33} = NnkT\lambda^3 \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) s_1(\lambda\omega) - 2 \left(1 + \frac{\epsilon}{5} \right) s_1(2\lambda\omega) + s_1(3\lambda\omega) \right] \right\} \quad (30)$$

where $L \equiv \lambda^2 \omega^2$ and:

$$f_1(x) \equiv \sum_{\alpha, \text{odd}} \frac{1}{(\pi^4 \alpha^4 + x^2)} = \frac{\phi_-\left(\sqrt{\frac{1}{2}x}\right)}{8x\sqrt{\frac{1}{2}x}} \quad (31)$$

$$s_1(x) \equiv \sum_{\alpha, \text{odd}} \frac{x}{\pi^2 \alpha^2 (\pi^4 \alpha^4 + x^2)} = \frac{1}{8x} \left[1 - \frac{\phi_+\left(\sqrt{\frac{1}{2}x}\right)}{\sqrt{\frac{1}{2}x}} \right] \quad (32)$$

where:

$$\phi_-(y) = \frac{\sinh y - \sin y}{\cosh y + \cos y} \quad (33)$$

$$\phi_+(y) = \frac{\sinh y + \sin y}{\cosh y + \cos y} \quad (34)$$

Substituting Eqs. (19) through (22) into Eq. (16), we obtain:

$$\begin{aligned} \tau_{yx} = & -\left(\eta'_{11}(\dot{\gamma}_0) + \eta'_{13}(\dot{\gamma}_0)^3 + \eta'_{15}(\dot{\gamma}_0)^5 + \dots\right) \cos \omega t \\ & -\left(\eta''_{11}(\dot{\gamma}_0) + \eta''_{13}(\dot{\gamma}_0)^3 + \eta''_{15}(\dot{\gamma}_0)^5 + \dots\right) \sin \omega t \\ & -\left(\eta'_{33}(\dot{\gamma}_0)^3 + \eta'_{35}(\dot{\gamma}_0)^5 + \eta'_{37}(\dot{\gamma}_0)^7 + \dots\right) \cos 3\omega t \\ & -\left(\eta''_{33}(\dot{\gamma}_0)^3 + \eta''_{35}(\dot{\gamma}_0)^5 + \eta''_{37}(\dot{\gamma}_0)^7 + \dots\right) \sin 3\omega t \\ & -\left(\eta'_{55}(\dot{\gamma}_0)^5 + \eta'_{57}(\dot{\gamma}_0)^7 + \eta'_{59}(\dot{\gamma}_0)^9 + \dots\right) \cos 5\omega t \\ & -\left(\eta''_{55}(\dot{\gamma}_0)^5 + \eta''_{57}(\dot{\gamma}_0)^7 + \eta''_{59}(\dot{\gamma}_0)^9 + \dots\right) \sin 5\omega t + \dots \end{aligned} \quad (35)$$

and neglecting all powers higher than $(\dot{\gamma}_0)^3$ yields:

$$\begin{aligned} \tau_{yx} = & -\left(\eta'_{11}(\dot{\gamma}_0) + \eta'_{13}(\dot{\gamma}_0)^3\right) \cos \omega t \\ & -\left(\eta''_{11}(\dot{\gamma}_0) + \eta''_{13}(\dot{\gamma}_0)^3\right) \sin \omega t \\ & -\eta'_{33}(\dot{\gamma}_0)^3 \cos 3\omega t \\ & -\eta''_{33}(\dot{\gamma}_0)^3 \sin 3\omega t \end{aligned} \quad (36)$$

Substituting Eqs. (25) through (30) into Eq. (36), we find:

$$\begin{aligned}
\tau_{yx} = & - \left(NnkT\lambda \left\{ \frac{8}{5} f_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} (\dot{\gamma}_0) \right. \\
& + NnkT\lambda^3 \left\{ \frac{4}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) f_1(2\lambda\omega) - \left(1 + \frac{2\epsilon}{5} \right) f_1(\lambda\omega) + \frac{1}{160} \epsilon \right] \right\} (\dot{\gamma}_0)^3 \cos \omega t \\
& - \left(NnkT\lambda \left\{ \frac{8}{5} s_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} (\dot{\gamma}_0) \right. \\
& + NnkT\lambda^3 \left\{ \frac{8}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) \left[\frac{1}{2} s_1(2\lambda\omega) - s_1(\lambda\omega) \right] \right] \right\} (\dot{\gamma}_0)^3 \sin \omega t \\
& - NnkT\lambda^3 \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) f_1(\lambda\omega) \right. \right. \\
& \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) f_1(2\lambda\omega) + f_1(3\lambda\omega) - \frac{1}{240} \epsilon \right] \right\} (\dot{\gamma}_0)^3 \cos 3\omega t \\
& - NnkT\lambda^3 \left\{ \frac{8}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) s_1(\lambda\omega) \right. \right. \\
& \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) s_1(2\lambda\omega) + s_1(3\lambda\omega) \right] \right\} (\dot{\gamma}_0)^3 \sin 3\omega t \right) \quad (37)
\end{aligned}$$

Simplifying and rearranging, we finally get:

$$\begin{aligned}
\frac{\tau_{yx}}{NnkT\lambda\dot{\gamma}_0} = & - \left(\left\{ \frac{8}{5} f_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \right. \\
& + \left\{ \frac{4}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) f_1(2\lambda\omega) - \left(1 + \frac{2\epsilon}{5} \right) f_1(\lambda\omega) + \frac{1}{160} \epsilon \right] \right\} (\lambda\dot{\gamma}_0)^2 \cos \omega t \\
& - \left(\left\{ \frac{8}{5} s_1(\lambda\omega) + \frac{1}{90} \epsilon \right\} \right. \\
& + \left\{ \frac{8}{7L} \left[\left(1 - \frac{\epsilon}{5} \right) \left[\frac{1}{2} s_1(2\lambda\omega) - s_1(\lambda\omega) \right] \right] \right\} (\lambda\dot{\gamma}_0)^2 \sin \omega t \\
& - \left\{ \frac{2}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) f_1(\lambda\omega) \right. \right. \\
& \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) f_1(2\lambda\omega) + f_1(3\lambda\omega) - \frac{1}{240} \epsilon \right] \right\} (\lambda\dot{\gamma}_0)^2 \cos 3\omega t \\
& - \left\{ \frac{8}{7L} \left[\left(1 + \frac{4\epsilon}{5} \right) s_1(\lambda\omega) \right. \right. \\
& \left. \left. - 2 \left(1 + \frac{\epsilon}{5} \right) s_1(2\lambda\omega) + s_1(3\lambda\omega) \right] \right\} (\lambda\dot{\gamma}_0)^2 \sin 3\omega t \right) \quad (38)
\end{aligned}$$

which is the expression for the shear stress in Curtiss-Bird theory (see Eq. 2.17 of [14]).

B. Reptation Through Slip-Links (With IAA)

Pearson and Rochefort investigated a simplification of the reptation model in large-amplitude oscillatory shear flow [37]. Called the slip-link model, the motion of the polymer chain is confined to a tube, but the tube then takes the shape of a random walk through a series of slip-links (each of which pins a tube position). Each slip-link represents an entanglement. The chain motion follows an independent alignment, an approximation that was later investigated in large-amplitude oscillatory shear flow by Helfand and Pearson [38]. We begin deriving an expression for the shear stress in Pearson and Rochefort slip-link theory with:

$$\tau_{yx} = \sum_{p,\text{odd}}^{\infty} \sum_{q,\text{odd}}^p \gamma_0^p \left[G'_{pq} \cos q\omega t + G''_{pq} \sin q\omega t \right] \quad (39)$$

$$\begin{aligned} \tau_{yx} = & \gamma_0 \left[G''_{11} \cos \omega t + G'_{11} \sin \omega t \right] \\ & + \gamma_0^3 \left[\begin{aligned} & G''_{31} \cos \omega t + G'_{31} \sin \omega t \\ & + G''_{33} \cos 3\omega t + G'_{33} \sin 3\omega t \end{aligned} \right] \\ & + \gamma_0^5 \left[\begin{aligned} & G''_{51} \cos \omega t + G'_{51} \sin \omega t \\ & + G''_{53} \cos 3\omega t + G'_{53} \sin 3\omega t \\ & + G''_{55} \cos 5\omega t + G'_{55} \sin 5\omega t \end{aligned} \right] + \dots \end{aligned} \quad (40)$$

an expansion of the shear stress in terms of strain amplitude, where:

$$\begin{aligned} G''_{11} &= \frac{3}{5} \frac{\rho k T}{N_e} \sum_{p,\text{odd}}^{\infty} \frac{8}{\pi^2} \frac{\lambda \omega}{p^4 + L} \\ &= \frac{3}{5} \frac{\rho k T}{N_e} f(\alpha, -\alpha) \end{aligned} \quad (41)$$

$$\begin{aligned} G'_{11} &= \frac{3}{5} \frac{\rho k T}{N_e} \sum_{p,\text{odd}}^{\infty} \frac{8}{\pi^2 p^2} \frac{L}{p^4 + L} \\ &= \frac{3}{5} \frac{\rho k T}{N_e} [1 - f(\alpha, \alpha)] \end{aligned} \quad (42)$$

$$\begin{aligned} G''_{31} &= -\frac{3}{14} \frac{\rho k T}{N_e} \sum_{p,\text{odd}}^{\infty} \frac{8}{\pi^2} \left(\frac{\lambda \omega}{p^4 + L} - \frac{\lambda \omega}{p^4 + 4L} \right) \\ &= -\frac{3}{14} \frac{\rho k T}{N_e} \left[f(\alpha, -\alpha) - \frac{1}{2} f(\sqrt{2}\alpha, -\sqrt{2}\alpha) \right] \end{aligned} \quad (43)$$

$$\begin{aligned} G'_{31} &= -\frac{3}{14} \frac{\rho k T}{N_e} \sum_{p,\text{odd}}^{\infty} \frac{8}{\pi^2 p^2} \left(\frac{2L}{p^4 + L} - \frac{2L}{p^4 + 4L} \right) \\ &= -\frac{3}{14} \frac{\rho k T}{N_e} \left[\frac{3}{2} - 2f(\alpha, \alpha) + \frac{1}{2} f(\sqrt{2}\alpha, \sqrt{2}\alpha) \right] \end{aligned} \quad (44)$$

$$\begin{aligned}
G''_{33} &= -\frac{3}{28} \frac{\rho kT}{N_e} \sum_{p,\text{odd}} \frac{8}{\pi^2} \left(\frac{\lambda\omega}{p^4 + L} - \frac{2\lambda\omega}{p^4 + 4L} + \frac{\lambda\omega}{p^4 + 9L} \right) \\
&= \frac{3}{28} \frac{\rho kT}{N_e} \left[f(\alpha, -\alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right]
\end{aligned} \tag{45}$$

and

$$\begin{aligned}
G'_{33} &= -\frac{3}{28} \frac{\rho kT}{N_e} \sum_{p,\text{odd}} \frac{8}{\pi^2} \left(\frac{L}{p^4 + L} - \frac{4L}{p^4 + 4L} + \frac{3L}{p^4 + 9L} \right) \\
&= \frac{3}{28} \frac{\rho kT}{N_e} \left[\frac{1}{3} f(\alpha, \alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right]
\end{aligned} \tag{46}$$

λ is the characteristic time for the slip-link model, $\alpha \equiv \pi\sqrt{\frac{1}{2}\lambda\omega}$, ρ is polymer molar density, N_e is the number of moles of polymer per slip-link, and (mindful of the errata appended to Ref. [37]):

$$f(x, y) \equiv \frac{1}{x} \frac{\sinh x + \sin y}{\cosh x + \cos y} \tag{47}$$

We can identify the ratio ρ/N_e introduced in Eqs. (41) through (46) with the n introduced in Eqs. (25) through (30) above. Substituting Eqs. (41) through (46) into Eq. (40), then neglecting all terms of higher order than γ_0^3 , we get (in terms of f):

$$\begin{aligned}
\tau_{yx} &= \gamma_0 \left[\frac{3}{5} \frac{\rho kT}{N_e} f(\alpha, -\alpha) \cos \omega t + \frac{3}{5} \frac{\rho kT}{N_e} [1 - f(\alpha, \alpha)] \sin \omega t \right] \\
&\quad + \gamma_0^3 \left[\begin{aligned} &-\frac{3}{14} \frac{\rho kT}{N_e} \left[f(\alpha, -\alpha) - \frac{1}{2} f(\sqrt{2}\alpha, -\sqrt{2}\alpha) \right] \cos \omega t \\ &-\frac{3}{14} \frac{\rho kT}{N_e} \left[\frac{3}{2} - 2f(\alpha, \alpha) + \frac{1}{2} f(\sqrt{2}\alpha, \sqrt{2}\alpha) \right] \sin \omega t \\ &+\frac{3}{28} \frac{\rho kT}{N_e} \left[f(\alpha, -\alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right] \cos 3\omega t \\ &+\frac{3}{28} \frac{\rho kT}{N_e} \left[\frac{1}{3} f(\alpha, \alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right] \sin 3\omega t \end{aligned} \right]
\end{aligned} \tag{48}$$

Simplifying and rearranging yields the expression for shear stress in slip-link theory:

$$\begin{aligned}
\frac{\tau_{yx}}{(\lambda\dot{\gamma}_0)\rho kT/N_e} &= \frac{3}{5\lambda\omega} \left[f(\alpha, -\alpha) \cos \omega t + [1 - f(\alpha, \alpha)] \sin \omega t \right] \\
&+ \frac{3(\lambda\dot{\gamma}_0)^2}{14(\lambda\omega)^3} \left[\begin{aligned} &-\left[f(\alpha, -\alpha) - \frac{1}{2} f(\sqrt{2}\alpha, -\sqrt{2}\alpha) \right] \cos \omega t \\ &-\left[\frac{3}{2} - 2f(\alpha, \alpha) + \frac{1}{2} f(\sqrt{2}\alpha, \sqrt{2}\alpha) \right] \sin \omega t \\ &+ \frac{1}{2} \left[f(\alpha, -\alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right] \cos 3\omega t \\ &+ \frac{1}{2} \left[\frac{1}{3} f(\alpha, \alpha) - f(\sqrt{2}\alpha, -\sqrt{2}\alpha) + \frac{1}{3} f(\sqrt{3}\alpha, -\sqrt{3}\alpha) \right] \sin 3\omega t \end{aligned} \right] \quad (49)
\end{aligned}$$

or, in terms of the summations:

$$\begin{aligned}
\frac{\tau_{yx}}{(\lambda\dot{\gamma}_0)\rho kT/N_e} &= \frac{24}{5} \left[\begin{aligned} &\frac{1}{\pi^2(p^4 + L)} \cos \omega t \\ &+ \frac{1}{\pi^2 p^2(p^4 + L)} \lambda \omega \sin \omega t \end{aligned} \right] \\
&- (\lambda\dot{\gamma}_0)^2 \frac{6}{7L} \left[\begin{aligned} &2 \sum_{p, \text{odd}} \frac{1}{\pi^2} \left(\frac{1}{p^4 + L} - \frac{1}{p^4 + 4L} \right) \cos \omega t \\ &+ 2 \sum_{p, \text{odd}} \frac{1}{\pi^2 p^2} \left(\frac{2}{p^4 + L} - \frac{2}{p^4 + 4L} \right) \lambda \omega \sin \omega t \\ &+ \sum_{p, \text{odd}} \frac{1}{\pi^2} \left(\frac{1}{p^4 + L} - \frac{2}{p^4 + 4L} + \frac{1}{p^4 + 9L} \right) \cos 3\omega t \\ &+ \sum_{p, \text{odd}} \frac{1}{\pi^2} \left(\frac{\textcolor{red}{1}}{p^4 + L} - \frac{\textcolor{red}{4}}{p^4 + 4L} + \frac{\textcolor{red}{3}}{p^4 + 9L} \right) \lambda \omega \sin 3\omega t \end{aligned} \right] \quad (50)
\end{aligned}$$

C. Reptation Through Slip-Links (Without IAA)

The analysis completed by Pearson and Rochefort uses the IAA, which does not correctly capture the behavior of a polymer undergoing reptation [37,38]. Therefore, Helfand and Pearson completed a more rigorous analysis of the slip link model without the use of this simplifying approximation. To develop an expression for the shear stress, we expand the stress in a similar fashion as the Pearson and Rochefort approach using the IAA:

$$\tau_{yx} = \Re \left\{ \begin{aligned} &\gamma_0 G_{11}^* e^{i\omega t} \\ &+ \gamma_0^3 \left[G_{31}^* e^{i\omega t} + G_{33}^* e^{3i\omega t} \right] \\ &+ \gamma_0^5 \left[G_{51}^* e^{i\omega t} + G_{53}^* e^{3i\omega t} + G_{55}^* e^{5i\omega t} \right] + \dots \end{aligned} \right\} \quad (51)$$

where real and imaginary parts of G_{11}^* are given by Eqs. (42) and (41), and where:

$$G_{3m}^* \equiv G_{3m}^{*(0)} + G_{3m}^{*(2)} \quad (52)$$

so that:

$$G_{31}^* \equiv G_{31}^{*(0)} + G_{31}^{*(2)} \quad (53)$$

$$G_{33}^* \equiv G_{33}^{*(0)} + G_{33}^{*(2)} \quad (54)$$

where the real and imaginary parts of $G_{31}^{*(0)}$ are given by Eqs. (44) and (43), and of $G_{33}^{*(0)}$, by Eqs. (46) and (45). For the higher order terms, $G_{3m}^{*(2)}$, that is, the departures from the independent alignment approximation, we have:

$$G_{31}^{*(2)} = \frac{1}{200} G_0 \begin{bmatrix} h_2 \left[(-i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2} \right] \\ -ih_2 \left[(-i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2}, (i\lambda\omega)^{1/2} \right] \\ +ih_2 \left[(i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2} \right] \end{bmatrix} \quad (55)$$

where:

$$G_0 \equiv \frac{\rho k T}{N_e} \quad (56)$$

and:

$$h_2(z_p, z_q, z_r) = \frac{2}{\cos \frac{1}{2} \pi z_p \cos \frac{1}{2} \pi z_q \cos \frac{1}{2} \pi z_r} \times \left\{ \begin{aligned} & \frac{1}{4} \left[h_3(z_p - z_q - z_r) + h_3(z_p + z_q - z_r) - h_3(z_p + z_q + z_r) - h_3(z_p - z_q + z_r) \right] \\ & + \frac{1}{2} \cos \frac{1}{2} \pi z_q \left[h_3(z_p + z_r) - h_3(z_p - z_r) \right] \\ & + \frac{1}{2} \pi z_p \cos \frac{1}{2} \pi z_p \cos \frac{1}{2} \pi z_q \left[h_4(z_r) \right] \\ & - \frac{1}{2} \left(\frac{1}{2} \pi z_p \right) \cos \frac{1}{2} \pi z_p \left[h_4(z_q + z_r) - h_4(z_q - z_r) \right] \end{aligned} \right\} \quad (57)$$

where:

$$h_3(z) = \frac{\sin \frac{1}{2} \pi z}{\frac{1}{2} \pi z} \quad (58)$$

$$h_4(z) = \frac{\sin \frac{1}{2} \pi z}{\left(\frac{1}{2} \pi z \right)^2} - \frac{\cos \frac{1}{2} \pi z}{\frac{1}{2} \pi z} \quad (59)$$

and:

$$G_{33}^{*(2)} = \frac{1}{40} G_0 h_2 \left[(-i\lambda\omega)^{1/2}, (-3i\lambda\omega)^{1/2}, (-i\lambda\omega)^{1/2} \right] \quad (60)$$

D. Paul and Mazo Plane-Polygonal Polymer

Paul and Mazo developed an expression of shear stress for a polygon of N sides that reside in a single plane without interaction using Kirkwood-Riseman theory. We can therefore directly use their solution for the shear stress from Eq. 19 of [33]:

$$\frac{(\tau - \tau^0)_{xy}}{c'\xi b^2} = \text{Re} \left\{ \left[\begin{aligned} & \frac{1}{60} \left(\xi_A + 6\xi_B + \frac{3}{1+i\omega\lambda} \xi_C \right) \dot{\gamma}_0 \exp(i\omega t) \\ & + \frac{\dot{\gamma}_0^2 \lambda^2}{1+\omega^2 \lambda^2} [1400(1+2i\omega\lambda)(5+3i\omega\lambda)]^{-1} \\ & \times \left[\begin{aligned} & \left[\begin{aligned} & 3\xi_A (10 - 3\omega^2 \lambda^2 + 18i\omega\lambda) \\ & -9\xi_B (5 - 2\omega^2 \lambda^2 + 11i\omega\lambda) \\ & -3\xi_C \left(\frac{95 - 51\omega^2 \lambda^2 + 158i\omega\lambda}{1+i\omega\lambda} \right) \end{aligned} \right] \dot{\gamma}_0 \exp(i\omega t) \\ & + \left[\begin{aligned} & 5\xi_A (2 + 3\omega^2 \lambda^2 + i\omega\lambda) \\ & -15\xi_B (1 - i\omega\lambda) \\ & -5\xi_C \left(\frac{19 + 15\omega^2 \lambda^2 - 4i\omega\lambda}{1+3i\omega\lambda} \right) \end{aligned} \right] \dot{\gamma}_0 \exp(3i\omega t) \end{aligned} \right] \right\} \quad (61)$$

where τ is the characteristic time and:

$$\xi_A = \left(1 + \frac{3}{2} S_1 - \frac{1}{2} S_0 \right)^{-1} \quad (62)$$

$$\xi_B = \frac{(1 + \frac{3}{2} S_3)}{\left[(1 + \frac{3}{2} S_3) (1 + \frac{3}{2} S_1) - \frac{1}{4} S_2^2 \right]} \quad (63)$$

$$\xi_C = (1 + S_1)^{-1} \quad (64)$$

where:

$$S_k = \frac{\xi}{4\pi\eta_0 b} (\ln N - \alpha_k) + O(N^{-1}) \quad (65)$$

and:

$$\alpha_k = \ln\left(\frac{1}{2}\pi\right) + 2 \sum_{l=0}^{k-1} (2l+1)^{-1} \quad (66)$$

which, for the first four values of k are:

$$\alpha_0 = 0.4516 \quad (67)$$

$$\alpha_1 = 2.4516 \quad (68)$$

$$\alpha_2 = 3.1182 \quad (69)$$

$$\alpha_3 = 3.5182 \quad (70)$$

Substituting Eqs. (66)-(70) into Eq. (65), we find:

$$S_0 = \frac{\xi}{4\pi\eta_0 b} (\ln N - 0.4516) \quad (71)$$

$$S_1 = \frac{\xi}{4\pi\eta_0 b} (\ln N - 2.4516) \quad (72)$$

$$S_2 = \frac{\xi}{4\pi\eta_0 b} (\ln N - 3.1182) \quad (73)$$

$$S_3 = \frac{\xi}{4\pi\eta_0 b} (\ln N - 3.5182) \quad (74)$$

Substituting Eqs. (71)-(74) into Eqs. (62)-(64) yields:

$$\xi_A = \left(1 + \frac{3}{2} \frac{\xi}{4\pi\eta b} (\ln N - 2.4516) - \frac{1}{2} \frac{\xi}{4\pi\eta b} (\ln N - 0.4516) \right)^{-1} \quad (75)$$

$$\xi_B = \frac{\left(1 + \frac{3}{2} \frac{\xi}{4\pi\eta b} (\ln N - 3.5182) \right)}{\left[\left(1 + \frac{3}{2} \frac{\xi}{4\pi\eta b} (\ln N - 3.5182) \right) \left(1 + \frac{3}{2} \frac{\xi}{4\pi\eta b} (\ln N - 2.4516) \right) \right]} \quad (76)$$

$$\xi_C = \left(1 + \frac{\xi}{4\pi\eta b} (\ln N - 2.4516) \right)^{-1} \quad (77)$$

Finally, taking the real part of Eq. (61), we get:

$$\begin{aligned}
\frac{(\tau - \tau^0)_{xy}}{c'\zeta b^2 \dot{\gamma}_0} = \text{Re} & \left\{ \frac{1}{60} \left(\frac{\xi_A + 6\xi_B + 3\xi_C + (\xi_A + 6\xi_B) \text{De}^2}{1 + \text{De}^2} \right) \cos(\omega t) + \frac{1}{60} \left(\frac{3\xi_C \text{De}}{1 + \text{De}^2} \right) \sin(\omega t) \right. \\
& + \frac{\text{Wi}^2}{1 + \text{De}^2} \left\{ \begin{aligned} & \left[\begin{aligned} & \frac{3\xi_A (50 + 159\text{De}^2 + 18\text{De}^4)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - \frac{9\xi_B (25 + 103\text{De}^2 + 12\text{De}^4)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - 3\xi_C \left(\frac{475 + 784\text{De}^2 - 9\text{De}^4}{1400(1 + \text{De}^2)(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right) \end{aligned} \right] \cos(\omega t) \\ & + \left[\begin{aligned} & \frac{3\xi_A (140 + 69\text{De}^2)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - \frac{9\xi_B (10 + 40\text{De}^2)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - 3\xi_C \left(\frac{920 + 2054\text{De}^2 + 306\text{De}^4}{1400(1 + \text{De}^2)(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \right) \end{aligned} \right] \text{Desin}(\omega t) \\ & + \left[\begin{aligned} & \frac{5\xi_A (10 + 16\text{De}^2 - 18\text{De}^4) - 15\xi_B (5 - 19\text{De}^2)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - \frac{5\xi_C (95 - 892\text{De}^2 - 603\text{De}^4)}{1400(1 + 9\text{De}^2)(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \end{aligned} \right] \cos(3\omega t) \\ & + \left[\begin{aligned} & \frac{5\xi_A (21 + 45\text{De}^2) - 15\xi_B (18 - 6\text{De}^2)}{1400(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \\ & - \frac{5\xi_C (552 - 102\text{De}^2 - 270\text{De}^4)}{1400(1 + \text{De}^2)(1 + 4\text{De}^2)(25 + 9\text{De}^2)} \end{aligned} \right] \text{Desin}(3\omega t) \end{aligned} \right\} \right\} \quad (78)
\end{aligned}$$

which is the final expression for the shear stress of plane-polygonal polymers.

E. Paul correction to Kirkwood and Plock

We examine the corrected shear stress solution in LAOS from Kirkwood and Plock [25] (see Eq. (1) of [30]):

$$\frac{(\tau - \tau^0)_{xy}}{n\zeta b^2} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(2 \sum_{l=-n}^n l\psi_l(2\lambda_0) + \frac{3}{1+i\omega\lambda} \sum_{l=-n}^n l\psi_l(\lambda_0) \right) \dot{\epsilon}_0 \exp(i\omega t) \\ & + \frac{3\dot{\gamma}_0^2 \lambda^2}{350(1+\omega^2 \lambda^2)} \left(\frac{10-3\omega^2 \lambda^2 + 19i\omega\lambda}{(1+2i\omega\lambda)(5+3i\omega\lambda)} \sum_{l=-n}^n l\psi_l(2\lambda_0) \right. \\ & \quad \left. - \frac{95-51\omega^2 \lambda^2 + 158i\omega\lambda}{2(1+i\omega\lambda)(1+2i\omega\lambda)(5+3i\omega\lambda)} \sum_{l=-n}^n l\psi_l(\lambda_0) \right) \dot{\gamma}_0 \exp(i\omega t) \\ & + \frac{\dot{\gamma}_0^2 \lambda^2}{70(1+\omega^2 \lambda^2)} \left(\frac{2+3\omega^2 \lambda^2 + i\omega\lambda}{(1+2i\omega\lambda)(5+3i\omega\lambda)} \sum_{l=-n}^n l\psi_l(2\lambda_0) \right. \\ & \quad \left. - \frac{19+15\omega^2 \lambda^2 - 4i\omega\lambda}{2(1+2i\omega\lambda)(1+3i\omega\lambda)(5+3i\omega\lambda)} \sum_{l=-n}^n l\psi_l(\lambda_0) \right) \dot{\gamma}_0 \exp(3i\omega t) \end{aligned} \right\} \quad (79)$$

where:

$$\sum_{l=-n}^{+n} l\psi_l(\lambda_0) = \frac{1}{2(1-\lambda_0)}; n = \frac{1}{2} \quad (80)$$

$$\sum_{l=-n}^{+n} l\psi_l(2\lambda_0) = \frac{1}{2(1-2\lambda_0)}; n = \frac{1}{2} \quad (81)$$

and we assume that $\lambda_0 \ll 1$, so that:

$$\sum_{l=-n}^{+n} l\psi_l(\lambda_0) = \sum_{l=-n}^{+n} l\psi_l(2\lambda_0) \approx \frac{1}{2}; n = \frac{1}{2} \quad (82)$$

which corresponds to the absence of hydrodynamic interactions. Inserting Eq. (82) into Eq. (79), we get:

$$\frac{(\tau - \tau^0)_{xy}}{n\zeta b^2 \dot{\gamma}_0} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(1 + \frac{3}{2(1+i\omega\lambda)} \right) \exp(i\omega t) \\ & + \frac{3\dot{\gamma}_0^2 \lambda^2}{350(1+\omega^2 \lambda^2)} \left(\frac{10-3\omega^2 \lambda^2 + 19i\omega\lambda}{2(1+2i\omega\lambda)(5+3i\omega\lambda)} \right. \\ & \quad \left. - \frac{95-51\omega^2 \lambda^2 + 158i\omega\lambda}{4(1+i\omega\lambda)(1+2i\omega\lambda)(5+3i\omega\lambda)} \right) \exp(i\omega t) \\ & + \frac{\dot{\gamma}_0^2 \lambda^2}{70(1+\omega^2 \lambda^2)} \left(\frac{2+3\omega^2 \lambda^2 + i\omega\lambda}{2(1+2i\omega\lambda)(5+3i\omega\lambda)} \right. \\ & \quad \left. - \frac{19+15\omega^2 \lambda^2 - 4i\omega\lambda}{4(1+2i\omega\lambda)(1+3i\omega\lambda)(5+3i\omega\lambda)} \right) \exp(3i\omega t) \end{aligned} \right\} \quad (83)$$

Expanding this into real and imaginary parts, we find:

$$\frac{(\tau - \tau^0)_{xy}}{n\xi b^2 \dot{\gamma}_0} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(1 + \frac{3}{2(1+i\text{De})} \right) (\cos \omega t + i \sin \omega t) \\ & + \frac{3\text{Wi}^2}{350(1+\text{De}^2)} \left(\frac{10-3\text{De}^2+19i\text{De}}{2(1+2i\text{De})(5+3i\text{De})} - \frac{95-51\text{De}^2+158i\text{De}}{4(1+i\text{De})(1+2i\text{De})(5+3i\text{De})} \right) (\cos \omega t + i \sin \omega t) \\ & + \frac{\text{Wi}^2}{140(1+\text{De}^2)} \left(\frac{2+3\text{De}^2+i\text{De}}{(1+2i\omega\lambda)(5+3i\omega\lambda)} - \frac{19+15\text{De}^2-4i\text{De}}{2(1+2i\text{De})(1+3i\text{De})(5+3i\text{De})} \right) (\cos 3\omega t + i \sin 3\omega t) \end{aligned} \right\} \quad (84)$$

Evaluating Eq. (84) for the real part, we get:

$$\frac{(\tau - \tau^0)_{xy}}{n\xi b^2 \dot{\gamma}_0} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(\frac{(4\text{De}^2+7)\cos \omega t + 3\text{De}\sin \omega t}{2(1+\text{De}^2)} \right) \\ & + \frac{3\text{Wi}^2}{350(1+\text{De}^2)} \left(\begin{aligned} & \left(\frac{-230\text{De}\sin \omega t}{(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} + \frac{35\text{De}\sin \omega t}{2(4\text{De}^2+1)(9\text{De}^2+25)} \right) \\ & - \left(\frac{196\text{De}^2 \cos \omega t}{(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} + \frac{86\text{De}^2 \cos \omega t}{(4\text{De}^2+1)(9\text{De}^2+25)} \right) \\ & - \left(\frac{475 \cos \omega t}{4(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} + \frac{25 \cos \omega t}{(4\text{De}^2+1)(9\text{De}^2+25)} \right) \\ & - \frac{153\text{De}^5 \sin \omega t}{2(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} \\ & - \frac{21\text{De}^4 \cos \omega t}{4(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} \\ & + \left(\frac{9\text{De}^4 \cos \omega t}{(4\text{De}^2+1)(9\text{De}^2+25)} - \frac{757\text{De}^3 \sin \omega t}{2(\text{De}^2+1)(4\text{De}^2+1)(9\text{De}^2+25)} \right) \\ & + \frac{75\text{De}^3 \sin \omega t}{2(4\text{De}^2+1)(9\text{De}^2+25)} \end{aligned} \right) \\ & + \frac{\text{Wi}^2}{140(1+\text{De}^2)} \left(\frac{2+3\text{De}^2+i\text{De}}{(5+13i\text{De}-6\text{De}^2)} - \frac{19+15\text{De}^2-4i\text{De}}{2(1+2i\text{De})(1+3i\text{De})(5+3i\text{De})} \right) (\cos 3\omega t + i \sin 3\omega t) \end{aligned} \right\} \quad (85)$$

which is the dimensionless shear stress expression without hydrodynamic interaction.

If we repeat this analysis with the inclusion hydrodynamic interaction, where $\lambda_0 \approx 1$, we begin with Eq. (79):

$$\frac{(\tau - \tau^0)_{xy}}{n\zeta b^2} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(2\beta'' + \frac{3\beta'}{(1+i\omega\lambda)} \right) \dot{\gamma}_0 \exp(i\omega t) \\ & + \frac{3\dot{\gamma}_0^2 \lambda^2}{350(1+\omega^2 \lambda^2)} \left(\begin{aligned} & \frac{10-3\omega^2 \lambda^2 + 19i\omega\lambda}{(1+2i\omega\lambda)(5+3i\omega\lambda)} \beta'' \\ & - \frac{95-51\omega^2 \lambda^2 + 158i\omega\lambda}{2(1+i\omega\lambda)(1+2i\omega\lambda)(5+3i\omega\lambda)} \beta' \end{aligned} \right) \dot{\gamma}_0 \exp(i\omega t) \\ & + \frac{\dot{\gamma}_0^2 \lambda^2}{70(1+\omega^2 \lambda^2)} \left(\begin{aligned} & \frac{2+3\omega^2 \lambda^2 + i\omega\lambda}{(1+2i\omega\lambda)(5+3i\omega\lambda)} \beta'' \\ & - \frac{19+15\omega^2 \lambda^2 - 4i\omega\lambda}{2(1+2i\omega\lambda)(1+3i\omega\lambda)(5+3i\omega\lambda)} \beta' \end{aligned} \right) \dot{\gamma}_0 \exp(3i\omega t) \end{aligned} \right\} \quad (86)$$

where:

$$\beta' \equiv \sum_{l=-n}^{+n} l\psi_l(\lambda_0) = \frac{1}{2(1-\lambda_0)}; n = \frac{1}{2} \quad (87)$$

$$\beta'' \equiv \sum_{l=-n}^{+n} l\psi_l(2\lambda_0) = \frac{1}{2(1-2\lambda_0)}; n = \frac{1}{2} \quad (88)$$

Expanding this into real and imaginary parts, we find:

$$\frac{(\tau - \tau^0)_{xy}}{n\zeta b^2 \dot{\gamma}_0} = \text{Re} \left\{ \begin{aligned} & \frac{1}{30} \left(2\beta'' + \frac{3}{(1+i\text{De})} \beta' \right) (\cos \omega t + i \sin \omega t) \\ & + \frac{3\text{Wi}^2}{350(1+\text{De}^2)} \left(\begin{aligned} & \frac{10-3\text{De}^2 + 19i\text{De}}{(1+2i\text{De})(5+3i\text{De})} \beta'' \\ & - \frac{95-51\text{De}^2 + 158i\text{De}}{2(1+i\text{De})(1+2i\text{De})(5+3i\text{De})} \beta' \end{aligned} \right) (\cos \omega t + i \sin \omega t) \\ & + \frac{\text{Wi}^2}{70(1+\text{De}^2)} \left(\begin{aligned} & \frac{2+3\text{De}^2 + i\text{De}}{(1+2i\text{De})(5+3i\text{De})} \beta'' \\ & - \frac{19+15\text{De}^2 - 4i\text{De}}{2(1+2i\text{De})(1+3i\text{De})(5+3i\text{De})} \beta' \end{aligned} \right) (\cos 3\omega t + i \sin 3\omega t) \end{aligned} \right\} \quad (89)$$

Solving for the real part of Eq. (89), we get:

$$\begin{aligned}
\frac{(\tau - \tau^0)_{xy}}{n\xi b^2 \dot{\gamma}_0} = & \frac{1}{30} \left(\frac{(2\beta'' + 3\beta' + 2\beta''De^2)\cos\omega t + 3\beta'D\sin\omega t}{(1 + De^2)} \right) \\
& + \frac{3Wi^2}{350(1 + De^2)} \left(\frac{\left(\frac{5(7\beta'' - 92\beta') + (110\beta'' - 757\beta')De^2 + 3(25\beta'' - 51\beta')De^4}{(1 + De^2)(1 + 4De^2)(25 + 9De^2)} \right) D\sin\omega t}{+ \frac{(25(4\beta'' - 19\beta') + 4(111\beta'' - 196\beta')De^2 + (380\beta'' - 21\beta')De^4 + 36\beta''De^6)}{2(1 + De^2)(1 + 4De^2)(25 + 9De^2)} \cos\omega t} \right) \\
& + \frac{Wi^2}{70(1 + De^2)} \left(\frac{3 \frac{45(3\beta'' + \beta')De^4 + (78\beta'' + 17\beta')De^2 + (7\beta'' - 92\beta')}{(1 + 4De^2)(1 + 9De^2)(25 + 9De^2)} D\sin 3\omega t}{- \frac{324\beta''De^6 - 9(28\beta'' + 67\beta')De^4 - 4(53\beta'' + 223\beta')De^2 - 5(4\beta'' - 19\beta')}{2(1 + 4De^2)(1 + 9De^2)(25 + 9De^2)} \cos 3\omega t} \right)
\end{aligned} \tag{90}$$

which is the solution for the shear stress response including hydrodynamic interaction.

VI. ACKNOWLEDGMENT

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Table I: Literature on Analytical Solutions for Molecular Models in LAOS

	Eq.	Model	First	Third	Fifth	Zeroth	Second	Fourth	Orientation	Notation Eq. of [24]	[Ref.] (Correction to)
			Shear Stress Harmonic			Normal Stress Difference Harmonic					
Kirkwood and Plock (1956, 1967); Plock (1957)		RD,SK	n						ψ	(157)	[25,26, 27]
Lodge (1961, 1964)		$L^\square$	ℓ	0	0	N_1	N_1	0			[28,29]
Paul (1969); Paul (1970); Bharadwaj (2012); Bharadwaj (2015)	(13)	RD,SK	n	X					ψ	(157)	[30,31,32, 13](25,27)
Paul and Mazo (1969), Paul (1970)	(14)	RR	n	X					ψ	(157)	[33,31]
Bird, Warner and Evans (1971)		RD	n			N_1 N_2	N_1 N_2		ψ	(157)	[34]
Bird <i>et al.</i> (1977)		BHS	ℓ	0	0				ψ		Table 11.4-2 [35]
Mou and Mazo (1977)		RR				N_1 N_2	N_1 N_2		ψ	(183)	[36](33)
Pearson and Rochefort (1982); Helfand and Pearson (1982)	(9)	$R^\square$	n	X						(147)	[37,38]
Fan and Bird (1984)	(8)	$CB^\square$	n	X						(157)	[39](37)
Hoyle (2010)		PP	n	X						(147)	[40]
Wagner <i>et al.</i> (2011)		R	n	X						(147)	[41]
Gurnon and Wagner (2012)		G	ℓ	X		N_1 N_2	N_1 N_2			(147)	[42]
Abbasi <i>et al.</i> (2013)		MSF	ℓ	X						(147)	[43]
Bird <i>et al.</i> (2014),		RD	n	X					ψ	(157)	[44]

Schmalzer et al. (2014)		RD				N_1 N_2	N_1 N_2		ψ		[45,46,47,48]
Bozorgi (2014); Bozorgi and Underhill (2014)		AS	n	X					ψ	(147)	[49,50]
Giacomin et al. (2014, 2015)		RD							ψ		[51,52]

Legend: AS = active rod suspension; BHS = Bead-Hookean spring; CB = Curtiss-Bird; G = Giesekus; L = Lodge rubberlike liquid; MSF = molecular stress function; PP = pompom; RD = rigid dumbbell; R = reptation; RR = planar rigid ring; SK = shish-kebab; N_1, N_2 = first and second normal stress differences; $n \equiv \eta^*(\omega, \gamma_0)$; $\ell \equiv \eta^*(\omega)$; $\square$ = multiple relaxation times.

Table II: Dimensional Variables

Angular frequency	t^{-1}	ω
Bead friction coefficient	M/t	ξ
Boltzmann constant	ML^2/t^2T	k
Coefficients of τ'_n, τ''_n expansions [14] [Eq. (16)]	Mt^{p-2}/L	η'_{np}, η''_{np}
Coefficients of stress expansion [14] [Eq. (16)]	M/Lt^2	τ'_n, τ''_n
Complex modulus non-dimensionalization constant	M/Lt^2	G_0
Complex viscosity	M/Lt	η^*
yx – component of extra stress tensor	M/Lt^2	τ_{yx}
yx – component of extra stress tensor reference value	M/Lt^2	τ_{yx}^0
yx – component of extra stress tensor, solvent	M/Lt^2	$\tau_{yx,s}$
Dynamic loss modulus expansion coefficients	M/Lt^2	G''_{pq}
Dynamic modulus expansion coefficients	M/Lt^2	G^*_{pq}
Dynamic storage modulus expansion coefficients	M/Lt^2	G'_{pq}
Length between beads/polygon side length	L	b
Molar concentration of dumbbells/chains	$dumbbells/L^3$	n
Number density of Paul plane-polygons [33]	$polygons/L^3$	c'
Number density of Pearson and Rochefort chain units [37]	$chain\ units/L^3$	ρ
Relaxation time of fluid	t	λ
Shear rate	t^{-1}	$\dot{\gamma}$
Shear rate amplitude	t^{-1}	$\dot{\gamma}_0$

Shear viscosity	M/Lt	η
Temperature	T	T
Time	t	t
Zero shear rate viscosity	M/Lt	η_0

Legend: M = mass; L = length; t = time; T = temperature

Table III: Dimensionless Variables and Groups

Angle of departure from Newtonian behavior	$\phi = \arctan \frac{Wi}{De}$
Arbitrary variables	x, y, z
Deborah number	$De = \lambda \omega$
Function for Paul rigid dumbbells [Eq. (87)]	$\beta' = \frac{1}{2(1 - \lambda_0)}$
Function for Paul rigid dumbbells [Eq. (88)]	$\beta'' = \frac{1}{2(1 - 2\lambda_0)}$
Function to determine Curtiss-Bird viscosity coefficients [Eq. (31)]	$f_1(x) = \frac{\phi_- \left(\sqrt{\frac{1}{2}} x \right)}{8x \sqrt{\frac{1}{2}} x}$
Function to determine Curtiss-Bird viscosity coefficients [Eq. (32)]	$s_1(x) = \frac{1}{8x} \left[1 - \frac{\phi_+ \left(\sqrt{\frac{1}{2}} x \right)}{\sqrt{\frac{1}{2}} x} \right]$
Function to determine Curtiss-Bird viscosity coefficients [Eq. (33)]	$\phi_-(y) = \frac{\sinh y - \sin y}{\cosh y + \cos y}$
Function to determine Curtiss-Bird viscosity coefficients [Eq. (34)]	$\phi_+(y) = \frac{\sinh y + \sin y}{\cosh y + \cos y}$
Function used by Pearson and Rochefort [Eq. (10)]	$f(x, y) = \frac{1}{x} \frac{\sinh x + \sin y}{\cosh x + \cos y}$
Generalized non-Newtonianness	$Gn = De + i Wi$
Helfand and Pearson functions [Eqs. (57) - (59)]	$h_n(z)$
Kirkwood and Plock hydrodynamic interaction parameter (Eq. 4 of [25])	$\lambda_0 = \frac{\xi}{8\pi\eta_0 b}$
Link tension coefficient	ϵ

Number of beads on Kramers chain [14]	N
Number of beads on rigid multi-bead rod [25]	$2n+1$
Number of chain units between slip links [37]	N_e
Paul and Mazo Function [Eq. (65)]	S_k
Paul and Mazo Functions [Eqs. (62) - (64)]	ξ_A, ξ_B, ξ_C
Paul and Mazo Variable [Eq. (66)]	α_k
Real part of complex number, W_i	$\text{Re}(W_i)$
Squared Deborah number	$L \equiv \text{De}^2$
Variable used by Pearson and Rochefort [Eq. (9)]	$\alpha \equiv \pi \sqrt{\frac{1}{2} \lambda \omega}$
Weissenberg number	$Wi \equiv \lambda \dot{\gamma}_0$

Table IV: Molecular models compared in this paper

Models	Eq.	Configuration	Hydrodynamic Interaction	Figures
Slip-Link Reptation	(9)	Figure 2b	x	Figure 15-Figure 17
Curtiss-Bird Chains	(8)	Figure 2a	$\epsilon = 0$	Figure 3-Figure 5
			$\epsilon = 1/8$	Figure 6-Figure 8
			$\epsilon = 3/8$	Figure 9-Figure 11
			$\epsilon = 1$	Figure 12-Figure 14
Kirkwood-Plock Rigid Dumbbells	(11)	Figure 2c	$\lambda_0 = 0.25$	Figure 24-Figure 26
	(13)		$\lambda_0 \ll 1$	Figure 21-Figure 23
Rigid Dumbbells	(82) of [44]	Figure 2c		Figure 18-Figure 20
Rigid Plane-Polygons	(14)	Figure 2d		Figure 27-Figure 29

Figure 1: Diagram for LAOS illustrating the complex, dimensionless generalized non-Newtonianness, Gn . Newtonian behavior is observed well inside the unit circle, where $|Gn| \ll 1$. The magnitude of Gn thus reflects how far the system departs from Newtonian behavior and the inclination ϕ identifies the type of departure.

Figure 2: Kramers freely-jointed chain (a), chain through slip-links (b), rigid dumbbell (c), and planar polygon (d).

Figure 3: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = 0$ corresponding to reptation.

Figure 4: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = 0$ corresponding to reptation.

Figure 5: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = 0$ corresponding to reptation.

Figure 6: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = \frac{1}{8}$.

Figure 7: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = \frac{1}{8}$.

Figure 8: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = \frac{1}{8}$.

Figure 9: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = \frac{3}{8}$.

Figure 10: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = \frac{3}{8}$.

Figure 11: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = \frac{3}{8}$.

Figure 12: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 0.1, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.

Figure 13: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 1.0, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.

Figure 14: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the Kramers freely-jointed chain (Curtiss-Bird) model [Eq. (8)] by increasing the Weissenberg number with a fixed Deborah number of 10, and for $\epsilon = 1$ corresponding to the dilute solution without hydrodynamic interaction.

Figure 15: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.

Figure 16: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 1.

Figure 17: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for Pearson and Rochefort reptation theory [Eq. (9)] by increasing the Weissenberg number with a fixed Deborah number of 10.

Figure 18: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 0.1.

Figure 19: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 1.0.

Figure 20: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for the rigid dumbbell model (see Eq. (82) of [44]) by increasing the Weissenberg number with a fixed Deborah number of 10.

Figure 21: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.

Figure 22: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 1.0.

Figure 23: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell without hydrodynamic interactions according to the Paul correction for Kirkwood and Plock solution [Eq. (13)] by increasing the Weissenberg number with a fixed Deborah number of 10.

Figure 24: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell according to the Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 0.1.

Figure 25: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell according to the Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 1.

Figure 26: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a rigid dumbbell according to the Paul correction for Kirkwood and Plock solution [Eq. (11)] with hydrodynamic interaction ($\lambda_0 = 0.25$) by increasing the Weissenberg number with a fixed Deborah number of 10.

Figure 27: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 0.1.

Figure 28: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 1.

Figure 29: Counterclockwise loops of dimensionless shear stress *versus* dimensionless shear rate calculated for a plane-polygon polymer according to Kirkwood-Riseman Theory [Eq. (14)] by increasing the Weissenberg number with a fixed Deborah number of 10.

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(119), " $(\zeta\alpha)$ " should be " $\zeta(\alpha)$ "; In Eq. (147), " $n-1$ " should be " $n=1$ "; In Eqs. (76) and (77), Ψ' and Ψ'' should be Ψ_1' and Ψ_1'' ; Throughout, Ψ_1^d , Ψ_1' and Ψ_1'' should be Ψ_1^d , Ψ_1' and Ψ_1'' ; In Eqs. (181) and (182), "1,21" should be "1,2".

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- ³⁷ Pearson, D.S. and W.E. Rochefort, "Behavior of concentrated polystyrene solutions in large-amplitude oscillating shear fields," *J. Polym. Sci.: Pol. Phys. Ed.*, **20**, 83 (1982); Errata: on p. 95, $e^{i\omega s}$ should be $e^{-i\omega s}$ in Eq. (A2); after Eq. (A10), α should be $\sqrt{\omega\tau_d/2}$; and in Eq. (A11), $\cos x$ should be $\cosh x$; in Eq. (A7), $\sqrt{2}\alpha$ should be $\sqrt{2}\alpha$.
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