QUEEN'S UNIVERSITY

POLYMERS RESEARCH GROUP

19 Division Street, Kingston, ON, K7L 3N6 Canada

COMPLEX POLYMER ORIENTATION

P.H. Gilbert¹ and A.J. Giacomini^{1,2,*}

¹Chemical Engineering Department and Polymers Research Group

²Mechanical and Materials Engineering Department
Queen's University, Kingston, Ontario, CANADA K7L 3N6

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*Corresponding author (giacomini@queensu.ca)

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ABSTRACT

Previously, we explored the dynamics of a dilute suspension of rigid dumbbells as a model for polymeric liquids in large-amplitude oscillatory shear (LAOS) flow. We derived the expression for the polymer orientation distribution, and then we decomposed this function into its first five harmonics (the zeroth, first, second, third and fourth harmonics). In this work, we separate each harmonic into its components in-phase and out-of-phase with $\cos n\omega t$, and then use three-dimensional imaging to investigate complex polymer motion in LAOS. Our analysis focuses on the nonlinear viscoelastic regime, specifically, where both $\lambda\omega$ and $\lambda\dot{\gamma}^0$ are unity. We learn that harmonic components, in-phase and out-of-phase with $\cos n\omega t$, contribute to orientation differently, and that out-of-phase components tend to give more probable orientation away from the flow direction. We also find that some orientation contributions are caused by interferences between complex components, some constructive and some destructive.

Keywords: polymer dynamics, polymer orientation, large-amplitude oscillatory shear flow, Fourier-transform rheology, rigid-dumbbell suspension, structure-property relations

*Corresponding author (giacomin@queensu.ca).

Orientation probability distribution component out-of-phase with $\cos 2\omega t$ for a polymer undergoing large-amplitude oscillatory shear (LAOS) at $\omega t = \pi^3/8$ with $\lambda\omega = 1$ and $\lambda\dot{\gamma}^0 = 10$, where red and blue correspond to high and low orientation probability.

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I. INTRODUCTION

The rigid dumbbell suspension seems to mimic the behavior of polymer solutions and melts, at least qualitatively, and this seems to be because the overall orientation of the polymer chains determines the longest time constant for polymeric liquids. A rigid dumbbell has both length and width, the two key geometric properties of a polymer molecule, and these confer orientation upon the polymer (see Figure 1 and Figure 2). Oscillatory shear flow [1,2,3,4,5,6] is by far the most common experiment for probing polymer orientation [7], and when performed at large-amplitude ([8,9,10,11,12,13]; see also Section 2 of [14]), this test is particularly informative. Table I classifies the literature on analytical solutions for orientation distribution in large-amplitude oscillatory shear flow (LAOS).

In our previous work, we developed an expression for polymer orientation in LAOS from the diffusion equation by expanding the orientation distribution in powers of shear rate amplitude [37,38,39,40,41,42]. We extended this work by decomposing the orientation distribution function into its first five (zeroth, first, second, third, fourth) harmonics. By *decomposing*, we mean rewriting the orientation distribution as:

$$\psi(\theta, \phi, t) = \sum_{n=0}^{\infty} [\psi'_n \cos n\omega t + \psi''_n \sin n\omega t] \quad (1)$$

where ψ'_n and ψ''_n are the Fourier coefficients of the orientation distribution function respectively in-phase and out-of-phase with $\cos n\omega t$. We can thus define *complex orientation* as:

$$\psi_n^*(\theta, \phi, t) \equiv \psi'_n - i\psi''_n \quad (2)$$

so that these Fourier coefficients of the orientation distribution function are respectively the real and minus the imaginary parts of the complex orientation, $\psi_n^*(\theta, \phi, t)$. We find that the frequency content of each harmonic contributes orientation differently. Particularly, only the zeroth and second harmonics contribute orientation in the flow direction, whereas odd harmonics provide orientation away from the flow direction and from the y – axis (see coordinates defined in Figure 1). We also identified the second harmonic as primarily contributing to the peanut-shape, or *lemniscoidal* shape, of the overall orientation distribution [45].

This paper concerns itself with the orientation distribution function of a suspension of rigid dumbbells, when the flow is given by the velocity field, $v_x(y, t)$, illustrated in Figure 1. We further restrict this paper to the periodic response, reached several cycles after startup of oscillatory shear, called alternance (see Section 6. of [15]; [16]). This work is an extension of recent articles [37, 38] wherein part of the orientation distribution is derived using the method of Bird and Armstrong [17] (see also Problem 11C.1 of [18]).

Here, we further extend our Fourier analysis [45] of the orientation distribution function by separating each harmonic into its components, in-phase and out-of-phase with $\cos n\omega t$. We deepen our understanding of the molecular motions by developing colored orientation distribution diagrams for the complex components of each harmonic. These distributions allow us to determine the contribution to orientation from each harmonic component. Our analysis includes only the case of nonlinear viscoelasticity.

a. The flow field

We are concerned with the particular case of the homogeneous shearing flow illustrated in Figure 1:

$$v_x = \dot{\gamma}^0 y f(t), v_y = v_z = 0 \quad (3)$$

called *simple shear flow*. Our symbols 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 time. This situation can be obtained by having the flow take place between two plates placed extremely close to one another [19,20].

We consider only the case where $f(t) = \cos \omega t$ so that Eq. (3) becomes [21,22]:

$$v_x = \dot{\gamma}^0 y \cos \omega t; v_y = v_z = 0 \quad (4)$$

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

$$\lambda \dot{\gamma}(t) = \lambda \dot{\gamma}^0 \cos \lambda \omega (t/\lambda) \quad (5)$$

in which the dimensionless shear rate $\lambda \dot{\gamma}^0$ (the Weissenberg number) and the dimensionless frequency $\lambda \omega$ (the Deborah number) appear [21,22,16]. All orientation distribution responses calculated herein are thus referred to this cosinusoidal shear rate (see Section V of [23]). 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:

$$\lambda = \frac{\xi L^2}{12kT} = \frac{(3\pi\eta_s b)L^2}{12kT} \quad (6)$$

and for rigid multibead-rods:

$$\lambda_N = \frac{\xi L^2 N(N+1)}{72(N-1)kT} \quad (7)$$

where N is the number of equally-spaced beads on the rod of length L , T is absolute temperature, 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). Eqs. (6) and (7) thus connect polymer molecular structure to the rheological properties; we call these *structure-property relations*. Eq. (5) applies for continua, and thus only applies when the gap, h , approaches or is much smaller than the molecular length, L . For a detailed study of small-amplitude oscillatory shear flow of a rigid dumbbell suspension in confined gaps, see Section 5. of [24] or Section 2.3.3 of [25].

In this paper, we consider the special case of Eq. (5) where higher harmonics arise in both the shear stress and in the normal stress difference responses.

b. Orientation distribution function

For simple shear flow, the *diffusion equation* for the orientation distribution function $\psi(\theta, \phi, t)$ is given by (see Eq. 5.1 of [26], Eq. (14.4-1) of [27]):

$$6\lambda \frac{\partial \psi}{\partial t} = \left[\frac{1}{S} \frac{\partial}{\partial \theta} \left(S \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{S^2} \frac{\partial^2 \psi}{\partial \phi^2} \right] - 6\lambda \dot{\gamma} \left[\frac{sc}{S} \frac{\partial}{\partial \theta} (S^2 C \psi) - \frac{\partial}{\partial \phi} (s^2 \psi) \right] \quad (8)$$

where $\lambda \dot{\gamma}$ is the dimensionless oscillatory shear rate [given by Eq. (5)]. In Eq. (8), we use the abbreviations $S \equiv \sin \theta$, $C \equiv \cos \theta$, $s \equiv \sin \phi$ and $c \equiv \cos \phi$. For ψ we adhere to the definition of Bird-Warner-Evans [26] which differs from that of [18,27]. The relation between the distribution function used here, ψ , and the

symbol used in the first [18] and second [27] editions of *Dynamics of Polymeric Liquids* is (see footnote 1 on p. 524 of [18]):

$$\psi_{\text{DPL},1e} = \psi_{\text{DPL},2e} = \psi \sin \theta \quad (9)$$

Also, whereas the symbol for the distribution function used here is ψ , that used in the second edition of *Dynamics of Polymeric Liquids* [27] is f .

The dumbbell orientation is thus given in terms of the spherical coordinates θ and ϕ , defined in Figure 2. When the fluid is at rest, all orientations are equally likely, and ψ is equal to a normalization constant, $1/4\pi$, so that:

$$\int_0^{2\pi} \int_0^\pi \psi(\theta, \phi, t) \sin \theta d\theta d\phi = 1 \quad (10)$$

In other words, when the fluid is at rest, $\psi(\theta, \phi)$ is spherically symmetric.

Although the orientation distribution function for rigid dumbbell suspensions has not been measured directly, its implications for rheological behaviors have been verified experimentally. Reasonable qualitative behavior for oscillatory shear flow are obtained for amplitudes both small [26] and large [37,38].

II. METHOD

Schmalzer and Giacomin [40,41,42] recently solved Eq. (8) analytically for large-amplitude oscillatory shear flow, including terms that do not contribute to the rheological responses, using the method of Bird and Armstrong [17]. This solution has the form:

$$\psi(\theta, \phi, t) = \frac{1}{4\pi} \left[1 + (6\lambda\dot{\gamma}^0) \psi_1(\theta, \phi, t) + (6\lambda\dot{\gamma}^0)^2 \psi_2(\theta, \phi, t) + (6\lambda\dot{\gamma}^0)^3 \psi_3(\theta, \phi, t) + (6\lambda\dot{\gamma}^0)^4 \psi_4(\theta, \phi, t) + \dots \right] \quad (11)$$

where ψ_1 through ψ_4 are given by Eqs. (36), (44), (52) and (61) of [40]. Giacomini et al. [45] undertook the laborious Fourier decomposition of these expressions for ψ_1 through ψ_4 , putting the resulting Fourier coefficients under common denominators. We deepen this Fourier analysis by exploring how the components in-phase and out-of-phase with $\cos n\omega t$ contribute to polymer orientation. To prevent introducing errors, we thus checked each result given below, numerically, by comparing the expressions before and after the Fourier decomposition (to 16 significant figures). Specifically, Eq. (11) plus Eqs. (36), (44), (52) and (61) of [40] checks with Eq. (1) plus Eqs. (12) through (20) to at least 16 significant figures.

III. RESULTS

From the results given in Subsections III.a through III.e, we see that in oscillatory shear flow the polymer orientation distribution decomposes into both even (starting with the zeroth) and odd (starting with the first) harmonics. Each of these harmonics contain contributions in-phase and out-of-phase with $\cos n\omega t$, except for the zeroth harmonic (which, by definition, does not depend on time). We identify the even harmonics of the polymer motion with the differences in the normal components of the extra stress tensor, whose Fourier components are also all even. We can further identify the odd harmonics of the orientation with the y_x – component of the extra stress tensor (called the shear stress), whose Fourier components are also all odd valued. Our analysis focuses on orientation in the nonlinear viscoelastic regime (where both $\lambda\omega$ and $\lambda\dot{\gamma}^0$ are unity), in-phase [Figure 3, Figure 4b, Figure 5b, Figure 6b, Figure 7b] and out-of-phase

[Figure 4c, Figure 5c, Figure 6c, Figure 7c] with $\cos n\omega t$, and we compare the complex orientation components with the contributions of each harmonic to the total orientation [Figure 4a, Figure 5a, Figure 6a, Figure 7a].

a. Zeroth Harmonic

The Fourier coefficient of the zeroth harmonic of the orientation distribution function for a rigid dumbbell suspension in large-amplitude oscillatory shear flow is given by:

$$\psi'_0 = \frac{1}{4\pi} \left[\begin{aligned} &1 - (6\lambda\dot{\gamma}^0)^2 \left\{ \frac{\left[-\frac{3}{4}(15C^4 + 30C^2 - 7) - 30(1 - C^2)c_2 + \frac{315}{28}(1 - C^2)^2 c_4 \right]}{1440(1 + W)} \right\} \\ &- (6\lambda\dot{\gamma}^0)^4 \left\{ \frac{\left[(1161W^3 + 14769W^2 + 74200W + 40000)(3C^2 - 1) + 11(1107W^3 + 19303W^2 + 60050W + 28750)(1 - C^2)c_2 \right]}{221760(W + 1)^2(4W + 1)(9W + 25)(9W + 100)} \right\} \end{aligned} \right] \quad (12)$$

Figure 3 illustrates the time steady orientation induced by the oscillatory shear deformation that is predicted by Eq. (12) in the nonlinear viscoelastic regime. The zeroth harmonic contains only a part in-phase with $\cos((0)\omega t) = 1$, because it contributes the base set of possible polymer orientations. The total orientation distribution begins with these marshmallows (Figure 3), and the higher harmonics then sculpt these into peanuts (Figure 8).

b. First Harmonic

The Fourier coefficients of the first harmonic of the orientation distribution function for a rigid dumbbell suspension in large-amplitude oscillatory shear flow are given by:

$$\psi'_1 = \frac{1}{4\pi} \left[\left(6\lambda\dot{\gamma}^0 \right) \frac{1}{4} (1-C^2) s_2 \left(\frac{1}{1+W} \right) + \left(6\lambda\dot{\gamma}^0 \right)^3 \left\{ \left[\begin{array}{l} -\frac{1}{3920} (75-37W)(W+49)(4W+1)(9W+100) \\ -\frac{15}{68992} (97W+860)(W+1)(W+49)(9W+25)(7C^2-1) \\ +\frac{7}{67584} (525-19W)(W+1)(4W+1)(9W+100)(33C^4-18C^2+1) \\ +\frac{5}{256} (160-W)(W+1)(W+49)(9W+25)(1-C^2) s_4 \\ -\frac{7}{6144} (525-19W)(W+1)(4W+1)(9W+100)(1-C^2)^2 s_6 \end{array} \right] s_2 \right\} (1-C^2) \right] \quad (13)$$

and:

$$\psi''_1 = \frac{1}{4\pi} \left[\left(6\lambda\dot{\gamma}^0 \right) \frac{1}{4} (1-C^2) s_2 \left(\frac{1}{1+W} \right) + \left(6\lambda\dot{\gamma}^0 \right)^3 \left\{ \left[\begin{array}{l} -\frac{1}{1680} (W+49)(9W+100)(153W^2+757W+460) \\ -\frac{45}{68992} (25W+256)(W+1)(W+49)(9W+25)(7C^2-1) \\ +\frac{7}{67584} (3W+355)(W+1)(4W+1)(9W+100)(33C^4-18C^2+1) \\ +\frac{3}{256} (13W+230)(W+1)(W+49)(9W+25)(1-C^2) s_4 \\ -\frac{7}{6144} (3W+355)(W+1)(4W+1)(9W+100)(1-C^2)^2 s_6 \end{array} \right] s_2 \right\} (1-C^2) \right] \lambda\omega \quad (14)$$

Figure 4A illustrates the total orientation distribution associated with the polymer motions contributed by the first harmonic, and predicted by Eqs. (13) and (14). Figure 4B and Figure 4C show the orientation associated with the first harmonic components in-phase and out-of-phase with $\cos\omega t$. As with the total first harmonic orientation distribution (Figure 4A), we see that the complex orientation components do not vary over a complete alternant cycle, and that the components in-phase and out-of-phase with $\cos\omega t$ contribute identically to orientation. Though orientation is identical for the complex components of the first harmonic, at $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}$ and at $\omega t = 0, \pi$, orientation contributions are entirely in-phase with $\cos\omega t$ and out-of-phase with $\cos\omega t$, respectively. Therefore, the components in-phase and out-of-phase with $\cos\omega t$ contribute the same shapes,

but unequally, in the course of one cycle. The three videos associated with Figure 4 verify the static behavior of each harmonic component, and we observe similar behavior at other values of $\lambda\omega$ and $\lambda\dot{\gamma}$. We encourage readers to view these videos.

c. Second Harmonic

The Fourier coefficients of the second harmonic of the orientation distribution function, for a rigid dumbbell suspension in large-amplitude oscillatory shear flow, are given by:

$$\psi'_2 = \frac{1}{4\pi} \left[\begin{aligned} & (6\lambda\dot{\gamma}^0)^2 \left\{ \begin{aligned} & \left[\frac{24}{7}(3C^2 - 1)(1 - 2W)(25 + 9W) \right. \\ & - \frac{9}{28}(35C^4 - 30C^2 + 3)(10 - 6W)(1 + 4W) \\ & - 24(1 - C^2)(1 - 2W)(25 + 9W)c_2 \\ & \left. + \frac{315}{28}(1 - C^2)^2(10 - 6W)(1 + 4W)c_4 \right] \\ & \left. - \frac{(72)16(1 + W)(1 + 4W)(25 + 9W)}{(72)16(1 + W)(1 + 4W)(25 + 9W)} \right\} \\ & + (6\lambda\dot{\gamma}^0)^4 \left\{ \begin{aligned} & \frac{\left(\begin{aligned} & 27917501148W^7 + 395970769863W^6 + 1359686945763W^5 \\ & + 1401100327677W^4 + 389057165809W^3 + 45722628300W^2 \\ & - 22856340000W - 1568000000 \end{aligned} \right) (3C^2 - 1)}{6519744(W + 1)^3(4W + 1)(9W + 1)(9W + 25)(9W + 100)(16W + 1)(81W + 100)} \\ & + \frac{\left(\begin{aligned} & 506797884W^7 + 6027824709W^6 + 19477775889W^5 \\ & + 19601882811W^4 + 5251665787W^3 + 424722600W^2 \\ & - 340140000W - 23000000 \end{aligned} \right) (1 - C^2)c_2}{120960(W + 1)^3(4W + 1)(9W + 1)(9W + 25)(16W + 1)(81W + 100)} \end{aligned} \right\} \end{aligned} \right] \quad (15)$$

and:

$$\psi_2'' = \frac{1}{4\pi} \left[\begin{aligned} & (6\lambda\dot{\gamma}^0)^2 \left\{ \frac{\left[\frac{9}{7}(3C^2-1)(25+9W) - \frac{9}{14}(35C^4-30C^2+3)(1+4W) \right]}{144(1+W)(1+4W)(25+9W)} \right. \\ & \left. - \frac{9(1-C^2)(25+9W)c_2 + \frac{630}{28}(1-C^2)^2(1+4W)c_4}{144(1+W)(1+4W)(25+9W)} \right\} \\ & + (6\lambda\dot{\gamma}^0)^4 \left[\frac{\begin{pmatrix} 4554095076W^7 + 54922330017W^6 + 62656044453W^5 \\ -366082940052W^4 - 649050340979W^3 - 299118407355W^2 \\ -75936742500W - 3787700000 \end{pmatrix} (3C^2-1)}{325987320(W+1)^3(4W+1)(9W+1)(9W+25)(9W+100)(16W+1)(81W+100)} \right. \\ & \left. + \frac{\begin{pmatrix} 73929348W^7 + 725310531W^6 + 487357884W^5 \\ -5792477481W^4 - 9601088132W^3 - 4427460420W^2 \\ -1076466750W - 53975000 \end{pmatrix} (1-C^2)c_2}{60480(W+1)^3(4W+1)(9W+1)(9W+25)(9W+100)(16W+1)(81W+100)} \right] \lambda\omega \end{aligned} \right] \quad (16)$$

Figure 5A illustrates the orientation distribution associated with the polymer motions at twice the test frequency, 2ω , induced by the oscillatory shear deformation, and predicted by Eqs. (15) and (16). From Figure 5B and Figure 5C, we see that at $\omega t = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$ only the component in-phase with $\cos 2\omega t$, $\psi_2' \cos 2\omega t$, contributes orientation. However, at $\omega t = \frac{\pi}{4}, \frac{3\pi}{4}, \frac{5\pi}{4}, \frac{7\pi}{4}$, only the component out-of-phase with $\cos 2\omega t$, $\psi_2'' \sin 2\omega t$, contributes orientation. When we examine $\psi_2' \cos 2\omega t$ at all values of ωt , we find that its orientation contribution remains constant over the cycle, and that it primarily contributes orientation in the flow direction. Further, $\psi_2'' \sin 2\omega t$ is responsible for all of the dynamic behavior in the total second harmonic orientation distribution. Also, $\psi_2'' \sin 2\omega t$ only contributes orientation away from the flow direction (in both the y or z directions, depending on ωt). The three videos associated with Figure 5 provide detailed colorful evidence of these orientation contributions, and we observe similar behavior at other values of $\lambda\omega$ and $\lambda\dot{\gamma}$.

d. Third Harmonic

The Fourier coefficients of the third harmonic of the orientation distribution function are given by:

$$\psi'_3 = \left\{ \left[\begin{array}{l} \frac{1}{2016}(603W^2 + 892W - 95)(9W + 49)(81W + 100) \\ + \frac{5}{9856}(19W - 5)(9W + 1)(9W + 49)(81W + 100)(7C^2 - 1) \\ + \frac{36}{13903}(7 - 9W)(4W + 1)(9W + 1)(81W + 100)(33C^4 - 18C^2 + 1) \end{array} \right] s_2 \right. \\ \left. \left[\begin{array}{l} - \frac{5}{768}(1647W^2 + 791W - 400)(9W + 1)(9W + 49)(1 - C^2)s_4 \\ + \frac{175}{6144}(9W - 7)(4W + 1)(9W + 1)(81W + 100)(1 - C^2)^2 s_6 \end{array} \right] \right\} (1 - C^2) \quad (17)$$

and:

$$\psi''_3 = \left\{ \left[\begin{array}{l} \frac{1}{336}(9W + 49)(81W + 100)(45W^2 + 17W - 92) \\ + \frac{15}{4928}(W - 3)(9W + 1)(9W + 49)(81W + 100)(7C^2 - 1) \\ + \frac{35}{67584}(71 - 9W)(4W + 1)(9W + 1)(81W + 100)(33C^4 - 18C^2 + 1) \end{array} \right] s_2 \right. \\ \left. \left[\begin{array}{l} - \frac{5}{128}(81W^2 - 220W - 225)(9W + 1)(9W + 49)(1 - C^2)s_4 \\ + \frac{35}{6144}(9W - 71)(4W + 1)(9W + 1)(81W + 100)(1 - C^2)^2 s_6 \end{array} \right] \right\} (1 - C^2) \lambda \omega \quad (18)$$

Figure 6A illustrates the orientation distribution associated with the polymer motions arising at thrice the test frequency, 3ω , and predicted by Eqs. (17) and (18). Figure 6B and Figure 6C show that both components, in-phase, $\psi'_3 \cos 3\omega t$, and out-of-phase, $\psi''_3 \sin 3\omega t$, with $\cos 3\omega t$, do not deform throughout an entire cycle, except at $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}$ and $\omega t = 0, \pi$ where $\psi'_3 \cos 3\omega t$ and $\psi''_3 \sin 3\omega t$ are zero, respectively. This finding is verified by the three movies associated with Figure

6, in which we see both $\psi'_3 \cos 3\omega t$ (B) and $\psi''_3 \sin 3\omega t$ (C) contributing significantly for most values of ωt . However, examination of the orientation distribution at particular times in the cycle, specifically at $\omega t = \frac{3\pi}{4}$, reveals orientations to which either the in-phase or out-of-phase part hardly contributes. This is why the small side wings in Figure 6C at $\omega t = \frac{3\pi}{4}$ disappear from the butterfly shaped total orientation in Figure 6A. Thus, $\psi'_3 \cos 3\omega t$ sometimes destructively interferes with $\psi''_3 \sin 3\omega t$. There are, therefore, polymer motions that are neither in-phase nor out-of-phase with $\cos 3\omega t$. After brief investigation, we found that orientation contributions from interference between in-phase and out-of-phase harmonic components also appear at other values of $\lambda\omega$ and $\lambda\dot{\gamma}$.

e. Fourth Harmonic

The Fourier coefficients of the fourth harmonic are given by:

$$\psi'_4 = \left\{ \begin{aligned} & -\frac{5(216W^3 - 201W^2 - 497W + 16)(3C^2 - 1)}{133056(W+1)(4W+1)(9W+1)(9W+25)(16W+1)} \\ & -\frac{5(17496W^4 - 20979W^3 - 58383W^2 - 31526W + 1150)(1-C^2)c_2}{12096(W+1)(4W+1)(9W+1)(9W+25)(16W+1)(81W+100)} \end{aligned} \right\} \quad (19)$$

and:

$$\psi''_4 = \left\{ \begin{aligned} & \frac{(18549162W^3 + 21819195W^2 + 7990963W - 3933950)(3C^2 - 1)}{6519744(W+1)(4W+1)(9W+1)(9W+25)(16W+1)(81W+100)} \\ & + \frac{(737586W^3 + 160560W^2 - 29711W - 63725)(1-C^2)c_2}{12096(W+1)(4W+1)(9W+1)(9W+25)(16W+1)(81W+100)} \end{aligned} \right\} \lambda\omega \quad (20)$$

Figure 7A illustrates the orientation distribution associated with the polymer motions arising at quadruple the test frequency, 4ω , that are induced by the

oscillatory shear deformation, and predicted by Eqs. (19) and (20). Figure 7A shows that the fourth harmonic contributes to total orientation along the y – axis, and transverse to the flow direction, and these contributions take the form of three-member shish-kebabs. Orientation distributions from the component in-phase with $\cos 4\omega t$, $\psi'_4 \cos 4\omega t$, shown in Figure 7B, all share the same general shape as those in Figure 7A. Though Figure 7C shows no orientation contribution from the component out-of-phase with $\cos 4\omega t$, $\psi''_4 \sin 4\omega t$, examination of $\psi''_4 \sin 4\omega t$ at other values of ωt reveals orientation contributions identical to those of $\psi'_4 \cos 4\omega t$. Therefore, the total fourth harmonic is qualitatively identical to both $\psi'_4 \cos 4\omega t$ and $\psi''_4 \sin 4\omega t$ without interference between the harmonic components. We observe similar behavior at other values of $\lambda\omega$ and $\lambda\dot{\gamma}$.

IV. DISCUSSION

Eqs. (12) through (20), along with Figure 4 through Figure 7, are the main results of this work. We sometimes find destructive interference between the complex parts of the total harmonic orientation as seen in Figure 6. However, in-phase and out-of-phase components do often constructively interfere (Figure 4, Figure 5, Figure 7). The dynamic response of some harmonic orientation distributions, over one alternant cycle, is caused by either (i) the changing relative influence of *both* complex components or (ii) the dynamic behavior of *just one* of the complex components (see Figure 5).

The second harmonic is the only instance where the changes in orientation distribution are just attributable to a single changing complex component. This is caused by the interference between the contributions from the second and fourth order terms in Eq. (11) to the second harmonic.

V. CONCLUSION

We have deepened our understanding of the molecular motion underlying large-amplitude oscillatory shear flow of polymeric liquids by decomposing the first five Fourier components (the zeroth, first, second, third and fourth harmonics) of the orientation distribution into their in-phase and out-of-phase constituents. We did so for the simplest polymer molecular model, the suspension of non-interacting rigid dumbbells in a Newtonian suspending fluid. We use three-dimensional imaging to explore each complex harmonic component of the polymer motion. Our analysis includes only the case of nonlinear viscoelasticity.

We find that the dynamic response of some harmonic orientation distributions, over one alternant cycle, is caused by either (i) the changing relative influence of *both* complex components or (ii) the dynamic behavior of *just one* of the complex components (see Figure 5).

We sometimes find destructive interference between the complex parts of the total harmonic orientation as seen in Figure 6. However, in-phase and out-of-phase components do often constructively interfere (Figure 4, Figure 5, Figure 7). Whereas the viscoelastic properties, be they linear $[\eta'(\omega), \eta''(\omega)]$ or $[\eta'(\omega, \dot{\gamma}_0),$

$\eta''(\omega, \dot{\gamma}_0)]$, never destructively interfere, their causes, lurking within the polymer orientation distribution, can destructively interfere.

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Table I: Literature on Analytical Solutions for Orientation Distribution in Large-Amplitude Oscillatory Shear Flow

	Model	Expansion Variable	Orientation Harmonic	Non-contributing Terms	Fourier Decomposition	[Ref.] (Correction to)
Kirkwood and Plock (1956, 1967); Plock (1957)	RD ^h , SK ^h	$\dot{\gamma}^0$	0,2,4,6			[28,29,30]
Paul (1969); Paul (1970); Bharadwaj (2012)	RD ^h , SK ^h	$\dot{\gamma}^0$	0,2,4,6			[31,32,33] (28,30)
Paul and Mazo (1969), Paul (1970)	RR	$\dot{\gamma}^0$	0,2,4,6			[34,32]
Bird, Warner and Evans (1971)	RD, SK	$\dot{\gamma}^0$	0,1,2,3			[26]
Mou and Mazo (1977)	RR	$\dot{\gamma}^0$	0,2,4,6			[35](34)
Helfand and Rochefort (1982)	R [†]	$\dot{\gamma}^0$	See Eq. (8)			[36]
Bird <i>et al.</i> (2014)	RD, SK	$\dot{\gamma}^0$	0,1,2,3			[37]
Schmalzer <i>et al.</i> (2014, 2015)	RD, SK	$\dot{\gamma}^0$	0,1,2,3,4			[38,39]
Schmalzer <i>et al.</i> (2014, 2015)	RD, SK	$\dot{\gamma}^0$	0,1,2,3,4	X		[40,41,42]
Bozorgi (2014); Bozorgi and Underhill (2014)	AS ^h	γ_0	0,1,2			Chapter 8 of [43]; [44]
Giacomin <i>et al.</i> (2015)	RD, SK	$\dot{\gamma}^0$	0,1,2,3,4	X	X	[45]
This paper	RD, SK	$\dot{\gamma}^0$	0,1',1'',2',2'',3',3'',4',4''	X	X	

Legend: AS = active rod suspensions; R = reptation; RD = rigid dumbbell; RR = planar rigid ring; SK = shish-kebab; † = mixtures; ^h = with hydrodynamic interaction; *n'* = in-phase with $\cos n\omega t$; *n''* = out-of-phase with $\cos n\omega t$.

Table II: Dimensional Variables

Velocity, i th component	L/t	v_i
Angular frequency	t^{-1}	ω
Bead center to center length of rigid dumbbell	L	L
Bead diameter	L	b
Bead friction coefficient	M/t	$\xi \equiv 3\pi b\eta_s$
Boltzmann constant	$ML^2/t^2T/dumbbell$	k
Cartesian coordinate, distance from stationary plate (Figure 1)	L	y
Cartesian coordinate, flow direction (Figure 1)	L	x
Cartesian coordinate, transverse to flow direction (Figure 1)	L	z
Gap	L	h
Relaxation time of fluid	t	λ
Shear rate amplitude	t^{-1}	$\dot{\gamma}^0$
Solvent viscosity	M/Lt	η_s
Temperature	T	T
Time	t	t

Legend: $M \equiv$ mass; $L \equiv$ length; $t \equiv$ time; $T \equiv$ temperature

Table III: Dimensionless Variables and Groups

Azimuthal angle	ϕ
Deborah number squared	$W \equiv (\lambda\omega)^2$
Deborah number, oscillatory shear	$\lambda\omega$
Number of equally-spaced beads on a rod of length $(L - b)$	N
Number of harmonic	n
Orientation distribution	$\psi(\theta, \phi, t)$
i th term of orientation distribution expansion	$\psi_i(\theta, \phi, t)$
Orientation distribution, Fourier component, in-phase with $\cos n\omega t$	$\psi'_n(\theta, \phi)$
Orientation distribution, Fourier component, out-of-phase with $\cos n\omega t$	$\psi''_n(\theta, \phi)$
Polar angle	θ
Time dependent part of shear rate for velocity profile, assumed linear in y [Eq. (3)]	$f(t)$
Weissenberg number, oscillatory shear	$\lambda\dot{\gamma}^0$

Figure 1: Orthomorphic sketch of alternating velocity profile in oscillatory shear between stationary and moving plates [Eqs. (3) or (4)]. 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: Zeroth harmonic of ψ , ψ'_0 , from Eq. (12), over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\dot{\gamma}^0 = 1$, where only ψ_2 and ψ_4 contribute. Nonlinear viscoelastic regime.

Figure 4: Total first harmonic of ψ (A), $\psi'_1 \cos \omega t + \psi''_1 \sin \omega t$ with Eqs. (13) and (14), and first harmonic components, in-phase (B) and out-of-phase (C) with the shear rate, over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\gamma^0 = 1$, and where only ψ_1 and ψ_3 contribute. Nonlinear viscoelastic regime.

Figure 5: Total second harmonic of ψ (A), $\psi'_2 \cos 2\omega t + \psi''_2 \sin 2\omega t$ with Eqs. (15) and (16), and second harmonic components, in-phase (B) and out-of-phase (C) with $\cos 2\omega t$, over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\dot{\gamma}^0 = 1$, and where only ψ_2 and ψ_4 contribute. Nonlinear viscoelastic regime.

Figure 6: Total third harmonic of ψ (A), $\psi'_3 \cos 3\omega t + \psi''_3 \sin 3\omega t$ with Eqs. (17) and (18), and third harmonic components, in-phase (B) and out-of-phase (C) with $\cos 3\omega t$, over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\gamma^0 = 1$, and where only ψ_3 contributes. Nonlinear viscoelastic regime.

Figure 7: Total fourth harmonic of ψ (A), $\psi'_4 \cos 4\omega t + \psi''_4 \sin 4\omega t$ with Eqs. (19) and (20), and fourth harmonic components, in-phase (B) and out-of-phase (C) with $\cos 4\omega t$, over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\dot{\gamma}^0 = 1$, and where only ψ_4 contributes. Nonlinear viscoelastic regime.

Figure 8: Sum of first five harmonics of ψ , $\sum_{n=0}^4 [\psi'_n \cos n\omega t + \psi''_n \sin n\omega t]$ with Eqs. (12) through (20), over a complete alternant cycle, $\omega t = 0$ to $\omega t = 2\pi$, with $\lambda\omega = 1$ and $\lambda\dot{\gamma}^0 = 1$. Nonlinear viscoelastic regime.

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