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NORMAL STRESS DIFFERENCES IN LARGE-AMPLITUDE OSCILLATORY SHEAR FLOW FOR DILUTE RIGID DUMBBELL SUSPENSIONS

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ABSTRACT

We examine the simplest relevant molecular model for large-amplitude oscillatory shear (LAOS) flow of a polymeric liquid: the suspension of rigid dumbbells in a Newtonian solvent. We find explicit analytical expressions for the shear rate amplitude and frequency dependences of the zeroth, second and fourth harmonics of the first and second normal stress difference responses. We include a detailed comparison of these predictions with the corresponding results for the simplest relevant continuum model: the corotational Maxwell model. We find that the responses of both models are qualitatively alike. The rigid dumbbell model relies entirely on the dumbbell orientation to explain the viscoelastic response of the polymeric liquid, including the higher harmonics in large-amplitude oscillatory shear flow. Our analysis employs the general method of Bird and Armstrong (1972) for analyzing the behavior of the rigid dumbbell model in any unsteady shear flow.

We derive the first three terms of the deviation of the orientational distribution function from the equilibrium state. Then, after getting the "paren functions," we use these for evaluating the normal stress differences for large amplitude oscillatory shear flow. We find the shapes of the first normal stress difference versus shear rate loops predicted to be reasonable [see Figure 1 (a)]. We find that the second normal stress difference is not proportional to the first, and that its shape differs markedly from that of the first [cf. Figures 1(a) and (b)]. we discover the same remarkable qualitative similarity between the predictions of the rigid dumbbell model and the corotational Maxwell model for the first normal stress difference. We find no qualitative similarities between the dumbbell and the continuum models for any of the predictions coefficients of the second normal stress differences in large-amplitude oscillatory shear flow.

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I. INTRODUCTION

Since its conception in the 1930s [1,2,3], and then the perfection of the measurement [4], oscillatory shear flow testing became, by far, the most common viscoelastic property measurement [5,6,7]. Only later, in his iconic Figure 14 of [8] did Weissenberg conceive, and then devise an experiment to measure, the normal stress differences in oscillatory shear flow ([9]; see also Section 2 of [10]). Since, a great deal of attention has been paid specifically to oscillatory shear testing performed at large shear rate amplitudes [11]. Here the preoccupations have been with the challenges in measuring [12,13,14] and with the difficulties in interpreting [15,16,17] the periodic shear stress response: a Fourier series of odd-valued harmonics. Much less attention has been paid to either the measurement ([18,19,20,21,²²]; see Section 1.23 of [23] and Section 10.1.4 of [24]) or the interpretations [see analysis in Section 6.2.3 of 25; 26] of the normal differences in large-amplitude oscillatory shear (LAOS) flow. See Table 1 of [26] for a summary of the literature on measurements of first, second, or third normal stress differences in LAOS flow (the third normal stress difference is the sum of the first and second (see Fig. 4.7 of [7];[27,28,29,30])). Table I summarizes the literature on analytical solutions for molecular models for the normal stress differences arising in large-amplitude oscillatory shear flow, which each arise as Fourier series of even-valued harmonics (see Section II.P. of [31]). For a review of the various notations from which to choose for reporting normal stress differences in LAOS flow, see Section 10 of [32]. Below, we derive new structure-property relations for these normal stress differences, and specifically, for the simplest relevant molecular model.

When a dilute suspension of rigid dumbbells is subjected to a shearing motion with large amplitude, the resulting shear stress and normal stress differences can be calculated. The rigid dumbbell suspension is chosen as a subject for study, inasmuch as it seems to mimic the behavior of polymer solutions and melts, at least qualitatively. This seems to be because the overall orientation of the polymer chains gives the longest time constant for the polymeric liquids. The dilute rigid dumbbell suspension is the simplest relevant structural model, in that it gives the appropriate higher harmonics in the shear stress and normal stress differences [33].

This paper concerns itself with the first and second normal stress differences, $\tau_{xx} - \tau_{yy}$ and $\tau_{yy} - \tau_{zz}$, when the flow is given by a velocity field $v_x(y, t)$. We further restrict this paper to the periodic response, reached several cycles after startup of oscillatory shear, called alternance [32]. This work is an extension of the recent article [33] wherein the expression for the shear stress response is derived using the method of Bird and Armstrong [34] (see also Problem 11C.1 of [35]).

a. The flow field

We are concerned here with a particular case of a homogeneous shearing flow (see Figure 1):

$$v_x = \dot{\gamma}^0 f(t) y, v_y = v_z = 0 \quad (1)$$

called simple shear flow. The symbols used here and elsewhere are defined, along with their dimensions, in Table II and Table III. The coefficient of proportionality between the velocity and position is $\dot{\gamma}^0 f(t)$, where the special variable f depends solely on the time. This situation can be obtained by having the flow take place between two plates placed extremely close to one another [36,37].

We consider only the case where $f(t) = \cos \omega t$ so that Eq. (1) becomes [38,39]:

$$v_x = \dot{\gamma}^0 \cos \omega t y; v_y = v_z = 0 \quad (2)$$

which we call oscillatory shear flow. That is, the shear rate may be written as:

$$\dot{\gamma}(t) = (\lambda \dot{\gamma}^0) \cos(\lambda \omega)(t/\lambda) \quad (3)$$

in which the dimensionless shear rate $\lambda \dot{\gamma}^0$ (the Weissenberg number) and the dimensionless frequency $\lambda \omega$ (the Deborah number), appear [32,40]. All normal stress difference responses calculated herein are thus referred to this cosinusoidal shear rate (see Section V of [41]). These dimensionless groups contain the characteristic time constant λ which, for the dilute suspension of rigid dumbbells in a Newtonian solvent of Newtonian viscosity η_s is:

$$\lambda \equiv \frac{\xi L^2}{12kT} = \frac{(3\pi\eta_s b)L^2}{12kT} \quad (4)$$

and for rigid multibead-rods:

$$\lambda_N = \frac{\xi L^2 N(N+1)}{72(N-1)kT} \quad (5)$$

where N is the number of equally-spaced beads on the rod of length L , T is absolute temperature, and k is Boltzmann's constant, ξ is the bead friction factor, given by Stokes' law, and b is the diameter of each of the beads of the dumbbell (see Figure 2).

In this paper, we consider the special case of Eq. (3) where higher harmonics arise in both the shear stress and in the normal stress differences. These arise when the ratio of the Weissenberg number to the Deborah number approaches or exceeds 1, and we call this large-amplitude oscillatory shear flow.

b. Previous results for the normal stress differences for rigid dumbbell suspensions

For the steady-state shear flow at *small shear rates*, a power series expression has been obtained for the first normal stress coefficient [53,42]:

$$\Psi_1(\dot{\gamma}) \equiv -\frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2} = \frac{6}{5}nkT\lambda^2 \left[1 - \frac{38}{35}(\lambda\dot{\gamma})^2 + \frac{38725}{25025}(\lambda\dot{\gamma})^4 - \dots \right] \quad (6)$$

At *large shear rates*, it was found by a collocation technique [43] that:

$$\Psi_1(\dot{\gamma}) = 1.20nkT\lambda^2 (\lambda\dot{\gamma})^{-4/3} \quad (7)$$

and analytically [44] that:

$$\Psi_1(\dot{\gamma}) = \left[\sqrt{\pi}/2^{2/3} \Gamma\left(\frac{z}{6}\right) \right] nkT \lambda^2 (\lambda \dot{\gamma})^{-4/3} \quad (8)$$

The rigid dumbbell suspension model gives exactly zero for the second normal stress coefficient $\Psi_2 \equiv -(\tau_{yy} - \tau_{zz})/\dot{\gamma}^2$ in steady-state shear flow, which agrees with the Weissenberg hypothesis, but disagrees with the current consensus of experimentalists (see Table 6.1 and Section 6.4. of [45]). However, it is anticipated that the second normal stress coefficient for unsteady shear flows will be predicted to be nonzero.

c. The expressions for the normal stress differences

The first and second normal stress differences, in terms of the paren functions, may be obtained from Eqs. (12) and (13) of [34], which are expressions for $(\tau_{xx} - \tau_{yy})$ and $(\tau_{xx} - \tau_{zz})$:

$$\frac{\tau_{xx} - \tau_{yy}}{nkT(\lambda \dot{\gamma}^0)^2} = \left[-\frac{6}{5}(0,1;t) + \left(\lambda \dot{\gamma}^0 \right)^2 \left(+\frac{276}{245}(0,0,0,1;t) + \frac{144}{245}(0,-\frac{z}{3},\frac{z}{3},1;t) + \frac{4}{7}\left(-\frac{z}{3},\frac{z}{3},0,1;t\right) - \left(\frac{z}{3},0,1;t\right) \cos \omega t \right) + \frac{8}{7}\left(-\frac{z}{3},0,\frac{z}{3},1;t\right) - \left(0,\frac{z}{3},1;t\right) \cos \omega t \right) \right] \quad (9)$$

$$\frac{\tau_{yy} - \tau_{zz}}{nkT(\lambda \dot{\gamma}^0)^2} = \frac{6}{1715} \left\{ \begin{aligned} & -98[-(0,1;t) + (1;t) \cos \omega t] \\ & + \left[\begin{aligned} & 92[-(0,0,0,1;t) + (0,0,1;t) \cos \omega t] \\ & + 48[-(0,-\frac{z}{3},\frac{z}{3},1;t) + (-\frac{z}{3},\frac{z}{3},1;t) \cos \omega t] \\ & + \frac{200}{3}[-(-\frac{z}{3},\frac{z}{3},0,1;t) + (\frac{z}{3},0,1;t) \cos \omega t] \\ & + \frac{4940}{33}[-(-\frac{z}{3},0,\frac{z}{3},1;t) + (0,\frac{z}{3},1;t) \cos \omega t] \end{aligned} \right] \end{aligned} \right\} (\lambda \dot{\gamma}^0)^2 \quad (10)$$

In these expressions, the “paren functions” of orders 1, 2, 3, and 4 of Bird and Armstrong [34] appear. For instance, the paren function of order 3 is:

$$(a,b,c;t) \equiv \frac{1}{\lambda^3} \int_{-\infty}^t \int_{-\infty}^{t'} \int_{-\infty}^{t''} e^{-a(t-t')/\lambda} e^{-b(t-t'')/\lambda} e^{-c(t-t''')/\lambda} f(t') f(t'') f(t''') dt''' dt'' dt' \quad (11)$$

The details of the integrations for the paren functions for LAOS are given in Section VIII of [33].

The first-order paren function multiplied by $\cos \omega t$ [Eq. (39)] and the second-order paren function [Eq. (40)] are given in Appendix A below. The four third-order paren functions multiplied by $\cos \omega t$ are given in Appendix B of this paper [Eqs. (44) through (47)]; the four fourth-order paren functions are summarized in Appendix C [Eqs. (51) through (52)]. When these paren functions are substituted into Eqs. (9) and (10) we get the desired expressions for the normal stress differences.

II. RESULTS

In the following subsections, we will develop the expressions for the first (Section II a.) and second (Section II b.) normal stress differences for the rigid dumbbell suspension.

a. First normal stress difference

When the expressions for the paren functions in Appendices A [Eq. (40)], B [Eqs. (46) and (47)], and C [Eqs. (51), (52), (53) and (54)] are substituted into Eq. (9) we get:

$$\frac{\tau_{xx} - \tau_{yy}}{n\dot{\gamma}^0} = \left[\begin{aligned} & -\frac{\frac{5}{9} \left[\frac{[1-2L] \cos 2\omega t + 3\lambda\omega \sin 2\omega t}{2(1+4L)(1+L)} + \frac{1}{2(1+L)} \right]}{+ \left(\lambda \dot{\gamma}^0 \right)^2} \\ & + \frac{\frac{276}{245} \left[\frac{(1-35L+24L^2)\cos 4\omega t}{8(1+16L)(1+9L)(1+4L)(1+L)} + \frac{(4-13L-32L^2-159L^3)\cos 2\omega t}{8(1+4L)(1+9L)(1+L)^3} + \frac{3}{8(1+4L)(1+L)} \right]}{+ \frac{\frac{144}{245} \left[\frac{(30-714L+216L^2)\cos 4\omega t}{8(1+16L)(1+9L)(100+36L)(1+L)} + \frac{3 \left[\begin{aligned} & \left(\frac{400+972L-9156L^2}{-23660L^3-4716L^4} \right) \cos 2\omega t \\ & + \left(\frac{1720+11576L+15472L^2}{-5544L^3-1944L^4} \right) \lambda\omega \sin 2\omega t \end{aligned} \right]}{(1+4L)(1+9L)(100+36L)(1+L)^3} + \frac{3(75-37L)}{20(1+L)(100+36L)(1+L)} \right]}{+ \frac{\frac{4}{7} \left[\frac{(30-609L+216L^2)\cos 4\omega t}{8(1+16L)(100+81L)(1+4L)(1+L)} + \frac{\left(\frac{12000-17040L-30786L^2}{-114093L^3-92340L^4} \right) \cos 2\omega t}{8(1+4L)^2(100+81L)(100+9L)(1+L)^2} + \frac{(90+153L)}{8(100+9L)(1+4L)(1+L)} \right]}{+ \frac{\frac{2}{7} \left[\frac{\left(\frac{[10-47L]\cos 4\omega t}{4(100+81L)(1+4L)(1+L)} + \frac{\left(\frac{[2000+1460L+1854L^2]\cos 2\omega t}{2(100+81L)(100+9L)(1+4L)(1+L)} + \frac{9}{4} \frac{10+17L}{(100+9L)(1+4L)(1+L)} \right)}{+ \frac{\frac{5}{7} \left[\frac{(900-10836L+1944L^2)\cos 4\omega t}{8(1+16L)(100+81L)(100+36L)(1+L)} + \frac{\frac{9}{20} \left[\begin{aligned} & \left(\frac{100000-72000L-475930L^2}{-330813L^3-62451L^4} \right) \cos 2\omega t \\ & + \left(\frac{325000+622150L+269979L^2}{-4725L^3-13122L^4} \right) \lambda\omega \sin 2\omega t \end{aligned} \right]}{(1+4L)(100+81L)(100+36L)(1+L)^2(100+9L)} + \frac{27}{2} \frac{(25-3L)}{(100+9L)(100+36L)(1+L)} \right]}{+ \frac{\frac{1}{7} \left[\frac{\left(\frac{[100-204L]\cos 4\omega t}{4(100+81)(100+36L)(1+L)} + \frac{\frac{9}{20} \left[\begin{aligned} & \left(\frac{[50000+1500L-5940L^2]\cos 2\omega t}{(100+9L)(100+81L)(25+9L)(1+L)} + \frac{1}{4} \frac{[675-81L]}{(100+9L)(25+9L)(1+L)} \right)} \right]} \right] \end{aligned} \right] \quad (12)$$

Rewriting Eq. (12) as a Fourier series, and finally, putting the coefficients of the trigonometric functions over common denominators, we get:

$$\begin{aligned}
\frac{\tau_{xx} - \tau_{yy}}{nkT} = & (\lambda\dot{\gamma}^0)^2 \left\{ -\left[\frac{3}{5(1+L)} \right] - \left[\frac{3(1-2L)}{5(1+4L)(1+L)} \right] \cos 2\omega t - \left[\frac{9}{5(1+4L)(1+L)} \right] \lambda\omega \sin 2\omega t \right\} \\
& + (\lambda\dot{\gamma}^0)^4 \left\{ \left[\frac{9(21L^2 + 784L + 475)}{350(L+1)^2(4L+1)(9L+25)} \right] \right. \\
& + \left[\frac{3 \begin{pmatrix} -177,820,596L^7 - 1,884,818,889L^6 - 6,101,765,361L^5 \\ -7,119,625,867L^4 - 3,192,891,587L^3 - 688,728,900L^2 \\ +25,370,000L + 19,000,000 \end{pmatrix}}{350(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right] \cos 2\omega t \\
& + \left[\frac{3 \begin{pmatrix} -27,634,932L^7 - 264,300,165L^6 - 431,971,812L^5 \\ +940,723,347L^4 + 2,233,642,922L^3 + 1,364,819,940L^2 \\ +431,340,000L + 50,600,000 \end{pmatrix}}{175(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right] \lambda\omega \sin 2\omega t \\
& + \left[\frac{3(272,160L^4 + 113,121L^3 - 152,944L^2 - 72,261L + 1,900)}{14(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \right] \cos 4\omega t \\
& + \left[\frac{3(174,960L^4 - 712,611L^3 - 909,195L^2 - 171,664L + 50,600)}{35(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \right] \lambda\omega \sin 4\omega t \left. \right\} \quad (13)
\end{aligned}$$

Eq. (13) is the first main result of this work. Putting the coefficients over common denominators is straightforward, but tedious. We checked Eq. (13) by performing the calculations for the graphs in Figure 3 through Figure 5 both before [Eq. (12)] and after [Eq. (13)] putting the coefficients over common denominators. Specifically, we have shown that for various ordered pairs $(\lambda\omega, \lambda\dot{\gamma}^0)$, Eqs. (12) and Eq. (13) are equal to 16 significant figures. Furthermore, setting all frequencies in Eq. (13) equal to zero, which causes all the sine terms and all the L s to drop out:

$$\frac{276}{245} + \left(\frac{144}{245} \right) \left(\frac{3}{10} \right) + \frac{4}{7} \left(\frac{24}{80} \right) - \frac{4}{7} \left(\frac{24}{80} \right) + \frac{8}{7} \left(\frac{72}{800} \right) - \frac{8}{7} \left(\frac{72}{800} \right) = \frac{228}{175} \quad (14)$$

the well-known result of Eq. (6) above, as it should.

Following [46,47,48] and then specifically Fig. 5. through Fig. 7. of [32], we now plot Lissajous-Bowditch loops [17], of $-(\tau_{xx} - \tau_{yy})/nkT\lambda\dot{\gamma}^0$ versus $\lambda\dot{\gamma}$ in Figure 3 through Figure 5. From Eq. (13), we get equations for the first normal stress displacement coefficient:

$$\frac{\Psi_1^d}{nkT\lambda^2} = -\left[\frac{3}{5(1+L)} \right] + (\lambda\dot{\gamma}^0)^2 \left[\frac{9(21L^2 + 784L + 475)}{350(L+1)^2(4L+1)(9L+25)} \right] \quad (15)$$

and for the real part:

$$\frac{\Psi_1'}{nkT\lambda^2} = -\left[\frac{3(1-2L)}{5(1+4L)(1+L)} \right] + (\lambda\dot{\gamma}^0)^2 \left[\frac{3 \begin{pmatrix} -177,820,596L^7 - 1,884,818,889L^6 - 6,101,765,361L^5 \\ -7,119,625,867L^4 - 3,192,891,587L^3 - 688,728,900L^2 \\ +25,370,000L + 19,000,000 \end{pmatrix}}{350(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right] \quad (16)$$

and minus the imaginary part:

$$\frac{\Psi''_{\dot{\gamma}^0}}{nkT\lambda} = -(\lambda\dot{\gamma}^0) \left[\frac{9}{5(1+4L)(1+L)} \right] + (\lambda\dot{\gamma}^0)^3 + \left(\frac{-27,634,932L^7 - 264,300,165L^6 - 431,971,812L^5 + 940,723,347L^4 + 2,233,642,922L^3 + 1,364,819,940L^2 + 431,340,000L + 50,600,000}{175(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right) \lambda\omega \quad (17)$$

of the first normal stress coefficient (which are associated with the second harmonic and which are defined in Table II).

We must keep in mind that there is also a term in $(\lambda\dot{\gamma}^0)^4$ in Eq. (13) involving the fourth harmonic. For the rigid dumbbell model, the coefficient of $(\lambda\dot{\gamma}^0)^4$ in the expressions for $\cos 4\omega t$ in Eq. (13) is:

$$\left(\frac{3(272,160L^4 + 113,121L^3 - 152,944L^2 - 72,261L + 1,900)}{14(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \right) \quad (18)$$

and for $\sin 4\omega t$:

$$\left(\frac{3(174,960L^4 - 712,611L^3 - 909,195L^2 - 171,664L + 50,600)}{35(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \right) \lambda\omega \quad (19)$$

which we will compare with the continuum model below.

b. Second normal stress difference

When the expressions for the paren functions in Appendices A [Eqs. (39) and (40)], B [Eqs. (44), (45), (46) and (47)], and C [Eqs. (51), (52), (53) and (54)] are

substituted into Eq. (10) we get:

$$\frac{\tau_{yy} - \tau_{zz}}{nkT(\lambda\dot{\gamma}^0)^2} = \frac{6}{1715} \left[\begin{aligned} &98 \left[\frac{(1-2L)\cos 2\omega t + 3\lambda\omega \sin 2\omega t}{2(1+4L)(1+L)} + \frac{1}{2(1+L)} \right] \\ &-92 \left[\frac{\cos 2\omega t + \lambda\omega \sin 2\omega t}{2(1+L)} - \frac{1}{2(1+L)} \right] \\ &+92 \left[\frac{(1-35L+24L^2)\cos 4\omega t}{8(1+16L)(1+9L)(1+4L)(1+L)} + \frac{(4-13L-32L^2-159L^3)\cos 2\omega t}{8(1+4L)(1+9L)(1+L)^3} + \frac{3}{8(1+4L)(1+L)} \right] \\ &+92 \left[\frac{[1-11L]\cos 4\omega t}{8(1+9L)(1+4L)(1+L)} + \frac{[1]\cos 2\omega t}{2(1+9L)(1+L)} + \frac{3}{8(1+4L)(1+L)} \right] \\ &-48 \left[\frac{(30-714L+216L^2)\cos 4\omega t}{8(1+16L)(1+9L)(100+36L)(1+L)} + \frac{3}{80} \left[\frac{(400+972L-9156L^2)\cos 2\omega t}{(1+4L)(1+9L)(100+36L)(1+L)^3} + \frac{(1720+11576L+15472L^2)\lambda\omega \sin 2\omega t}{(-5544L^3-1944L^4)} \right] + \frac{3(75-37L)}{20(1+L)(100+36L)(1+L)} \right] \\ &+48 \left[\frac{3}{16} \frac{[5-27L]\cos 4\omega t}{(1+9L)(25+9L)(1+L)} + \frac{3}{40} \frac{[2-117L^2+132L+25]\cos 2\omega t}{(1+L)^2(1+9L)(25+9L)} + \frac{3}{80} \frac{75-37L}{(1+L)^2(25+9L)} \right] \\ &- \frac{200}{3} \left[\frac{(30-609L+216L^2)\cos 4\omega t}{8(1+16L)(100+81L)(1+4L)(1+L)} + \frac{(12000-17040L-30786L^2)\cos 2\omega t}{8(1+4L)^2(100+81L)(100+9L)(1+L)^2} + \frac{(47400+105150L+191643L^2)\lambda\omega \sin 2\omega t}{(-114093L^3-92340L^4)} + \frac{(90+153L)}{8(100+9L)(1+4L)(1+L)} \right] \\ &+ \frac{200}{3} \left[\frac{3}{8} \frac{[10-47L]\cos 4\omega t}{(100+81L)(1+4L)(1+L)} + \frac{3}{4} \frac{[3900+1755L+648L^2]\cos 2\omega t}{(100+81L)(100+9L)(1+4L)(1+L)} + \frac{9}{8} \frac{10+17L}{(100+9L)(1+4L)(1+L)} \right] \\ &- \frac{4940}{33} \left[\frac{(900-10836L+1944L^2)\cos 4\omega t}{8(1+16L)(100+81L)(100+36L)(1+L)} + \frac{9}{20} \left[\frac{(100000-72000L-475930L^2)\cos 2\omega t}{(1+4L)(100+81L)(100+36L)(1+L)^2(100+9L)} + \frac{(325000+622150L+269979L^2)\lambda\omega \sin 2\omega t}{(-4725L^3-13122L^4)} \right] + \frac{27}{2} \frac{(25-3L)}{(100+9L)(100+36L)(1+L)} \right] \\ &+ \frac{4940}{33} \left[\frac{9}{16} \frac{[50-102L]\cos 4\omega t}{(100+81L)(25+9L)(1+L)} + \frac{9}{40} \frac{[50000+1500L-5940L^2]\cos 2\omega t}{(100+9L)(100+81L)(25+9L)(1+L)} + \frac{27}{8} \frac{(25-3L)}{(100+9L)(25+9L)(1+L)} \right] \end{aligned} \right] (\lambda\dot{\gamma}^0)^2 \quad (20)$$

and then rewriting the result as a Fourier series, and finally, putting the coefficients of the trigonometric functions over common denominators, we get:

$$\frac{(\tau_{yy} - \tau_{zz})\lambda}{nkT} = (\lambda\dot{\gamma}^0)^2 \left[-\frac{36L}{35(L+1)(4L+1)} \cos 2\omega t + \frac{12(1-2L)}{35(L+1)(4L+1)} \lambda\omega \sin 2\omega t \right] \\ + \frac{3}{3850} (\lambda\dot{\gamma}^0)^4 \left[\begin{aligned} &L \left[\frac{(676,141,668L^6 + 6,726,036,285L^5 + 22,879,515,861L^4 + 30,153,680,741L^3 + 17,670,955,395L^2 + 5,725,307,250L + 664,775,000)}{(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \cos 2\omega t + \right. \\ &\left. \frac{(278,553,816L^7 + 3,170,611,026L^6 + 10,488,789,819L^5 + 10,645,327,725L^4 + 2,763,261,389L^3 - 250,144,875L^2 - 835,447,500L - 157,000,000)}{(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \lambda\omega \sin 2\omega t \right] \\ &- \left[\frac{20L(2,241,432L^3 + 2258595L^2 + 330,218L - 361,825)}{(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \cos 4\omega t + 200 \left[\frac{69,984L^4 - 123,363L^3 - 230,571L^2 - 100,787L + 3,925}{(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \lambda\omega \sin 4\omega t \right] \right] \end{aligned} \right] \quad (21)$$

Eq. (21) is the second main result of this work. Putting the coefficients over common denominators is straightforward, but tedious. We checked Eq. (21) by performing the calculations for the graphs in Figure 6 through Figure 8 both before [Eq. (20)] and after [Eq. (21)] putting the coefficients over common denominators. Specifically, we have shown that for various ordered pairs $(\lambda\omega, \lambda\dot{\gamma}^0)$, Eqs. (20) and (21) are equal to 16 significant figures. Further, at steady

state, we set the frequency in Eq. (21) equal to zero and make use of the paren functions in the appendices to get:

$$-98[-1+1]+92[-1+1]+48\left(-\frac{12}{80}+\frac{12}{80}\right)+\frac{200}{3}\left(-\frac{24}{80}+\frac{24}{80}\right)+\frac{4940}{33}\left(-\frac{72}{800}+\frac{72}{800}\right)=0 \quad (22)$$

which is a well-known result for steady state, as it should. .

Following Fig. 5. through Fig. 7. of [32], we now plot Lissajous-Bowditch loops of $-(\tau_{yy} - \tau_{zz})/nkT\lambda\dot{\gamma}^0$ versus $\lambda\dot{\gamma}$ in Figure 3 through Figure 5. From Eq.(21), we get equations for the second normal stress displacement coefficient:

$$\frac{\Psi_2^{d\dot{\gamma}^0}}{nkT\lambda} = 0 \quad (23)$$

and for the real part:

$$\frac{\Psi_2^{\prime\dot{\gamma}^0}}{nkT\lambda} = -(\lambda\dot{\gamma}^0) \left[-\frac{36L}{35(L+1)(4L+1)} \right] + (\lambda\dot{\gamma}^0)^3 \frac{3}{3850} \left[\frac{L \left(676,141,668L^6 + 6,726,036,285L^5 + 22,879,515,861L^4 + 30,153,680,741L^3 + 17,670,955,395L^2 + 5,725,307,250L + 664,775,000 \right)}{(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right] \quad (24)$$

and minus the imaginary part:

$$\frac{\Psi_2^{\prime\prime\dot{\gamma}^0}}{nkT\lambda} = (\lambda\dot{\gamma}^0) \left[\frac{12(1-2L)}{35(L+1)(4L+1)} \right] + (\lambda\dot{\gamma}^0)^3 \frac{3}{3850} \left[\frac{\left(278,553,816L^7 + 3,170,611,026L^6 + 10,488,789,819L^5 + 10,645,327,725L^4 + 2,763,261,389L^3 - 250,144,875L^2 - 835,447,500L - 157,000,000 \right)}{(L+1)^3(4L+1)^2(9L+1)(9L+25)(9L+100)(81L+100)} \right] \lambda\omega \quad (25)$$

of the second normal stress coefficient (which are associated with the second harmonic and which are defined in Table II).

We must keep in mind that there is also a term in $(\lambda\dot{\gamma}^0)^4$ in Eq. (21) involving the fourth harmonic. For the rigid dumbbell model, the coefficient of $(\lambda\dot{\gamma}^0)^4$ in the expressions for $\cos 4\omega t$ in Eq. (21) is:

$$\frac{20L \left(2,241,432L^3 + 2,258,595L^2 + 330,218L - 361,825 \right)}{(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \quad (26)$$

and for $\sin 4\omega t$:

$$\frac{200 \left(69,984L^4 - 123,363L^3 - 230,571L^2 - 100,787L + 3,925 \right)}{(L+1)(4L+1)(9L+1)(9L+25)(16L+1)(81L+100)} \lambda\omega \quad (27)$$

which we will compare with the continuum model below.

III. COMPARISON WITH CONTINUUM MODEL

It is interesting to compare the above results with a two-constant (η_0 and λ) continuum model, namely the corotational Maxwell model. The latter is the simplest relevant continuum model, in that it predicts a shear-rate dependent viscosity and normal stress, as well as describing the higher harmonics in LAOS

flows. For the corresponding comparison for the shear stress response, see Section X of [33]. Of course, the corotational Maxwell model also has limitations, such as, for instance, its non-monotonicity of the shear stress versus shear rate in steady shear flow (see Eq. (25) of [32] or Eq. (15) of [26]). For the normal stress differences in steady shear flow, no such non-monotonicity is predicted.

Whereas both the corotational Maxwell model and the rigid dumbbell suspension model give roughly the same results in linear viscoelasticity for the shear stress (see Eqs. (84) through (87) of [33]), there are significant differences in the responses of the two models in large-amplitude oscillatory motion, for both the shear stress (Section X of [33]) and the normal stress differences. The comparison for the normal stress differences is summarized below for the first and second normal stress differences.

Furthermore, the corotational Maxwell model gives us no information about the structural changes within the fluid that can be associated with the rheological behavior, whereas the rigid dumbbell suspension model gives information about the alignment of the constituent.

For the corotational Maxwell model, from Eq. (66) of [32] we get, for the first and second normal stress differences:

$$\begin{aligned} \frac{(\tau_{xx} - \tau_{yy})\lambda}{\eta_0} &= -2 \frac{(\tau_{yy} - \tau_{zz})\lambda}{\eta_0} \\ &= -(\lambda\dot{\gamma}^0)^2 \left[\frac{1}{1+L} + \frac{(1-2L)\cos 2\omega t + 3\lambda\omega \sin 2\omega t}{(1+L)(1+4L)} \right] \\ &\quad + \frac{(\lambda\dot{\gamma}^0)^4}{4} \left[\frac{3}{(1+L)(1+4L)} + \frac{(4-24L)\cos 2\omega t + 20\lambda\omega \sin 2\omega t}{(1+L)(1+4L)(1+9L)} \right. \\ &\quad \left. + \frac{(1-35L+24L^2)\cos 4\omega t + (10L-50L^2)\lambda\omega \sin 4\omega t}{(1+L)(1+4L)(1+9L)(1+16L)} \right] \end{aligned} \quad (28)$$

which has the same number of terms as our Eqs. (13) and (21) above. If we identify $nkT\lambda$ on the left side of Eqs. (13) and (21) with η_0 , we can then compare with the corotational Maxwell solution, Eq. (28). From Eq. (28), we see that one further limitation of the corotational Maxwell model is that the second normal stress difference is exactly minus one half of the second, whereas the measured values are normally nearer minus one seventh [26].

To compare the rigid dumbbell suspension model to the corotational Maxwell model, graphically, we follow the form of the left sides of Eqs. (75), (76) and (77) of [32], we plot $\Psi_1^d(\lambda\omega)\dot{\gamma}^0/nkT\lambda$, $\Psi_1'(\lambda\omega)\dot{\gamma}^0/nkT\lambda$ and $\Psi_1''(\lambda\omega)\dot{\gamma}^0/nkT\lambda$ versus $\lambda\omega$ in Figure 9 through Figure 11 for the first normal stress difference coefficients, and we plot $\Psi_2^d(\lambda\omega)\dot{\gamma}^0/nkT\lambda$, $\Psi_2'(\lambda\omega)\dot{\gamma}^0/nkT\lambda$ and $\Psi_2''(\lambda\omega)\dot{\gamma}^0/nkT\lambda$ versus $\lambda\omega$ in Figure 12 through Figure 14 for the first normal stress difference coefficients.

a. First normal stress difference

From Eq. (28), for the coefficients of the corotational Maxwell model we get, for the displacement value:

$$\frac{\Psi_1^d}{\eta_0 \lambda} = -\left[\frac{1}{1+L} \right] + (\lambda \dot{\gamma}^0)^2 \left[\frac{3}{4(1+4L)(1+L)} \right] \quad (29)$$

and for the real:

$$\frac{\Psi_1'}{\eta_0 \lambda} = -\left[\frac{(1-2L)}{(1+L)(1+4L)} \right] + (\lambda \dot{\gamma}^0)^2 \left[\frac{(1-2L)}{4(1+L)(1+4L)(1+9L)} \right] \quad (30)$$

and imaginary:

$$\frac{\Psi_1''}{\eta_0 \lambda} = -\left[\frac{3\lambda\omega}{(1+L)(1+4L)} \right] + \frac{(\lambda \dot{\gamma}^0)^2}{4} \left[\frac{3\lambda\omega}{(1+L)(1+4L)(1+9L)} \right] \quad (31)$$

parts of the second normal stress coefficient (which is associated with the second harmonic). Figure 9

There is also a term in $(\dot{\gamma}^0)^4$ in Eq. (28) involving the fourth harmonic. For the rigid dumbbell model, the coefficient of $(\dot{\gamma}^0)^4$ in the expressions for $\cos 4\omega t$ is:

$$\frac{(1-35L+24L^2)}{4(1+L)(1+4L)(1+9L)(1+16L)} \quad (32)$$

and for $\sin 4\omega t$:

$$\frac{(10L-50L^2)}{4(1+L)(1+4L)(1+9L)(1+16L)} \quad (33)$$

Examining Figure 9 through Figure 11, we find that interesting intercepts arise in our comparison of the coefficients of the first normal stress difference.

For instance, in Figure 9, for both models, Ψ_1' crosses the abscissa at $\lambda\omega = 1/\sqrt{2}$. We find this same intercept reported for the Oldroyd 3-constant model (see after Eq. (7) of [49]; see also after Eq. (62) of [50]). Table IV summarizes where these sign changes arise for each normal stress coefficient (first three rows for the first normal stress difference, last three rows for the second normal stress difference), and for each model.

From Figure 9 we learn that the behaviors of $\Psi_1^d(\lambda\omega)$ [Eq. (15) versus Eq. (29)], $\Psi_1'(\lambda\omega)$ [Eq. (16) versus Eq. (30)] and $\Psi_1''(\lambda\omega)$ [Eq. (17) versus Eq. (31)] for the two models are strikingly similar. We find this to be remarkable, given the very different origins of the models: one molecular, the other continuum.

From Figure 10 we learn that the coefficients of $(\lambda \dot{\gamma}^0)^3$ in the expressions for $\Psi_1^d(\lambda\omega)$ [Eq. (15) versus Eq. (29)], $\Psi_1'(\lambda\omega)$ [Eq. (16) versus Eq. (30)] and $\Psi_1''(\lambda\omega)$ [Eq. (17) versus Eq. (31)] are also strikingly alike. Finally, from Figure 11 we learn that the coefficients of $(\lambda \dot{\gamma}^0)^4$ in Eq. (13) for $\cos 4\omega t$ [Eq. (18) versus Eq. (32)], and for $\sin 4\omega t$ [Eq. (19) versus Eq. (33)] are strikingly similar. In other

words, even the behaviors of the coefficients of the fourth harmonics of the first normal stress differences are qualitatively alike. The $\lambda\omega$ values for the seven interesting intercepts arising in our equations for the coefficients of the first normal stress difference are listed in the first three rows of Table IV, and for each model.

The Lissajous-Bowditch loops of Figure 15 through Figure 17 for the corotational Maxwell model, can be compared with Figure 3 through Figure 5 for the rigid dumbbell model. We see that for low values of $\lambda\omega$ the shapes match (Figure 15 versus Figure 3), but for higher values, the shapes differ. In view of the striking qualitative similarity of the two models, from this part of the comparison we learn that the shapes of the Lissajous-Bowditch loops can be particularly sensitive to the quantitative differences between models.

b. Second normal stress difference

From Eq. (28), for the coefficients of the corotational Maxwell model we get, for the displacement value:

$$\frac{\Psi_2^d \dot{\gamma}^0}{nkT\lambda} = (\lambda\dot{\gamma}^0) \left[\frac{1}{2(1+L)} \right] - (\lambda\dot{\gamma}^0)^3 \left[\frac{3}{8(1+4L)(1+L)} \right] \quad (34)$$

$$\frac{\Psi_2'^d \dot{\gamma}^0}{nkT\lambda} = (\lambda\dot{\gamma}^0) \left[\frac{(1-2L)}{2(1+L)(1+4L)} \right] - (\lambda\dot{\gamma}^0)^3 \left[\frac{(1-2L)}{8(1+L)(1+4L)(1+9L)} \right] \quad (35)$$

$$\frac{\Psi_2''^d \dot{\gamma}^0}{nkT\lambda} = (\lambda\dot{\gamma}^0) \left[\frac{3\lambda\omega}{2(1+L)(1+4L)} \right] - (\lambda\dot{\gamma}^0)^3 \left[\frac{3\lambda\omega}{8(1+L)(1+4L)(1+9L)} \right] \quad (36)$$

There is also a term in $(\dot{\gamma}^0)^4$ involving the fourth harmonic. For the rigid dumbbell model, the coefficient of $(\dot{\gamma}^0)^4$ in the expressions for $\cos 4\omega t$ is:

$$\frac{(1 - 35L + 24L^2)}{8(1+L)(1+4L)(1+9L)(1+16L)} \quad (37)$$

and for $\sin 4\omega t$:

$$\frac{(10L - 50L^2)}{8(1+L)(1+4L)(1+9L)(1+16L)} \quad (38)$$

Examining Figure 12 through Figure 14, we find that interesting intercepts arise in our comparison of the coefficients of the second normal stress difference.

For instance, in Figure 12, for just the corotational Maxwell model, Ψ_1' crosses the abscissa at $\lambda\omega = 1/\sqrt{2}$. Table IV summarizes where these sign changes arise for each normal stress coefficient (first three rows for the first normal stress difference, last three rows for the second normal stress difference), and for each model.

From Figure 12 we learn that the behaviors of $\Psi_2^d(\lambda\omega)$ [Eq. (23) versus Eq. (34)], $\Psi_2'^d(\lambda\omega)$ [Eq. (24) versus Eq. (35)] and $\Psi_2''^d(\lambda\omega)$ [Eq. (25) versus Eq. (36)].

for the two models are strikingly different. Whereas $\Psi_2^d(\lambda\omega) = 0$ for the rigid dumbbell model, $\Psi_2^d(\lambda\omega)$ descends monotonically and asymptotically to zero for the continuum model. For $\Psi_2'(\lambda\omega)$, we find nearly opposite behaviors, and for $\Psi_2''(\lambda\omega)$ we find the dumbbell model intercept at the origin, and the continuum model intercept at $\lambda\omega = 1/\sqrt{2}$. From Figure 13 we see that the coefficients of $(\lambda\dot{\gamma}^0)^3$ in expressions for $\Psi_2^d(\lambda\omega)$ [Eq. (23) versus Eq. (34)], $\Psi_2'(\lambda\omega)$ [Eq. (24) versus Eq. (35)] and $\Psi_2''(\lambda\omega)$ [Eq. (25) versus Eq. (36)] all differ, even

qualitatively. Similarly, from Figure 14, we find that the coefficients of $(\lambda\dot{\gamma}^0)^4$ in Eq. (21) for $\cos 4\omega t$ [Eq. (24) versus Eq. (37)], and for $\sin 4\omega t$ [Eq. (25) versus Eq. (38)] also all differ, even qualitatively. The $\lambda\omega$ values for the eight interesting intercepts arising in our equations for the coefficients of the second normal stress difference are listed in the last three rows of Table IV, and for each model.

The shapes of the Lissajous-Bowditch loops of Figure 15 through Figure 17 for the corotational Maxwell model, can be compared with Figure 6 through Figure 8 for the second normal stress difference of the rigid dumbbell suspension. We find that the shapes predicted for the second normal stress difference for the molecular model differ markedly from those of the continuum model.

IV. CONCLUSION

In our previous work on the shear stress response in large-amplitude oscillatory shear, we discovered a remarkable qualitative similarity between the predictions of the rigid dumbbell model and the corotational Maxwell model. The qualitative similarity is held for all coefficients of both the first and the third harmonics of the shear stress.

In this paper, we discover the same remarkable qualitative similarity between the predictions of the rigid dumbbell model and the corotational Maxwell model for the first normal stress difference. We find no qualitative similarities between the dumbbell and the continuum models for any of the predictions coefficients of the second normal stress differences in large-amplitude oscillatory shear flow. This suggests that the rarely-attempted experimental measurement of the second normal stress difference in large-amplitude oscillatory shear flow might be particularly interesting.

Eq. (13) is, to our knowledge, the first structure-property relation from a molecular model to include the fourth harmonic of the first normal stress difference in large-amplitude oscillatory shear flow. Eq. (21) is, to our knowledge, the first structure-property relation from a molecular model for the second normal stress difference in large-amplitude oscillatory shear flow. Eq. (21) also includes an expression for the fourth harmonic of the second normal stress difference, a quantity that has yet to be measured.

We close by noting that the sum of Eq. (13) and Eq. (21) gives an expression for what is normally called the third normal stress difference, and that some experiments give this particular normal stress difference in oscillatory shear

[7,27,28,29,30]. So Eqs. (13) and (21) provide a means for evaluating the rigid dumbbell model for the third normal stress difference.

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VI. DEDICATION

This paper is dedicated to Distinguished Research Professor Kenneth Walters of the Institute of Non-Newtonian Fluid Mechanics, and of the Department of Mathematics and Physics of Aberystwyth University, in celebration of his 80th birthday, September 14, 2014.

VII. APPENDIX A. FIRST AND SECOND ORDER PAREN FUNCTIONS

For calculating the normal stresses we need:

$$(1;t)\cos \omega t = \frac{1}{2} \frac{\cos 2\omega t + \lambda\omega \sin 2\omega t}{1+L} + \frac{1}{2} \frac{1}{1+L} \quad (39)$$

$$(0,1;t) = \frac{[1-2L] \cos 2\omega t + 3\lambda\omega \sin 2\omega t}{2(1+4L)(1+L)} + \frac{1}{2(1+L)} \quad (40)$$

in which $L = (\lambda\omega)^2$.

VIII. APPENDIX B. THE THIRD ORDER PAREN FUNCTIONS MULTIPLIED BY $\cos\omega t$

For any values of a , b , or c we have:

$$\begin{aligned}
(a, b, c; t) \cos \omega t &\equiv [A, B, 1; t] \cos \omega t \\
&= \frac{1}{2} \left[\begin{aligned} &\frac{[AB - \{2A + 3B + 6\}L] (\cos 4\omega t + \cos 2\omega t) + [\{AB + 2A + 3B\} - 6L] \lambda \omega (\sin 4\omega t + \sin 2\omega t)}{4(A^2 + 9L)(B^2 + 4L)(1 + L)} \\ &+ \frac{[3AB^2 - (2AB + B^2 + 2B - 8A)L](1 + \cos 2\omega t)}{4(A^2 + L)B(B^2 + 4L)(1 + L)} \\ &+ \frac{[(AB^2 + 2AB + 3B^2) + (8 - 2B)L] \lambda \omega \sin 2\omega t}{4(A^2 + L)B(B^2 + 4L)(1 + L)} \end{aligned} \right] \quad (41)
\end{aligned}$$

$$\begin{aligned}
(a, b, c; t) \cos \omega t &\equiv [A, B, 1; t] \cos \omega t \\
&= \left[\begin{aligned} &\frac{[AB - \{2A + 3B + 6\}L] \cos 4\omega t + [\{AB + 2A + 3B\} - 6L] \lambda \omega \sin 4\omega t}{8(A^2 + 9L)(B^2 + 4L)(1 + L)} \\ &+ \left\{ \frac{[4A^3B^2 + (8A^3 + 28AB^2 - 4A^3B - 4A^2B^2 - 8A^2B)L] + (72A - 20AB - 12B^2 - 24B)L^2}{8(A^2 + 9L)(B^2 + 4L)(1 + L)(A^2 + L)B} \right\} \cos 2\omega t \\ &+ \left\{ \frac{[(2A^3B^2 + 4A^3B + 6A^2B^2) + (8A^2 + 10AB^2 + 20AB + 30B^2 - 8A^2B)L + (72 - 24B)L^2]}{8(A^2 + 9L)(B^2 + 4L)(1 + L)(A^2 + L)B} \right\} \lambda \omega \sin 2\omega t \\ &+ \frac{[3AB^2 + (8A - 2AB - B^2 - 2B)L]}{8(A^2 + L)B(B^2 + 4L)(1 + L)} \end{aligned} \right] \quad (42)
\end{aligned}$$

where the “bracket functions” are given in terms of $A \equiv a + b + c$, $B \equiv b + c$, and $C = c = 1$ (the only case for c that is needed).

$$\begin{aligned}
(a, b, 1; t) \cos \omega t &\equiv [A, B, 1; t] \cos \omega t \\
&= \left[\begin{aligned}
&\frac{[AB - \{2A + 3B + 6\}L] \cos 4\omega t + [\{AB + 2A + 3B\} - 6L] \lambda \omega \sin 4\omega t}{8(A^2 + 9L)(B^2 + 4L)(1 + L)} \\
&+ \left\{ \frac{[4A^3B^2 + (8A^3 + 28AB^2 - 4A^3B - 4A^2B^2 - 8A^2B)L]}{8(A^2 + 9L)(B^2 + 4L)(1 + L)(A^2 + L)B} \right\} \cos 2\omega t \\
&+ \left\{ \frac{[(2A^3B^2 + 4A^3B + 6A^2B^2) + (8A^2 + 10AB^2 + 20AB + 30B^2 - 8A^2B)L + (72 - 24B)L^2]}{8(A^2 + 9L)(B^2 + 4L)(1 + L)(A^2 + L)B} \right\} \lambda \omega \sin 2\omega t \\
&+ \frac{[3AB^2 + (8A - 2AB - B^2 - 2B)L]}{8(A^2 + L)B(B^2 + 4L)(1 + L)}
\end{aligned} \right] \quad (43)
\end{aligned}$$

The four specific cases that are necessary for the evaluation of the normal stress differences are:

$$(0, 0, 1; t) \cos \omega t \equiv [1, 1, 1; t] \cos \omega t = \left[\begin{aligned}
&\frac{1}{8} \cdot \frac{[1 - 11L] \cos 4\omega t + [6 - 6L] \lambda \omega \sin 4\omega t}{(1 + 9L)(1 + 4L)(1 + L)} \\
&+ \frac{1}{2} \cdot \frac{[1 + 5L + 4L^2] \cos 2\omega t + [3 + 15L + 12L^2] \lambda \omega \sin 2\omega t}{(1 + 9L)(1 + 4L)(1 + L)^2} \\
&+ \frac{3}{8} \cdot \frac{1}{(1 + 4L)(1 + L)}
\end{aligned} \right] \quad (44)$$

$$\begin{aligned}
(-\frac{z}{3}, \frac{z}{3}, 1; t) \cos \omega t &\equiv [1, \frac{10}{3}, 1; t] \cos \omega t = \left[\begin{aligned}
&\frac{3}{8} \cdot \frac{[10 - 54L] \cos 4\omega t + [46 - 18L] \lambda \omega \sin 4\omega t}{(1 + 9L)(100 + 36L)(1 + L)} \\
&+ \frac{3}{20} \cdot \frac{\left\{ \frac{[100 + 528L - 468L^2] \cos 2\omega t}{(100 + 36L)(100 + 9L)(1 + L)^2} + [230 + 1108L - 18L^2] \lambda \omega \sin 2\omega t \right\}}{(100 + 36L)(100 + 9L)(1 + L)^2} \\
&+ \frac{3}{20} \cdot \frac{75 - 37L}{(100 + 36L)(1 + L)^2}
\end{aligned} \right] \quad (45)
\end{aligned}$$

$$\begin{aligned}
(\frac{z}{3}, 0, 1; t) \cos \omega t &\equiv [\frac{10}{3}, 1, 1; t] \cos \omega t = \left[\begin{aligned}
&\frac{3}{8} \cdot \frac{[10 - 47L] \cos 4\omega t + [39 - 18L] \lambda \omega \sin 4\omega t}{(100 + 81L)(1 + 4L)(1 + L)} \\
&+ \frac{3}{8} \cdot \frac{\left\{ \frac{[4000 + 2920L + 3708L^2] \cos 2\omega t}{(100 - 9L)(100 + 81L)(1 + 4L)(1 + L)} + [7800 + 3510L + 1296L^2] \lambda \omega \sin 2\omega t \right\}}{(100 - 9L)(100 + 81L)(1 + 4L)(1 + L)} \\
&+ \frac{9}{8} \cdot \frac{10 + 17L}{(100 + 9L)(1 + L)(1 + 4L)}
\end{aligned} \right] \quad (46)
\end{aligned}$$

$$\begin{aligned}
(0, \frac{7}{3}, 1; t) \cos \omega t \equiv & \left[\frac{10}{3}, \frac{10}{3}, 1; t \right] \cos \omega t = \left[\begin{aligned} & \frac{9}{8} \cdot \frac{(100 - 204L) \cos 4\omega t + [250 - 54L] \lambda \omega \sin 4\omega t}{(100 + 81L)(100 + 36L)(1 + L)} \\ & + \frac{9}{10} \cdot \frac{\left\{ \begin{aligned} & [50000 + 1500L - 5940L^2] \cos 2\omega t \\ & + [62500 + 21825L - 243L^2] \lambda \omega \sin 2\omega t \end{aligned} \right\}}{(100 + 9L)(100 + 81L)(100 + 36L)(1 + L)} \\ & + \frac{27}{2} \cdot \frac{(25 - 3L)}{(100 + 9L)(100 + 36L)(1 + L)} \end{aligned} \right] \quad (47)
\end{aligned}$$

IX. APPENDIX C. THE FOURTH ORDER PAREN FUNCTIONS MULTIPLIED BY $(a, b, c, d; t)$

$$\begin{aligned}
 (a, b, c, d; t) = & \frac{\left(\left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 12(\lambda\omega)^2 \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \\ & - \left[3(a+b+c+d) + 4(b+c+d) \right] \left[(c+d) + 2d \right] (\lambda\omega)^2 \end{aligned} \right] \cos 4\omega t \\ & + \left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 12(\lambda\omega)^2 \right] \left[(c+d) + 2d \right] \\ & + \left[3(a+b+c+d) + 4(b+c+d) \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \end{aligned} \right] \lambda\omega \sin 4\omega t \right)}{8 \left((a+b+c+d)^2 + 16(\lambda\omega)^2 \right) \left((b+c+d)^2 + 9(\lambda\omega)^2 \right) \left((c+d)^2 + 4(\lambda\omega)^2 \right) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{\left(\left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 6(\lambda\omega)^2 \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \\ & - \left[3(a+b+c+d) + 2(b+c+d) \right] \left[(c+d) + 2d \right] (\lambda\omega)^2 \end{aligned} \right] \cos 2\omega t \\ & + \left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 6(\lambda\omega)^2 \right] \left[(c+d) + 2d \right] \\ & + \left[3(a+b+c+d) + 2(b+c+d) \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \end{aligned} \right] \lambda\omega \sin 2\omega t \right)}{8 \left((a+b+c+d)^2 + 4(\lambda\omega)^2 \right) \left((b+c+d)^2 + 9(\lambda\omega)^2 \right) \left((c+d)^2 + 4(\lambda\omega)^2 \right) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{\left(\left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \\ & - \left[(a+b+c+d) + 2(b+c+d) \right] \left[(c+d) + 2d \right] (\lambda\omega)^2 \end{aligned} \right] \cos 2\omega t \\ & + \left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] \left[(c+d) + 2d \right] \\ & + \left[(a+b+c+d) + 2(b+c+d) \right] \left[(c+d)d - 2(\lambda\omega)^2 \right] \end{aligned} \right] \lambda\omega \sin 2\omega t \right)}{8 \left((a+b+c+d)^2 + 4(\lambda\omega)^2 \right) \left((b+c+d)^2 + (\lambda\omega)^2 \right) \left((c+d)^2 + 4(\lambda\omega)^2 \right) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{\left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] d - \left[(a+b+c+d) + 2(b+c+d) \right] (\lambda\omega)^2 \cos 2\omega t \\ & + \left[\left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] + \left[(a+b+c+d) + 2(b+c+d) \right] d \right] \lambda\omega \sin 2\omega t \end{aligned} \right]}{8 \left((a+b+c+d)^2 + (\lambda\omega)^2 \right) \left((b+c+d)^2 + (\lambda\omega)^2 \right) (c+d) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{\left[\begin{aligned} & \left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] d + \left[(a+b+c+d) + 2(b+c+d) \right] (\lambda\omega)^2 \cos 2\omega t \\ & - \left[\left[(a+b+c+d)(b+c+d) - 2(\lambda\omega)^2 \right] - \left[(a+b+c+d) + 2(b+c+d) \right] d \right] \lambda\omega \sin 2\omega t \end{aligned} \right]}{8 \left((a+b+c+d)^2 + 4(\lambda\omega)^2 \right) \left((b+c+d)^2 + (\lambda\omega)^2 \right) (c+d) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{\left[(b+c+d)(c+d) - 2(\lambda\omega)^2 \right] d - \left[2(b+c+d) + (c+d) \right] (\lambda\omega)^2}{8(a+b+c+d) \left((b+c+d)^2 + (\lambda\omega)^2 \right) \left((c+d)^2 + 4(\lambda\omega)^2 \right) \left(d^2 + (\lambda\omega)^2 \right)} \\
 & + \frac{2(b+c+d)d}{8(a+b+c+d) \left((b+c+d)^2 + (\lambda\omega)^2 \right) (c+d) \left(d^2 + (\lambda\omega)^2 \right)}
 \end{aligned} \tag{48}$$

For any values of a , b , c , and d (but with $d=1$, the only case of interest here), and with, $A \equiv a+b+c+d$, $B \equiv b+c+d$, $C \equiv c+d$ and $D \equiv d=1$ we have:

$$\begin{aligned}
(a, b, c, 1; t) = [A, B, C, 1; t] = & \frac{\left(\begin{aligned} & \{[B-12L][C-2L] - [3+4B][C+2]L\} \cos 4\omega t \\ & + \{[B-12L][C+2] + [3+4B][C-2L]\} \lambda \omega \sin 4\omega t \end{aligned} \right)}{8[1+16L][B^2+9L][C^2+4L][1+L]} \\
& + \frac{\left(\begin{aligned} & \{[B-6L][C-2L] - [3+2B][C+2]L\} \cos 2\omega t \\ & + \{[B-6L][C+2] + [3+2B][C-2L]\} \lambda \omega \sin 2\omega t \end{aligned} \right)}{8[1+4L][B^2+9L][C^2+4L][1+L]} \\
& + \frac{\left(\begin{aligned} & \{[B-2L][C-2L] - [1+2B][C+2]L\} \cos 2\omega t \\ & + \{[B-2L][C+2] + [1+2B][C-2L]\} \lambda \omega \sin 2\omega t \end{aligned} \right)}{8[1+4L][B^2+L][C^2+4L][1+L]} \\
& + \frac{\{[B-2L] - [1+2B]L\} \cos 2\omega t + \{[B-2L] + [1+2B]\} \lambda \omega \sin 2\omega t}{8[1+L][B^2+L]C[1+L]} \\
& + \frac{\{[B-2L] + [1+2B]L\} \cos 2\omega t - \{[B-2L] - [1+2B]\} \lambda \omega \sin 2\omega t}{8[1+4L][B^2+L]C[1+L]} \\
& + \frac{\{[BC-2L] - [2B+C]L\} C + 2B[C^2+4L]}{8[B^2+L][C^2+4L][1+L]C} + \frac{2B}{8[B^2+L]C[1+L]}
\end{aligned} \tag{49}$$

$$\begin{aligned}
(a, b, c, 1; t) &= [A, B, C, 1; t] = \frac{\{[B-12L][C-2x] - [3+4B][C+2]L\} \cos 4\omega t}{8[1+16L][B^2+9L][C^2+4L][1+L]} \\
&+ \frac{\left[\begin{aligned} &\{[B-6L][C-2L] - [3+2B][C+2]L\} \cdot [B^2+L][1+L]C \\ &+ \{[B-2L][C-2L] - [1+2B][C+2]L\} \cdot [B^2+9L][1+L]C \\ &+ \{[B-2L] - [1+2B]L\} \cdot [1+4L][B^2+9L][C^2+4L] \\ &+ \{[B-2L] + [1+2B]L\} \cdot [B^2+9L][C^2+4L][1+L] \end{aligned} \right]}{8[1+4L][B^2+9L][C^2+4L][1+L]^2[B^2+L]C} \cos 2\omega t \\
&+ \frac{\left[\begin{aligned} &\{[B-6L][C+2] + [3+2B][C-2L]\} \cdot [B^2+L][1+L]C \\ &+ \{[B-2L][C+2] + [1+2B][C-2L]\} \cdot [B^2+9L][1+L]C \\ &+ \{[B-2L] + [1+2B]\} \cdot [1+4L][B^2+9L][C^2+4L] \\ &- \{[B-2L] - [1+2B]\} \cdot [B^2+9L][C^2+4L][1+L] \end{aligned} \right]}{8[1+4L][B^2+9L][C^2+4L][1+L]^2[B^2+L]C} \lambda \omega \sin 2\omega t \\
&+ \frac{3BC^2 + (8B - 2C - 2BC - C^2)L}{8[B^2+L][C^2+4L][1+L]C}
\end{aligned} \tag{50}$$

Next we evaluate the $(a, b, c, 1; t) = [A, B, C, 1; t]$ for the cases we need for getting the normal stress differences:

$$\begin{aligned}
(0, 0, 0, 1; t) &= [1, 1, 1, 1; t] = \frac{1}{8} \cdot \frac{(1 - 35L + 24L^2) \cos 4\omega t + (10 - 50L) \lambda \omega \sin 4\omega t}{(1+16L)(1+9L)(1+4L)(1+L)} \\
&+ \frac{1}{8} \cdot \frac{(4 - 13L - 32L^2 - 159L^3) \cos 2\omega t + 2(10 + 26L + 61L^2 - 27L^3) \lambda \omega \sin 2\omega t}{(1+4L)(1+9L)(1+L)^3} \\
&+ \frac{3}{8} \cdot \frac{1}{(1+4L)(1+L)}
\end{aligned} \tag{51}$$

$$\begin{aligned}
(0, -\frac{7}{3}, \frac{7}{3}, 1; t) &= [1, 1, \frac{10}{3}, 1; t] \\
&= \frac{3}{4} \cdot \frac{(5 - 119L + 36L^2) \cos 4\omega t + (43 - 117L) \lambda \omega \sin 4\omega t}{(1 + 16L)(1 + 9L)(100 + 36L)(1 + L)} \\
&\quad + \frac{3}{20} \cdot \frac{\left[(100 + 243L - 2289L^2 - 5915L^3 - 1179L^4) \cos 2\omega t \right.}{(1 + 4L)(1 + 9L)(100 + 36L)(1 + L)^3} \\
&\quad \left. + 2(215 + 1447L + 1934L^2 - 693L^3 - 243L^4) \lambda \omega \sin 2\omega t \right] \\
&\quad + \frac{3}{20} \cdot \frac{(75 - 37L)}{(1 + L)^2 (100 + 36L)}
\end{aligned} \tag{52}$$

$$\begin{aligned}
(-\frac{7}{3}, \frac{7}{3}, 0, 1; t) &= [1, \frac{10}{3}, 1, 1; t] \\
&= \frac{3}{8} \cdot \frac{(10 - 203L + 72L^2) \cos 4\omega t + (79 - 206L) \lambda \omega \sin 4\omega t}{(1 + 16L)(100 + 81L)(1 + 4L)(1 + L)} \\
&\quad + \frac{3}{8} \cdot \frac{\left[(4000 - 5680L - 10262L^2 - 38031L^3 - 30780L^4) \cos 2\omega t \right.}{(1 + 16L)(100 + 81L)(1 + 4L)(1 + L)^2 (100 + 9L)} \\
&\quad \left. + (15800 + 35050L + 63881L^2 + 32130L^3 - 5832L^4) \lambda \omega \sin 2\omega t \right] \\
&\quad + \frac{9}{8} \cdot \frac{(10 + 17L)}{(100 + 9L)(1 + 4L)(1 + L)}
\end{aligned} \tag{53}$$

$$\begin{aligned}
(-\frac{7}{3}, 0, \frac{7}{3}, 1; t) &= [1, \frac{10}{3}, \frac{10}{3}, 1; t] \\
&= \frac{9}{4} \cdot \frac{2(25 - 301L + 54L^2) \cos 4\omega t + 5(65 - 87L) \lambda \omega \sin 4\omega t}{(1 + 16L)(100 + 81L)(100 + 36L)(1 + L)} \\
&\quad + \frac{9}{20} \cdot \frac{\left[(100000 - 72000L - 475930L^2 - 330813L^3 - 62451L^4) \cos 2\omega t \right.}{(1 + 4L)(100 + 81L)(100 + 36L)(1 + L)^2 (100 + 9L)} \\
&\quad \left. + (325000 + 622150L + 269979L^2 - 4725L^3 - 13122L^4) \lambda \omega \sin 2\omega t \right] \\
&\quad + \frac{27}{2} \cdot \frac{(25 - 3L)}{(100 + 9L)(100 + 36L)(1 + L)}
\end{aligned} \tag{54}$$

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

	Model	First	Third	Fifth	Zeroth	Second	Fourth	Startup	Notation Eq. of [32]	[Ref.] (Correction to)
		Shear Stress Harmonic			Normal Stress Difference Harmonic					
Lodge (1961, 1964)	$L^{\dagger}$	ℓ	0	0	N_1	N_1	0			[51,52]
Bird, Warner and Evans (1971)	RD, SK	n			N_1 N_2	N_1 N_2			(157)	[53]
Mou and Mazo (1977)	RR				N_1 N_2	N_1 N_2			(183)	[54](55)
Gurnon and Wagner (2012)	G	ℓ	X		N_1 N_2	N_1 N_2			(147)	[56]
This paper	RD, SK	n	X		N_1 N_2	N_1 N_2	N_1 N_2		(157)	

Legend: G $\equiv$ Giesekus; L $\equiv$ Lodge rubberlike liquid; RD $\equiv$ rigid dumbbell; RR $\equiv$ planar rigid ring; SK $\equiv$ shish-kebab; $N_1, N_2 \equiv$ first and second normal stress differences; $n \equiv \eta^*(\omega, \gamma_0)$; $\ell \equiv \eta^*(\omega)$; $^{\dagger} \equiv$ multiple relaxation times.

Table II: Dimensional Variables

<i>i</i> th component of velocity	L/t	v_i
Angular frequency	t^{-1}	ω
Bead friction coefficient	M/t	$\zeta \equiv 3\pi b\eta_s$
Boltzmann constant	$ML^2/t^2T/\text{dumbbell}$	k
Cartesian coordinate, flow direction (Figure 1)	L	x
Cartesian coordinate, distance from stationary plate (Figure 1)	L	y
Cartesian coordinate, transverse to flow direction (Figure 1)	L	z
<i>ij</i> – component of extra stress tensor*	M/Lt^2	τ_{ij}
Bead diameter	L	b
First normal stress coefficient, steady shear flow	M/L	$\Psi_1 \equiv -(\tau_{xx} - \tau_{yy})/\dot{\gamma}^2$
First normal stress coefficient, component in-phase with $\cos 2\omega t$ **	M/L	Ψ'_1
First normal stress coefficient, component in-phase with $\sin 2\omega t$ **	M/L	Ψ''_1
First normal stress displacement coefficient**	M/L	Ψ_1^d
Molar concentration of dumbbells	$\text{dumbbells}/L^3$	n
Past time	t	t', t'', t'''
Relaxation time of fluid	t	λ
Second normal stress coefficient, steady shear flow	M/L	$\Psi_2 \equiv (\tau_{yy} - \tau_{zz})/\dot{\gamma}^2$

Second normal stress coefficient, component in-phase with $\cos 2\omega t$	M/L	$-\Psi'_2$
Second normal stress coefficient, component in-phase with $\sin 2\omega t$	M/L	$-\Psi''_2$
Second normal stress displacement coefficient	M/L	$-\Psi_1^d$
Shear rate amplitude	t^{-1}	$\dot{\gamma}^0$
Solvent viscosity	M/Lt	η_s
Temperature	T	T
Time	t	t

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

* Where τ_{ij} is the force exerted in the j th direction on a unit area of fluid surface of constant x_i by fluid in the region lesser x_i on fluid in the region greater x_i [57].

**See Eqs. (4.4-14) and (4.4-15) and also NOTATION FOR VOLUME 1: Greek Symbols of [58].

Table III: Dimensionless Variables and Groups

Deborah number, oscillatory shear	$\lambda\omega$
Deborah number squared	$L = (\lambda\omega)^2$
Number of equally-spaced beads on a rod of length L	N
Paren function, first order	$(a;t)$
Paren function, second order	$(a,b;t)$
Paren function, third order	$(a,b,c;t)$
Paren function, fourth order	$(a,b,c,d;t)$
Time dependent part of the shear rate for assumed velocity profile linear in y [Eq. (1)]	$f(t)$
Weissenberg number, oscillatory shear	$\lambda\dot{\gamma}^0$

Table IV: Intercepts arising in normal stress difference equations.

	Function	Rigid dumbbell model (Equation)	Corotational Maxwell model (Equation)
Figure 9	Ψ'_1	$\lambda\omega = 1/\sqrt{2}$ (16)	$\lambda\omega = 1/\sqrt{2}$ (30)
Figure 10	$\cos 2\omega t$ coefficient, $(\lambda\dot{\gamma}^0)^2$ in Ψ'_1	$\lambda\omega \cong 0.3653$ (16)	$\lambda\omega = 1/\sqrt{2}$ (30)
Figure 11	$\cos 4\omega t$ coefficient	$\lambda\omega \cong 0.1581$ $\lambda\omega \cong .8732$ (18)	$\lambda\omega = \sqrt{\frac{1}{48}(35 - \sqrt{1129})} \cong 0.1707$ $\lambda\omega = \sqrt{\frac{1}{48}(35 + \sqrt{1129})} \cong 1.1955$ (32)
Figure 11	$\sin 4\omega t$ coefficient	$\lambda\omega = 0$ $\lambda\omega \cong 0.3927$ $\lambda\omega \cong 2.2633$ (19)	$\lambda\omega = 0$ $\lambda\omega = 1/\sqrt{5}$ (33)
Figure 12	Ψ'_2	$\lambda\omega = 0$ (24)	$\lambda\omega = 1/\sqrt{2}$ (35)
Figure 13	$\cos 2\omega t$ coefficient, $(\lambda\dot{\gamma}^0)^2$ in Ψ'_2	$\lambda\omega = 0$ (24)	$\lambda\omega = 1/\sqrt{2}$ (35)
Figure 13	$\sin 2\omega t$ coefficient, $(\lambda\dot{\gamma}^0)^2$ in Ψ''_2	$\lambda\omega = 0$ $\lambda\omega \cong 0.6254$ (25)	$\lambda\omega = 0$ (35)
Figure 14	$\cos 4\omega t$ coefficient	$\lambda\omega = 0$ $\lambda\omega \cong 0.5473$ (26)	$\lambda\omega = \sqrt{\frac{1}{48}(35 - \sqrt{1129})} \cong 0.1707$ $\lambda\omega = \sqrt{\frac{1}{48}(35 + \sqrt{1129})} \cong 1.1955$ (37)
Figure 14	$\sin 4\omega t$ coefficient	$\lambda\omega = 0$ $\lambda\omega \cong 0.1896$ $\lambda\omega \cong 1.7358$ (27)	$\lambda\omega = 0$ $\lambda\omega = 1/\sqrt{5}$ (38)

Figure 1: Orthomorphic sketch of alternating velocity profile in oscillatory shear between stationary and moving plates [Eqs. (1) or (2)]. Cartesian coordinates with origin on the stationary plate.

Figure 2: The dumbbell consists of identical beads (of identical mass and of identical diameter) connected by one thin, absolutely rigid (dimensionless, massless) rod.

Figure 3: Loops of dimensionless first normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = \frac{1}{10}$.

Figure 4: Loops of dimensionless first normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = 1$.

Figure 5: Loops of dimensionless first normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = 10$.

Figure 6: Loops of dimensionless second normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = \frac{1}{10}$

Figure 7: Loops of dimensionless second normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = 1$.

Figure 8: Loops of dimensionless second normal stress differences *versus* dimensionless shear rate calculated for the rigid dumbbell model by increasing the Weissenberg number with a fixed Deborah number of $\lambda\omega = 10$.

Figure 9: First normal stress coefficients for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for small-amplitude oscillatory shear flow: $\Psi_1^d(\lambda\omega)$ [Eq. (15) versus Eq. (29)], $\Psi_1'(\lambda\omega)$ [Eq. (16) versus Eq. (30)] and $\Psi_1''(\lambda\omega)$ [Eq. (17) versus Eq. (31)].

Figure 10: Coefficients of $(\lambda \dot{\gamma}^0)^2$ in expressions for $\Psi_1^d(\lambda \omega)$ [Eq. (15) versus Eq. (29)], $\Psi_1'(\lambda \omega)$ [Eq. (16) versus Eq. (30)] and $\Psi_1''(\lambda \omega)$ [Eq. (17) versus Eq. (31)] for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for large-amplitude oscillatory shear flow.

Figure 11: Coefficients of $(\lambda\dot{\gamma}^0)^4$ in Eqs. (13) and (28) for $\cos 4\omega t$ [Eq. (18) versus Eq. (32)], and for $\sin 4\omega t$ [Eq. (19) versus Eq. (33)] for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for large-amplitude oscillatory shear flow.

Figure 12: Second normal stress coefficients for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for small-amplitude oscillatory shear flow: $\Psi_2^d(\lambda\omega)$ [Eq. (23) versus Eq. (34)], $\Psi_2'(\lambda\omega)$ [Eq. (24) versus Eq. (35)] and $\Psi_2''(\lambda\omega)$ [Eq. (25) versus Eq. (36)].

Figure 13: Coefficients of $(\lambda \dot{\gamma}^0)^2$ in expressions for $\Psi_2^d(\lambda \omega)$ [Eq. (23) versus Eq. (34)], $\Psi_2'(\lambda \omega)$ [Eq. (24) versus Eq. (35)] and $\Psi_2''(\lambda \omega)$ [Eq. (25) versus Eq. (36)] for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for large-amplitude oscillatory shear flow.

Figure 14: Coefficients of $(\lambda\dot{\gamma}^0)^4$ in Eqs. (21) and (28) for $\cos 4\omega t$ [Eq. (26) versus Eq. (37)], and for $\sin 4\omega t$ [Eq. (27) versus Eq. (38)] for the rigid dumbbell model (blue) versus the corotational Maxwell model (red) for large-amplitude oscillatory shear flow.

Figure 15: Dimensionless first normal stress differences versus dimensionless shear rate loops calculated for the 2-constant corotational Maxwell model for five Weissenberg numbers with a fixed $\lambda\omega = 0.1$.

Figure 16: Dimensionless first normal stress differences versus dimensionless shear rate loops calculated for the 2-contant corotational Maxwell model for five Weissenberg numbers with a fixed Deborah number of $\lambda\omega = 1.0$.

Figure 17: Dimensionless first normal stress differences versus dimensionless shear rate loops calculated for the 2-constant corotational Maxwell model for five Weissenberg numbers with a fixed Deborah number of $\lambda\omega = 10$.

X. REFERENCES

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Addendum: In Eq. (8), the term $-\frac{1}{432}\left[\frac{3}{49}\left(\frac{7}{3}, 0, 1\right); t + \frac{3}{537}\left(0, \frac{7}{3}, 1; t\right)\right]P_4^2 s_2$ should be inserted just before the "+ additional terms".

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Erratum: On p. 409 of the first printing, the $(n + m)!$ in the denominator should be $(n - m)!$.

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